THE VISCOSITY OF AQUEOUS ELECTROLYTES
AND
VISCOMETRIC TITRATIONS

BY

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HIERDIE WERK WORD MET LIEFDE AAN
MY OUERS, FLIP EN TIEN CROUSE, OPGEDRA.

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P.L.C.

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ABSTRACT

The thesis attempts to find the most appropriate equation from which to calculate the viscosities of mixtures of aqueous electrolytes so as to predict the course of viscometric titration curves for new systems, to interpret viscometric data already published, and to use in the possible determination of equilibrium constants where other methods are not applicable.

An extensive literature survey is included in the introduction (section 1), including not only material directly related to the main objective of the thesis, but material published on the subject of the viscosity of electrolytes in general.

In section 2 the fundamental principles and experimental techniques employed are discussed. Sources of error in capillary viscometry are discussed with reference to the apparatus used.

In section 3 an extended form of the Jones-Dole equation for a simple strong binary electrolyte

i.e. $\eta/\eta_0 = 1 + A\sqrt{c} + Bc$

(where c is the molar concentration and A and B are constants) is proposed,

viz. $\eta/\eta_0 = 1 + a\sqrt{\Gamma} + b\Gamma$.

Γ /...

Γ is the ional strength (i.e. twice the conventional ionic strength) and a and b are constants. The calculation of the electrostatic constant, a, from the theory of Onsager and Fuoss is discussed. The A-coefficient in the original Jones-Dole equation is shown to be non-additive. The Falkenhagen equation for calculating A is presented as a special case of the Onsager and Fuoss theory. A qualitative interpretation of the B-coefficient, which is attributed to ion-solvent interaction, is given. B is shown to be additive and in a mixture b can be computed from

$$b = \sum_i b_i \Gamma_i / \Gamma$$

where b_i is calculated from B_i, the ionic B-coefficient of the i-th ionic species present.

In section 4 the proposed equation is shown to be applicable to weak electrolytes, provided the concentration of every species in solution is known. A value for the B-coefficient of HSO_4^- is computed. Anomalies in the viscosity data reported in the literature for H_2SO_4 and mixtures of $CuSO_4$ and H_2SO_4 are explained in terms of the difference in value of the B-coefficients of HSO_4^- and SO_4^{2-}. The B-coefficients of acetic acid and the acetate ion are determined. $B_{\text{acetic acid}}$ is determined in a mixture of acetic acid and HCl, the latter being added to suppress the dissociation of acetic acid. B_{acetate} is evaluated in a mixture of acetic acid and

NaOH,/...

NaOH, the latter being added in excess in order to prevent hydrolysis. The values arrived at are compared with values reported in the literature. The viscometric titration curves of acetic and sulphuric acid with NaOH are interpreted in terms of the B_i - values obtained.

Several equations proposed for concentrated solutions of electrolytes are examined in section 5. Special attention is given to the equation developed by Goldsack and Franchetto. The disadvantages of viscosity work at high concentrations are pointed out.

Viscometric titrations of Zn^{2+}, Cd^{2+}, and Hg^{2+} are reported in section 6. Discontinuities in the titration curves are correlated with maxima in the computed speciation curves. A method is suggested of extending the equation proposed in section 3 to apply to cases where complex formation occurs.

1. INTRODUCTION

One main objective of this thesis is to be able to predict the viscosities of mixtures of electrolytes so as to be able to predict the course of viscometric titration curves for new systems which could be of practical analytical value and to interpret those already published. Since a number of published equations are discussed an overview of the development of the subject as a whole will be given, pointing out the areas of conflict which this work will attempt to resolve.

The variation of the viscosity of aqueous solutions of electrolytes has been a subject of study for more than a hundred years. In 1876 Sprung |95| published measurements on many salts at many temperatures. His viscosity-concentration curves are approximately linear, but with an upward trend at higher concentrations. Arrhenius |2| found the same linear relationship at high dilution, with the viscosity increasing more rapidly than the concentration at higher concentration. He proposed an equation of the form

$$\eta_{\mathrm{rel}} = A^{c} \qquad (1.1)$$

where A is an empirical constant for a given salt, and η_{rel} and c the relative viscosity and concentration of the solution.

Equation (1.1) is only a rough approximation, holding in a very limited concentration range. Furthermore it does not account for the fact that some solutes, like KCl, diminish the viscosity of water under certain conditions.

Einstein/...

Einstein |24| deduced from the principles of hydrodynamics that if the solute could be regarded as made up of spherical incompressible uncharged particles which are large in comparison with the water molecules, the viscosity of the solute would be

$$\eta_{rel} = 1 + 2{,}5\theta \qquad (1.2)$$

where θ is the total volume of the solute particles per unit volume. A linear relationship is predicted. Finkelstein |33| extended Einstein's treatment to solutions of binary electrolytes in polar solvents. He studied the effect on the viscosity of the relaxation time of the solvent dipoles, and predicted a linear increase of viscosity with concentration. Neither Einstein's nor Finkelstein's theory could explain negative viscosity increments.

Grüneisen |43| improved current experimental techniques in order to extend viscosity measurements to lower dilution and found that for salts, deviations from the linear law became more pronounced at low concentration instead of disappearing. Subsequently this departure from linearity at high dilution became known as the "Grüneisen effect". His attempts to express viscosity as a function of concentration were unsuccessful, however.

The Grüneisen effect was found always to increase the viscosity, regardless of whether at higher concentration the salt eventually increases or decreases the viscosity. It occurred to Jones and Dole

that the/...

that the Debye-Hückel theory of interionic attraction might be extended to apply to this problem, and that the Grüneisen effect might be dependent upon the square root of the concentration. In their classic paper of 1929 |49| they showed that for solutions of $BaCl_2$ and $LiNO_3$ plots of $(\phi - 1)/\sqrt{c}$ against $\sqrt{c}$ are perfectly linear, where ϕ is the relative fluidity of the solution and is the reciprocal of the relative viscosity.

Their now famous equation was given in its first form,

$$\phi = 1 + A\sqrt{c} + Bc \qquad (1.3)$$

where A is always negative, and B either positive or negative. This equation has subsequently been used in the more convenient form,

$$\eta_{rel} = 1 + A\sqrt{c} + Bc \qquad (1.4)$$

where A and B have approximately the same moduli as the coefficients in equation (1.3) but are of opposite sign. The term, $A\sqrt{c}$, is due to interionic electrostatic forces, while the term, Bc, is a measure of ion-solvent interaction.

Working on KCl solutions Joy and Wolfenden |58| soon confirmed the Jones-Dole equation. Numerous papers by Jones and his colleagues followed giving A and B-coefficients for various salts |e.g. 50-58|.

All agreed that the proposed equation holds well for strong electrolytes in the concentration range 0,0 to 0,1 M and that the term, $A\sqrt{c}$, is positive in all cases.

Falkenhagen *et al.* |25- 32| initiated the theoretical calculation of A using the Debye-Hückel equilibrium theory as a starting point. An expression for A for simple strong electrolytes was obtained which yielded theoretical values agreeing well with those obtained experimentally. Their general equation will be discussed in section 3.1.

Onsager and Fuoss, in their paper on irreversible processes in electrolytes |79|, extended the Falkenhagen theory to include any mixture of strong electrolytes. The viscosity will now depend on the total and on the relative concentrations of the various ionic species present and no simple expression in c comparable to equation (1.4) is applicable. On the contrary, the Onsager and Fuoss equation for the electrostatic contribution to the relative viscosity, as represented by Asmus |6|, is given as

$$\eta_{\mathrm{rel}} = 1 + a\sqrt{\Gamma} \qquad (1.5)$$

where the a-coefficient is a general constant corresponding to A in equation (1.4) and Γ is, by definition, twice the conventional ionic strength, I,

i.e. $$\Gamma = \sum_i c_i z_i^2 \qquad (1.6)$$

z_i and c_i being the valency and the molar concentration of the i-th ionic species respectively. Γ will be referred to as the total ional strength to distinguish it from I, the ionic strength.

The Falkenhagen equation has been tested extensively by Asmus |3-5| and others | e.g. 22, 67, 73, 86 | and has invariably predicted accurate values for the A-coefficient. Asmus even used it to obtain a more correct value for the conductivity of the ferrocyanide ion |7|. He also obtained satisfactory results when testing the Onsager and Fuoss theory experimentally | 6, 8 |. His presentation of their equation, as well as his experimental results, will be given detailed attention in section 3.2.

Chakravarti *et al.* |17, 18, 19| experimented extensively on the viscosities of mixtures of electrolytes. They found that, provided the proportions of the various ionic species in solution remain unchanged, a solution of a mixture of electrolytes behaves like that of a single salt, obeying the Jones-Dole equation which can now be rewritten as

$$\eta_{\mathrm{rel}} = 1 + A^{*}\sqrt{c} + B^{*}c. \qquad (1.7)$$

Furthermore, they claimed that A* is a constant varying linearly with composition. This means that A* in, for example, a binary mixture of electrolytes can easily be obtained by linear interpolation, using the two values of A for the individual electrolytes. Yusufova *et al.* |108| make the same claim. They give the electrostatic contribution to viscosity as

$$\eta_{rel} = 1 + A\sqrt{\Gamma} \qquad (1.8)$$

with $A = \sum_i x_i A_i$

where A_i and x_i are the A-coefficient and the molal portion of the ionai strength of the i-th ionic species respectively. x_i is defined by

$$x_i = \Gamma_i/\Gamma \qquad (1.9)$$

Since this would make the formidable calculations involved in obtaining values for the a-coefficient redundant, the validity of these claims will be investigated.

Many attempts have been made at finding a quantitative theory for the B-coefficient. Asmus pointed out relationships among values of B, deviations from Walden's rule, the entropies of hydration and lyotropic numbers |9|. Nightingale related the B-coefficient to the effective radii of hydrated ions |74|, and to energies and entropies of activation for viscous flow |75, 76| for example. Various studies of the variation of the viscosity of electrolytic solutions as a function of temperature have also been published |37, 38, 46, 59-63, 80, 81, 88|. From these different sources emerged a good qualitative understanding of ion-solvent interaction which is represented by the B-coefficient. However, all quantitative theories for B have had only very limited success up to now. The B-coefficient is discussed in detail in section 3.2.

Various/...

Various ways of calculating the B-coefficient for mixtures of electrolytes from the reported values of individual ionic species are also examined. Chakravarti |19| claims that B*, like A* in equation (1.7), varies linearly with composition. Simpson |92| gives the contribution to the change in viscosity due to ion-solvent interaction as the sum of the individual Bc terms for each ion

i.e. $$\eta_{\text{rel}} = 1 + a\sqrt{\Gamma} + \sum_i B_i c_i \qquad (1.10)$$

Asmus, on the other hand, in his paper on the Onsager and Fuoss theory |6| found experimentally that the relationship

$$\eta_{\text{rel}} = 1 + a\sqrt{\Gamma} + b\Gamma \qquad (1.11)$$

holds good, the a-coefficient agreeing well with theory. However, he could find no simple way of obtaining the b-coefficient from the B values for the individual ionic species in solution. These different proposals will be looked at in order to find the most convenient expression for B in mixtures.

In a paper on the fluidity of electrolytes, Bingham |12| showed that the fluidity of an electrolyte can be represented as

$$\phi = \phi_w + c(\Delta_a + \Delta_c) \qquad (1.12)$$

where c is the molal concentration, Δ_a and Δ_c are the equivalent

ionic/...

ionic elevations in the fluidity of water produced by one equivalent weight of anions and cations respectively in a normal solution at 25°C, and ϕ_W is the fluidity of water alone. He determined the ionic elevations for several ionic species and on the basis of these predicted viscometric titration curves for NaOH and KOH with HCl and HNO_3, all of which showed sharp end-points. It should be noted that equation (1.12) neglects the electrostatic coefficient and is inaccurate at very high dilutions. Nevertheless, Bingham's predictions that viscometric titrations with sharp stoicheiometric end-points were possible, were experimentally confirmed by Simpson, Irving and Smith, who had designed and built a fully automatic viscometer which made such titrations viable |93|. This same automatic viscometer was used for the experimental work in this thesis, and will be described in section 2, along with the experimental techniques used and the fundamental principles of viscometry.

Few articles on the viscosity of weak electrolytes have been published |e.g. 11, 96|. One such example is that of Srinivasan and Prasad |96| who used the expression

$$\eta_{rel} = 1 + A\sqrt{\alpha c} + \beta(1 - \alpha)c \qquad (1.13)$$

where α is the degree of dissociation, β is a constant applicable to the undissociated molecule, and A has its usual meaning. A large discrepancy was found between calculated and experimental values of A. Attention is given to the viscosity of weak electrolytes in section 4.

Extensive/...

Extensive research on concentrated solutions of strong electrolytes has been carried out. Examples are that of Singh and Tikoo |94|, Satoh and Hayashi |90|, Suryanarayana and Venkatesan |98|, Sahu and Behera |89|, Carbonell |15|, Galinker *et al.* |36|, Isono |48|, Breslau *et al.* |13, 14|, Moulik and Rakshit |72|, and Goldsack and Franchetto |40, 41|. A common approach has been |e.g. 51, 51| to extend the Jones-Dole equation to higher terms in c, e.g.

$$\eta_{\text{rel}} = 1 + A\sqrt{c} + Bc + Dc^2 \qquad (1.14)$$

Recently Martinus *et al.* |70| found the presence of the term, Dc^2, influences the accuracy with which B may be determined, and proposed a statistical technique for obtaining B more accurately. Various expressions for calculating viscosity at high concentration are discussed in section 5. Special attention is given to the work of Goldsack and Franchetto |40, 41| who extended the absolute rate theory of Eyring *et al.* |39| to the viscosity of electrolytes, and derived a two parameter equation which can be used to predict the viscosity of concentrated solutions of strong electrolytes. These two parameters are derived from viscosity data. Their approach has been extended to apply to mixtures |41, 78|.

Galinker *et al.* |41| studied the effect of complex formation on viscosity in mixtures of $CdCl_2$ and various chlorides. They could draw no unambiguous conclusions, however. Their work is discussed in section 6 where zinc, cadmium and mercury chloride complexes are studied using viscometric titrations.

For the/...

For the sake of completeness a number of articles which are either of interest but not of direct importance to this work, or which appear to be of importance, but whose contents have not yet been obtainable, or are inaccessible because of language difficulty, should be mentioned. Guveli found a regular increase per methylene group in the B-coefficient of alkyltrimethyl-ammonium bromides |45|. Noel *et al.* reported B-coefficients for metal chelates and selected ligands |77|. These might prove useful in viscometric determinations of equilibrium constants. Tollert used viscometric data to prove the presence of molecules of higher order in aqueous solution |102, 104| and to determine the basicity of cerium earth nitrates |103|. He also recorded some anomalies in the specific viscosities of some ionic species which might be of biological interest |101|. Golik *et al.* |42| used viscometry to investigate the configuration of water molecules surrounding a cation. Kraeft |65| reported theoretical work on short range forces between ions which might effect viscosity. Serdyuk and Shavaev |91| describe a method for calculating solution properties of mixed aqueous salt systems from binary solution properties and solubility data, and 2 or 3 of these properties along the saturation curve. Zaitsev *et al.* |109| discuss various methods for calculating viscosity parameters in mixed solutions. Penkina published work on the temperature and concentration dependence of electrolytes |82, 85|, the energy of activation of viscous flow |84| and proposed an alternative way of calculating viscosities |83|.

Finally it should be mentioned that general reviews of the subject have been published by Finkelstein |33|, Stokes and Mills |97| and Spiro and King |47|.

Note/...

Note that throughout the thesis the convention is adopted that $|\ \ |$ = square brackets. Hence $|HCl|$ indicates the molar concentration of hydrochloric acid, for example.

2. FUNDAMENTAL PRINCIPLES AND EXPERIMENTAL TECHNIQUES

2.1 DEFINITIONS AND NOMENCLATURE

Flow

Flow is defined as the irreversible deformation of a body, in contrast to the spontaneously reversible deformation known as 'elasticity'. The work done in order to sustain flow is dissipated as heat and is not mechanically recoverable. During viscous flow mechanical energy is converted into heat and therefore the resistance to flow of a fluid is sometimes called 'internal friction'.

Shear

This term is defined as the process in which infinitely thin, parallel planes or concentric cylinders slide over each other. Viscous deformation is expressed in terms of 'rate of shear', which is the change in velocity of flow with a distance measured at right angles to the direction of flow.

Stress

In order to produce flow, a stress has to be applied. It is defined as force per unit area, and when applied tangentially to the area of the body deformed, it is known as a shearing stress.

Absolute Viscosity

The absolute viscosites for ideal viscous bodies is defined as the force per unit area required to maintain unit difference in velocity between two parallel layers of the fluid which are unit distance apart. In definitive terms, it is the ratio of the applied shearing stress to the rate of shear. The dimensions of absolute viscosity are $ML^{-1}T^{-1}$, which in SI units is 10^{-1}kg $m^{-1}s^{-1}$. The basic unit is termed the poise, although, in practice the centipoise (cP) is commonly used. The symbol for absolute viscosity is η.

Kinematic Viscosity

The kinematic viscosity, ν, is the ratio of the absolute viscosity to the density of the fluid,

viz. $\nu = \eta/d$.

d is the density. The dimensions are L^2T^{-1}, which in SI units is $10^{-4}m^2s^{-1}$. The unit is called the stoke, although in practice the centistoke is most commonly used.

Relative viscosity

This is the ratio of the absolute viscosity of a solution to that of the pure solvent under the same conditions,

viz. $\eta_{rel} = \eta/\eta_o$.

Fluidity

Fluidity, ϕ, is the reciprocal of absolute viscosity,

viz. $\phi = {}^1/_\eta$.

2.2/...

2.2 EXPERIMENTAL TECHNIQUES

The measurement of viscosity with capillary type viscometers depends on a relationship between the rate of flow of liquids under an applied pressure and the dimensions of the capillary through which they are forced.

$$\eta = \frac{\pi R^4 (p_o - p_1) t}{8 \, v\ell} \qquad (2.1)$$

where v is the volume of the liquid flowing through the tube in time t. p_o and p_1 are the pressures at the two ends of the capillary which is of radius R and length ℓ.

The following conditions have to be met in order to derive the above equation:

(i) the flow is everywhere parallel to the axis of the tube;
(ii) the flow is steady, initial disturbances due to accelerations from rest having been damped out;
(iii) There is no slip at the walls of the capillary;
(iv) the fluid is incompressible;
(v) the fluid will flow even when subjected to an infinitely small pressure.

Conditions (i) and (ii) relate to the requirements of streamlined flow, (iii) and (iv) are important in multi-phase liquids and high-pressures respectively and do not concern this work while (v) is concerned with surface tension effects.

The/...

The Ubbelohde suspended-level viscometer (Fig. 2.1) satisfies conditions (i) - (v) most closely and is invariably used for precise measurement on liquids of low viscosity. In this case it is the hydrostatic pressure of the liquid that causes it to flow through the capillary and equation (2.1) becomes

$$\eta = \frac{\pi R^4 \ (h_m \ gd)t}{8v\ell} \qquad (2.2)$$

where h_m is the mean height of the liquid column, g is the acceleration due to gravity and d is the density of the liquid. Viscometers, like the Ubbelohde and Ostwald viscometers, which utilise the head of the liquid itself to produce the pressure differential across the capillary are called 'kinematic' viscometers. Measurements of viscosity with these instruments need to be associated with accurate determination of densities.

With reference to figure 2.1 and equation (2.2), V is the volume of liquid contained between timing marks X and Y, above and below reservoir bulb R. t is the time taken for the meniscus of the liquid to pass from X to Y and equation (2.2) may therefore be rewritten as

$$\eta = K.d.t. \qquad (2.3)$$

Thus $\nu = K.t.$ (2.4)

The/...

The kinematic viscosity, ν, of a liquid is, therefore, directly proportional to the flow time of that liquid in a particular viscometer. The constant, K, may be determined by calibration of the instrument with liquids of known viscosity, but this is required only when absolute viscosities are to be measured. When determining relative viscosities this constant need not be known since

$$\eta_{rel} = \eta/\eta_{o} = d.t/d_{0}t_{0} \qquad 2.5$$

where d_0 and t_0 are the density and flow time respectively of the pure solvent.

2.2.1 Errors and their correction in capillary viscometry

The kinetic energy effect, which is the largest single cause of deviation from equation (2.2), arises when some of the hydrostatic or applied pressure is used to accelerate the liquid in the entrance reservoir from rest to the velocity distribution in the capillary. This error is most apparent when measuring absolute viscosities, since the test and calibrating liquids may have greatly different flow rates. In measurements of relative viscosity, especially of aqueous electrolytes, this is not the case and the error is negligible. The observed pressure is corrected for the loss of kinetic energy by an additional term in equation (2.2), which becomes

η /...

$$\eta = \frac{\pi R^4 h_m g d t}{8 v \ell} - \frac{m d v}{8 \pi \ell t} \qquad (2.6)$$

where m is a numerical coefficient ($\cong 1$) which takes account of the shape of the capillary.

Equation 2.4 is thus modified to

$$\nu = K.t - M/t \qquad (2.7)$$

where the constants K and M may be found from a plot of $^{\nu}/t$ against - $^{1}/t^{2}$ in the calibration of the viscometer. The numerical values K and M were found to be 0,016 and 0,014 respectively in the viscometer used. Although the correction to the absolute kinematic viscosity, ν, may not be insignificant, the final results in this study are given in the form of relative viscosity and the resultant error in η_{rel} was found to be negligible in practice (< 0,00001).

Drainage errors constitute a problem peculiar to glass viscometers. Jones and Ferrell |55| have studied this effect and have shown that the volume of liquid on the walls after a particular time is inversely proportional to flow-time and to the kinematic viscosity of the liquid, and independent of surface tension. The effect may be minimised by thorough cleaning. In the case of relative viscosity it is hardly apparent since the time for drainage will be virtually constant.

The Couette correction allows for the viscous energy used in the formation of streamlines at the entrance and exit of the capillary. It is expressed as an increase, λ, in the effective length of the capillary. In equations (2.2) and (2.6) ℓ is thus replaced by $(\ell + \lambda)$. If the viscometer is calibrated, or if it is used to obtain values for relative viscosity, this correction is made automatically.

Errors due to surface tension effects at the entrance and exit of the capillary may be important for measurements of absolute viscosity, although it is claimed that the suspended level at the exit reservoir of the Ubbelohde viscometer does much to compensate for forces operating in the entrance reservoir. This error is once again negligible in measurements of relative viscosity unless the solute appreciably changes the surface tension of the solvent.

2.2.2 Measurements of Relative Viscosity

The measurements necessary for the calculation of relative viscosities, i.e. flow times and densities, were determined in the same water thermostat capable of maintaining a constant temperature of 25°C with a deviation of less than ± 0,005°C.

2.2.2.1 Determinations of Flow-times

The Ubbelohde viscometer (fig. 2.1) used for measurement of flow-times was mounted in a stand designed to hold it rigidly with the capillary in a vertical position. The perspex top of the stand was fitted with a three point levelling arrangement. The capillary viscometer used was incorporated into an assembly which forms an automatic capillary viscometer. Its construction and operation have been comprehensively described by Simpson |92| and will not be discussed in great detail here.

The instrument combines the electronic measurement of the flow time with an automation of the processes of (i) taking a predetermined number of successive measurements on a particular solution, (ii) adding a predetermined quantity of any liquid to the viscometer from an automatic burette and (iii) mixing the contents of the viscometer. The sequence of operations followed in this work involved transferring a known volume of liquid, usually 20 ml, into the reservoir, the U-tube, of the viscometer. Valves C and D are of the normally closed type, while valves A and B are of the normally open type (fig. 2.1). Thus by energising valves A, B and C the liquid is forced up the capillary by compressed nitrogen just past the mark, X, when filling stops. After a preset time delay, during which the valves return to their normal positions, the liquid is allowed to fall freely under gravity. The passage of the meniscus past the upper (start) and lower (stop) levels, X and Y, is detected using silicon planar phototransistors, BPX 25, incorporated into a waterproof fibre optic light guide system (fig. 2.2). As long as the capillary is filled with liquid the phototransistors are illumined. However, the moment the liquid level falls and the liquid is replaced by air, the light is scattered at the internal glass/air interface and the intensity of the transmitted light beam is reduced, enabling the phototransistors to trigger off and start (or stop) on electronic timing device. The apparatus proved reliable in practice. The standard deviation obtained for fifteen readings for distilled water (155,234 ±0,004^{1}s or ±0,002^{6}%) is comparable with that reported by Simpson |92| for ten runs with acetone at the same temperature (392,545 ±0,012^{0}s or ±0,003^{1}%) These flow times (in seconds) are compared in table 2.1.

Whenever the viscometer reservoir received an aliquot portion of a liquid from the autoburette, either in order to dilute the solution or to alter its composition, the whole was mixed by bubbling nitrogen through it. Adequacy of mixing and the attainment of a constant temperature were at once monitored by the successive flow times which, after an initial run, rarely differed from one another by more than 0,008 seconds.

Two techniques were used to measure flow times:

Method 1. This technique was used especially for the determination of the a and b-coefficients in the Jones-Dole type equation (1.11) for electrolytes at 25°C.

Distilled water (20,0 ml) was transferred into the viscometer reservoir using a calibrated pipette and allowed to reach thermal equilibrium with the thermostat bath (20-30 minutes). The difference between successive flow times indicated whether equilibrium had been attained. An aliquot portion of the concentrated electrolyte stock solution was now added from the autoburette and the flow time was measured at least thrice after it had become steady before the next addition of stock solution. The mean of the three flow times was used to calculate the relative viscosity of the solution of known concentration using the expression:

$$\eta_{rel} = \frac{t}{t_0} \times d_{rel} \qquad (2.8)$$

where t and t_0 are the flow-times of the solution and pure solvent respectively and d_{rel} the relative density which was determined independently. Plots of $(\eta_{rel}-1)/\Gamma^{\frac{1}{2}}$ against $\Gamma^{\frac{1}{2}}$ gave excellent straight lines. In each case a least squares analysis was performed on the data. The intercept gave the *a*-coefficient and the slope the *b*-coefficient.

<u>Method 2.</u> This technique was used for titrations. A known volume of sample solution (usually 20 ml) was placed in the viscometer reservoir and allowed to reach thermal equilibrium as before. Flow-times only were used to indicate changes in viscosity and density determinations were therefore not required, which simplified the problem considerably. Aliquot portions of titrant were now added from the autoburette and flow-times recorded after each addition. The flow-times were plotted against the volume of the titrant added, which gave the various titration curves shown in the text.

To prevent evaporation and contamination of its contents, the viscometer was kept closed to the atmosphere except when measurements of

flow-time/...

flow-time were being undertaken. During the course of the work the viscometer was rigorously cleaned at regular intervals with hot chromic acid and then rinsed thoroughly with distilled water followed by AnalaR grade acetone which had been filtered through a No.4 porosity sintered glass funnel.

2.2.2.2 Density Determinations.

These were carried out using a pair of Bingham pycnometers (figure 2.3) which were immersed in the water thermostat. Before commencing a particular group of measurements, the pycnometers were cleaned with chromic acid, followed by water and filtered AnalaR grade acetone. Internal drying was effected by vacuum pump. Flushing with water and acetone was found to be adequate between individual measurements within a set. The solution whose density was to be measured was added to the pycnometer using a hypodermic syringe which was also used to adjust the level in the capillary to the calibration level after 20 minutes in the water thermostat. Before weighing the pycnometers were thoroughly rinsed externally and allowed to stand in the balance case for about 20 minutes. Care was taken to ensure that no droplets of liquid remained in the capillary above the calibration mark. An initial calibration at 25°C was performed with glass distilled water. The two pycnometers were found to contain 16,1797 ±0,0005 and 17,0160 ±0,0004 g of water respectively.

The values of $d^{25^\circ \mathrm{soln}}_{4^\circ\ H_2O}$ for test liquids were calculated using the expression:

d/...

$$d^{25°soln}_{4°\ H_2O} = \frac{W'}{W} . d^{25°H_2O}_{4°\ H_2O} - \frac{0,001185\ (W'-W)}{W} \qquad (2.9)$$

where W' and W are the apparent weight of the solution and of distilled water respectively contained in the viscometer, and 0,001185 is the mean density of air at one atmosphere pressure. The second term on the right corrects for the boyancy of air. Relative density (d_{rel}), i.e. the density of the solution at temperature T° relative to the density of pure solvent at the same temperature T°, is then obtained from

$$d_{rel} = \frac{d^{25°soln}_{4°\ H_2O}}{d^{25°\ H_2O}_{4°\ H_2O}} \quad . \qquad (2.10)$$

$d^{25°\ H_2O}_{4°\ H_2O}$ was taken as 0.99707 |107|.

Relative density was found to have a linear dependence upon concentration, c, in all cases. Measurement of density at five or more different concentrations were found to be adequate to obtain the value for the constant, κ, in the expression

$$d_{rel} = 1 + \kappa \cdot c \, . \qquad (2.11)$$

In each case a least squares analysis was performed. Since, by definition, the intercept in equation (2.11) has to be unity, κ can be calculated from

κ/...

$$\kappa = \frac{\sum_{1}^{n} c_i d_{\mathrm{rel}\,i} - \sum_{1}^{n} c_i}{\sum_{1}^{n} c_i^2} \qquad (2.12)$$

Since the concentration was known for each recorded flow-time, d_{rel} and hence η_{rel} could be calculated from equations (2.11) and (2.8).

2.2.3 Preparation and standardisation of Solutions

In all cases AnalaR grade reagents and glass distilled water were used. The acetic acid, hydrochloric acid, sulphuric acid and sodium hydroxide solutions were all standardised potentiometrically, using a Metrohm Dosimat Titroprocessor. In all cases freshly prepared sodium hydroxide solutions were used and care was taken not to expose them to the atmosphere. The acids were all titrated with the sodium hydroxide solution, which in turn was standardised with potassium hydrogen phthalate.

All zinc, cadmium and mercury solutions were standardised by titration with EDTA. A commercially prepared EDTA solution was used. Its concentration was determined with a solution of Ca^{2+} prepared from pure calcite ($CaCO_3$) and buffered to pH 10, using Eriochrome Black T as indicator, with a small volume of a Mg-EDTA solution to increase the sharpness of the end-point. The zinc and

cadmium solutions/...

cadmium solutions were determined by direct titrations, buffered to pH 10 and using Eriochrome Black T as indicator in each case. The mercury solution was back titrated with the zinc solution, using xylenol orange as indicator and buffered to pH 6.

TABLE 2.1

Flow-times of water through the viscometer used in this work compared with the values obtained by Simpson |92|.

This work (water)	Simpson (acetone)
Temperature = 25 ± 0,002°C	Temperature = 25 ± 0,002°C
155,235	392,541
155,239	392,544
155,235	392,551
155,234	392,549
155,236	392,559
155,231	392,552
155,239	392,544
155,227	392,541
155,237	392,540
155,233	392,534
155,237	
155,230	
155,231	
155,232	
155,230	

Mean = 392,546 s

Standard deviation = ± $0,012^0$s

= ± $0,003^1$%.

Mean = 155,234 s

Standard deviation = ± $0,004^1$s

= ± $0,002^6$ %

FIGURE 2.1

UBBELOHDE SUSPENDED-LEVEL VISCOMETER

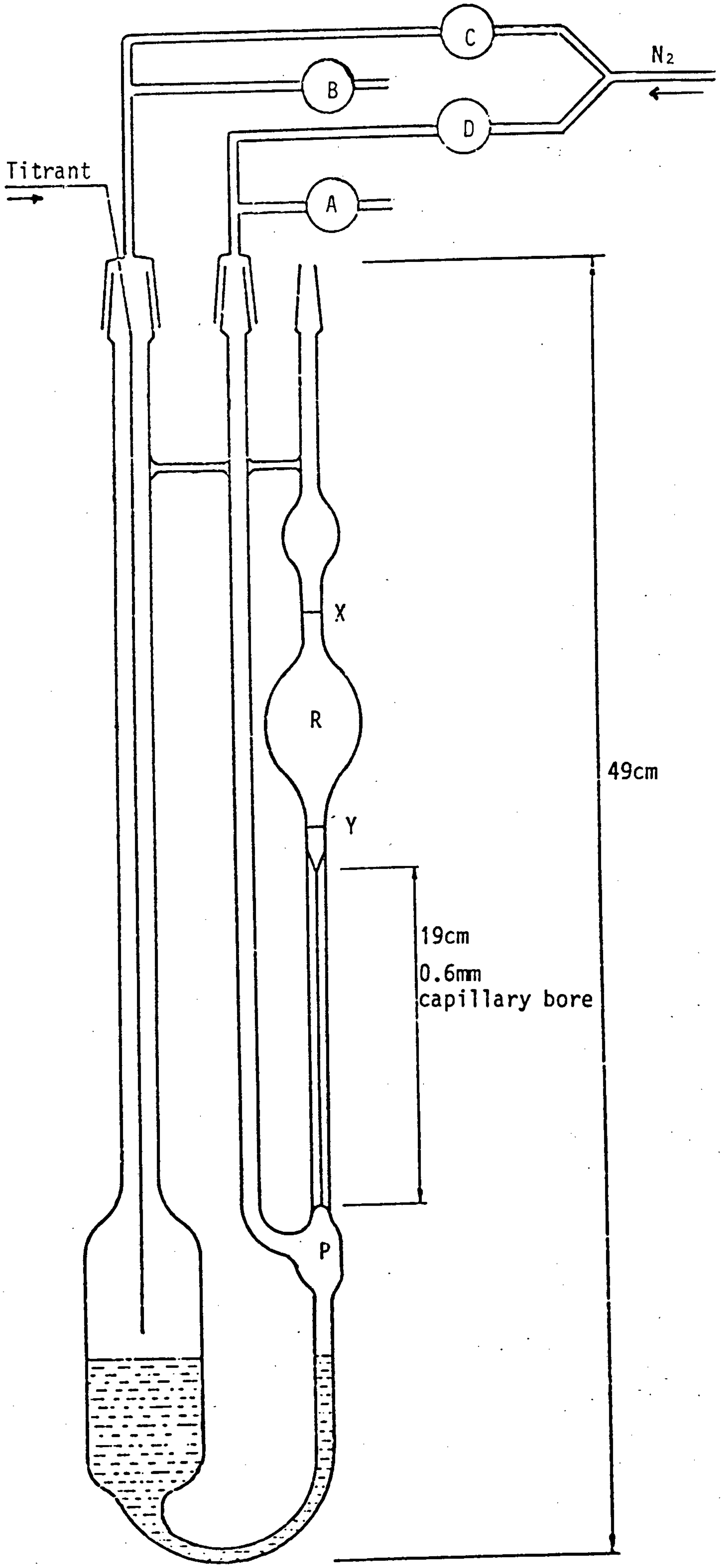


FIGURE 2.2

OPTICAL SYSTEM

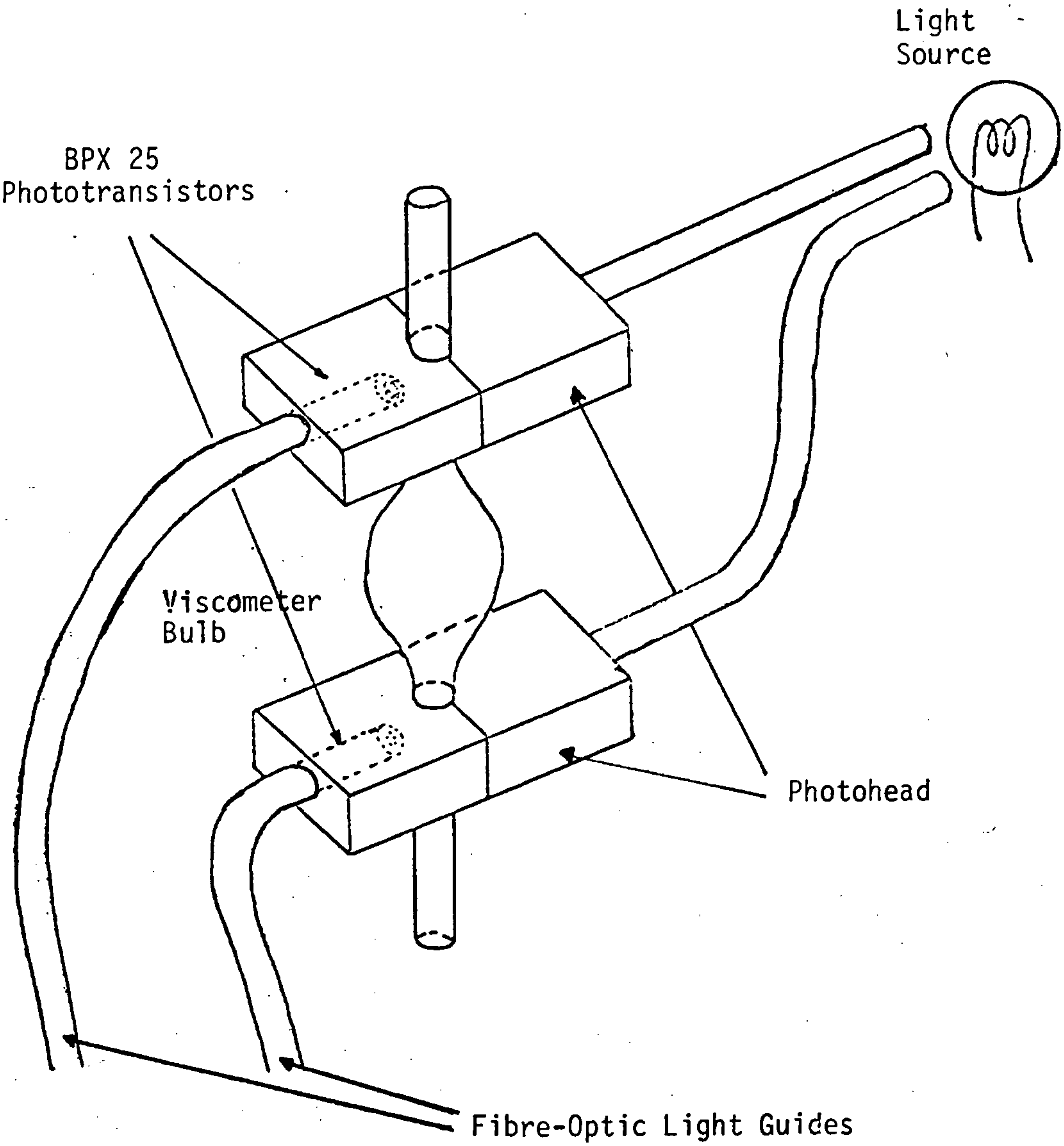
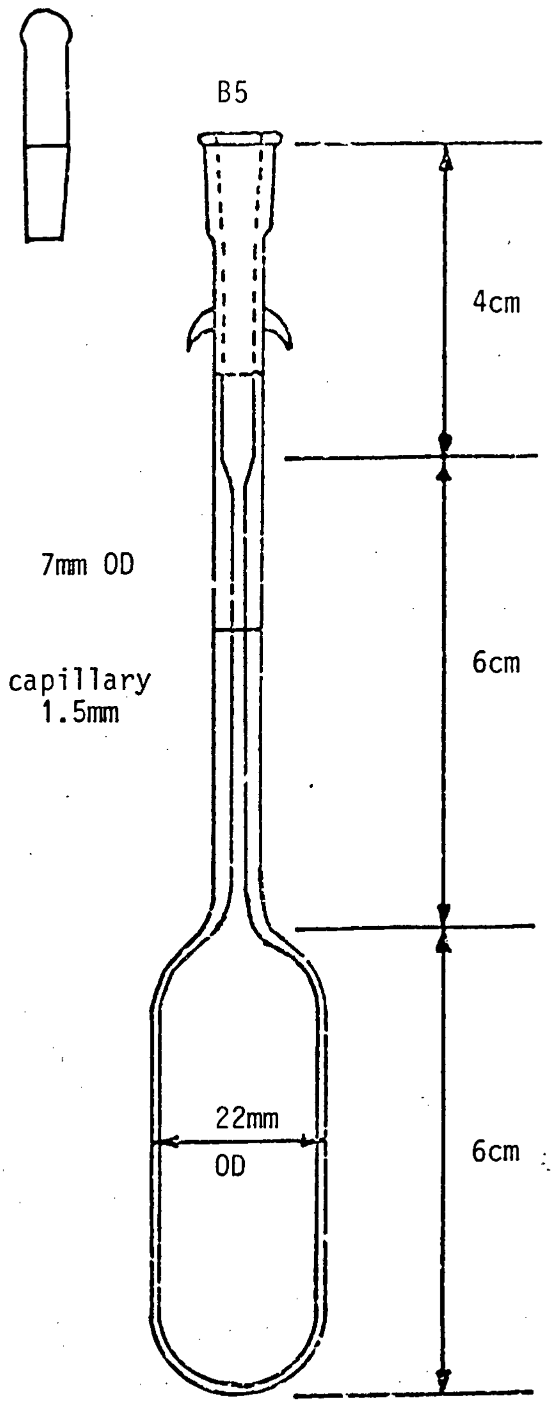


FIGURE 2.3

BINGHAM PYCNOMETER

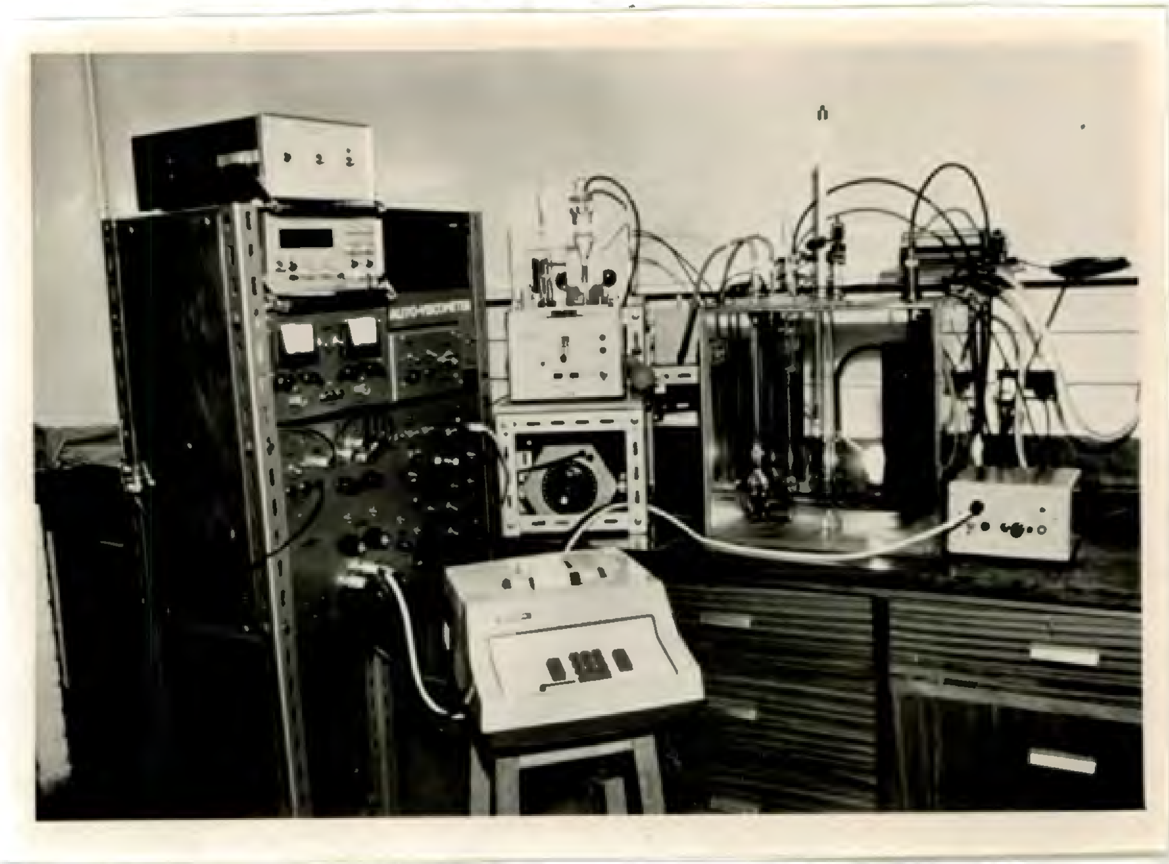


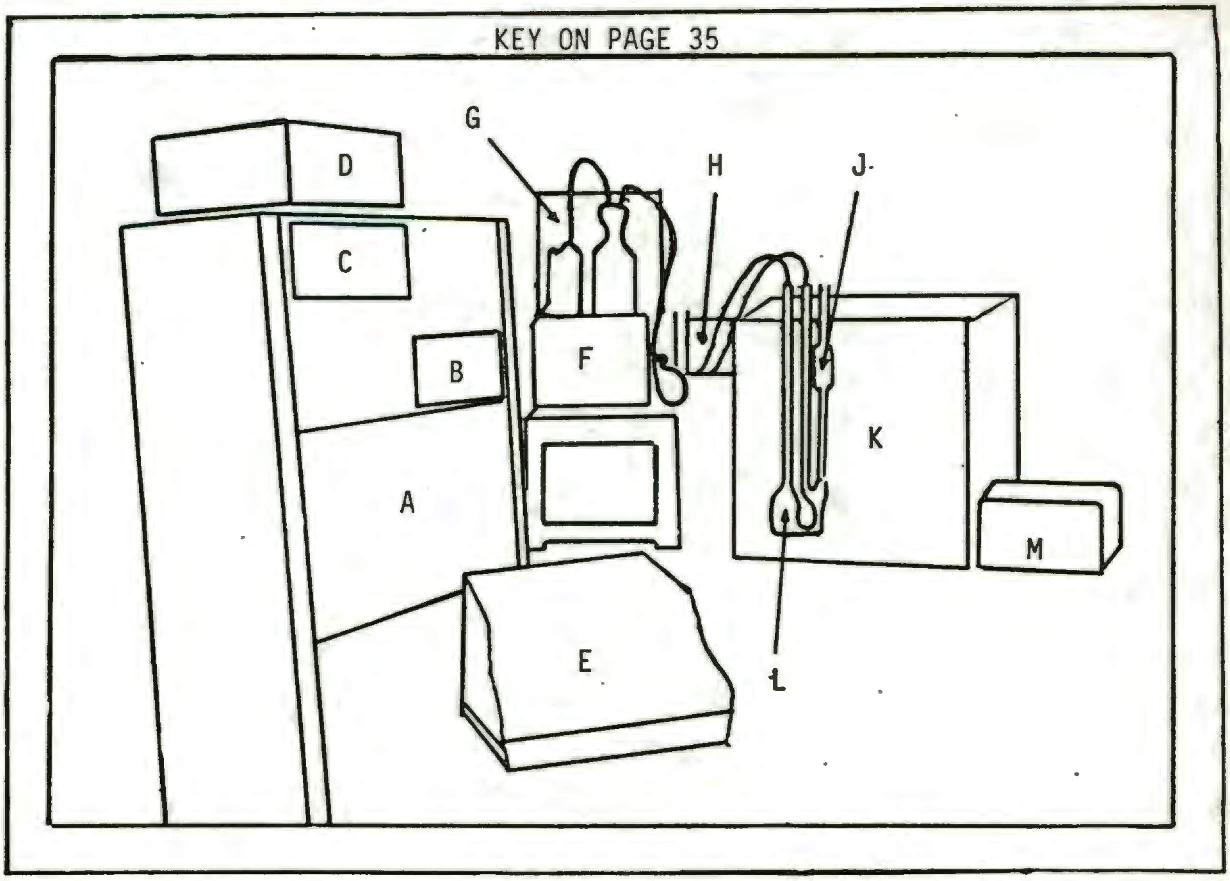
KEY TO FIGURE 2.4

A	Main control Unit - houses logic circuitry, PSU 61, stabilised 24 V PSU, output stage and neon indicators.
B	Output stage power supply (PSU).
C	Venner TSA 6616/MZ digital timer.
D	Venner TSA 301 serialiser (printer control unit).
E	Addo-X printer.
F	Radiometer autoburette ABU 12 b.
G	Variable intensity light source.
H	Solenoid valve assembly.
J	Photohead (stainless steel).
K	Thermostat both (water at 25°±0,005°C).
L	Suspended-level viscometer.
M	Fail-safe device.

FIGURE 2.4

LABORATORY SET-UP




KEY ON PAGE 35

3. THE VISCOSITY OF DILUTE SOLUTIONS OF STRONG ELECTROLYTES

In dilute solutions ($\lesssim$ 0,1 M) there are two effects which contribute to the relative viscosity of strong electrolytes *viz.* long range electrostatic forces and ion-solvent interaction. As has already been mentioned the equations for calculating both A for simple electrolytes, and the a-coefficient for mixtures have been derived from first principles using the interionic attraction theory developed by Debye and Hückel as starting point. For these derivations the reader is referred to the relevant papers |25-31, 79, 97|. Since the mathematical manipulations involved in obtaining values for a can be rather confusing, and since the expression for A is often given in different forms in different papers, both will be illustrated in detail.

3.1 LONG-RANGE ELECTROSTATIC FORCES

Since the ratio of the Jones-Dole coefficients $|A|/|B|$ is generally quite small (∿0,1) the electrostatic contribution to the viscosity increment is soon swamped by the term, Bc, as the concentration of an electrolyte solution increases. However, as the concentration approaches zero the square root term becomes predominant and the Jones-Dole equation (1.4) approximates to

$$\eta_{rel} = 1 + A\sqrt{c} \quad . \tag{3.1}$$

In very dilute solutions the electrostatic contribution to the viscosity is important, and both the expressions for A and a will be dealt with in this section. Asmus' terminology will be retained throughout for the sake of consistency as his representation |6| of the Onsager and Fuoss equation |79| constitutes the largest part of the discussion.

3.1.1 Calculation of A for simple strong electrolytes

The general expression for the A-coefficient of any single electrolyte solution as derived by Falkenhagen and Vernon |31| is given in a slightly rearranged form as:

$$A = \frac{\varepsilon\sqrt{N}}{30\sqrt{4000k\pi}} \times \frac{1}{\eta_o\sqrt{DT}} \times \sqrt{\frac{\nu_1 z_1}{z_1 + z_2}} \times \frac{1}{u_1 u_2}\left[\frac{u_1 z_2 + u_2 z_1}{4} - \frac{z_1 z_2 (u_1 - u_2)^2}{\left(\sqrt{u_1 z_1 + u_2 z_2} + \sqrt{(u_1 + u_2)(z_1 + z_2)}\right)^2}\right] (\text{mol/litre})^{-\frac{1}{2}} \qquad (3.2)$$

where N = Avogadro's number (6,022 045x10^{23} mol^{-1})

ν_1, ν_2 = the dissociation numbers of ions

z_1, z_2 = absolute values of the valencies of ions

k = Boltzman constant (1,380 662x10^{-16} erg deg.$^{-1}$)

u_1, u_2 = absolute mobilities of ions

D = dielectric constant of solvent

ε = electronic charge (4,804 98x10^{-10} esu)

η_o/...

η_o = viscosity of pure solvent in poise

T = absolute temperature

Since this expression is normally rewritten in a more convenient form in terms of equivalent conductivities (e.g. Kaminsky |59|), this alternative formula will now be derived.

The absolute mobility of the i-th ion, u_i, is related to the molar ionic conductivity at infinite dilution, L_i, by the following expression |31 p.547|:

$$L_i = u_i N \varepsilon^2 z_i^2 / c^2 \times 10^{-9} \qquad (3.3)$$

(L_i in units of $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$)

Since the electronic charge = $4{,}803 \times 10^{-10}$ esu

$$= e \times c \qquad (3.4)$$

where e = electronic charge = $1{,}602\ 1 \times 10^{-20}$ emu (c.g.s. units)

$c = 2{,}997\ 9 \times 10^{10}\ \text{cm s}^{-1}$

we can write

$$L_i = u_i N e^2 z_i^2 10^9 \qquad (3.5)$$

Since $\Lambda_i = L_i / z_i$ (3.6)

where Λ_i is the equivalent conductivity in $\text{ohm}^{-1}\ \text{cm}^2\ \text{equiv.}^{-1}$

we have

$$u_i = \Lambda_i / N e^2 z_i 10^9 \qquad (3.7)$$

Substituting (3.7) into (3.2) one obtains

A/...

$$A = \frac{1{,}458}{\eta_\circ\sqrt{DT}} \sqrt{\frac{\nu_1 z_1}{(z_1 + z_2)}} \times \frac{1}{\Lambda_1 \Lambda_2} \left[\frac{\Lambda_1 z_2^2 + \Lambda_2 z_1^2}{4} - \frac{(\Lambda_1 z_2 - \Lambda_2 z_1)^2}{\left\{\sqrt{\Lambda_1 + \Lambda_2} + \sqrt{\Lambda_1 z_2 + \Lambda_2 z_1} \times \sqrt{\frac{(z_1 + z_2)}{z_1 z_2}}\right\}^2} \right] (\text{mol/litre})^{-\frac{1}{2}} \qquad (3.8)$$

Theoretical values calculated for A using equation (3.8) are generally in good agreement with experimental values.

At 25°C D = 78,3, $\eta_\circ$ = 0,008 904 poise, $\Lambda(Na^+)$ = 50,9, $\Lambda(Cl^-)$ =75,5, $\Lambda(Li^+)$ = 40, $\Lambda(SO_4^{2-})$ = 79, and substitution into (3.8) yields A values of 0,006 1 and 0,016 5 for NaCl and Li_2SO_4 respectively. This compares well indeed with the experimentally determined values of 0,006 2 and 0,016 7.

3.1.2 Calculation of "a" for mixtures of electrolytes

Onsager and Fuoss |79| derived theoretically from hydrodynamical considerations and the Debye-Hückel equilibrium theory an equation to evaluate the elctrostatic contribution towards the viscosity of a multiionic solution. Asmus |6| represents this electrostatic increment in viscosity for a mixture of *i* ionic species as

$$\Delta\eta = \eta - \eta_\circ = 0{,}362 \left[\frac{\Gamma}{DT}\right]^{\frac{1}{2}} \left[\sum_i \frac{\mu_i z_i}{\Lambda_i} - 4\underline{\underline{r}} \sum_{n=0}^{\infty} \alpha_n \underline{\underline{s}}^{(n)} \right] \qquad (3.9)$$

where $\Gamma = \sum_i c_i z_i^2$ (twice the conventional 'ionic strength'), D is the dielectric constant of the pure solvent, c_i the molar concentration, z_i the absolute value of the valency, and Λ_i the equivalent conductivity of the i-th ionic species.

μ_i represents the contribution of the i-th ionic species to Γ such that

$$\mu_i = \Gamma_i/\Gamma = c_i z_i^2 / \sum_i c_i z_i^2 \quad . \tag{3.10}$$

Equation (3.9) is of the form

$$n/n_o = 1 + a\Gamma^{\frac{1}{2}} \tag{1.5}$$

with the coefficient a independent of Γ, but dependent upon the composition of the mixture, and thus clearly identifiable with the A coefficient of the Jones-Dole equation (1.4).

The first term in the brackets of equation (3.9) is the most important. The second becomes more significant the greater the differences between the equivalent conductivities of the different ions become. The second term is the scalar product of a row vector $\underline{\underline{r}}$ and an infinite sum of column vectors $\underline{\underline{s}}^{(n)}$ multiplied by $4\alpha_n$ where α_n is a numerical factor.

The factors, α_n, are calculated according to the scheme:

$$\left.\begin{aligned} \alpha_o &= -3 + 2\sqrt{2} \\ \alpha_n &= -4 + 2\sqrt{2} \sum_{p=0}^{n} \binom{\frac{1}{2}}{p} \text{ for } n \geq 1 \end{aligned}\right\} \tag{3.11}$$

For/...

For the first eight coefficients α takes the following values:

$\alpha_0 = -0{,}171\ 572\ 9$ $\qquad$ $\alpha_1 = 0{,}242\ 640\ 7$

$\alpha_2 = -0{,}110\ 912\ 7$ $\qquad$ $\alpha_3 = 0{,}065\ 864\ 0$

$\alpha_4 = -0{,}044\ 621\ 4$ $\qquad$ $\alpha_5 = 0{,}032\ 718\ 4$

$\alpha_6 = -0{,}025\ 286\ 6$ $\qquad$ $\alpha_7 = 0{,}020\ 288\ 6$

$\alpha_8 = -0{,}016\ 741\ 5$ $\qquad$ $\alpha_9 = 0{,}014\ 116\ 8$

In the original paper by Asmus |6| the numerical factors, α_n, are unfortunately listed with α_0 in place of α_1 and α_n in place of α_{n-1}. The correct values are as above.

The components of the vector $\underline{\underline{r}}$ are defined by

$$\underline{\underline{r}}_i = 1 - \left[(z_i/\Lambda_i)/\ (\overline{z/\Lambda}\,) \right] \tag{3.12}$$

There are as many terms as there are ionic species in the system. $(\overline{z/\Lambda})$ is a mean value defined by:

$$\begin{aligned}(\overline{z/\Lambda}) &= (\sum_i \Gamma_i (z_i/\Lambda_i))/\sum_i \Gamma_i \\ &= \sum_i \Gamma_i\ (z_i/\Lambda_i)/\Gamma \\ &= \sum_i \mu_i (z_i/\Lambda_i)\end{aligned} \tag{3.13}$$

Of the components of the vectors $\underline{\underline{s}}^{(n)}$, only those of the first vector, $\underline{\underline{s}}^{(o)}$, are easy to calculate. They are defined by:

$$s_i^{(o)} = \mu_i \left[z_i/\Lambda_i - \overline{(z/\Lambda)^2}/(\overline{z/\Lambda}) \right] \tag{3.14}$$

where/...

where $\overline{(z/\Lambda)^2}$ is a second mean value defined by:

$$\overline{(z/\Lambda)^2} = \sum_i \mu_i (z_i/\Lambda_i)^2 \tag{3.15}$$

Values of $\underline{\underline{s}}^{(n)}$ for all n ≥ 1 are calculated from the recursion formula:

$$\underline{\underline{s}}^{(n)} = (2H - E)\underline{\underline{s}}^{(n-1)} \tag{3.16}$$

where E is the identity matrix

$$\text{i.e. } E = \begin{vmatrix} 1 & 0 & . & 0 \\ 0 & 1 & . & . \\ . & . & . & . \\ 0 & . & . & 1 \end{vmatrix}$$

and H is a matrix whose elements are given by:

$$h_{ji} = \delta_{ji}\left[\sum_i \mu_i \frac{(\Lambda_i/z_i)}{\{(\Lambda_i/z_i) + (\Lambda_j/z_j)\}}\right] + \mu_j \frac{(\Lambda_j/z_j)}{\{(\Lambda_i/z_i) + (\Lambda_j/z_j)\}} \tag{3.17}$$

$$\text{where } \delta_{ji} = \begin{array}{l} 0 \text{ when } i \neq j \\ 1 \text{ when } i = j \end{array}$$

If there are n different ions in the mixed electrolyte H will be an n x n matrix with n^2 components. A useful simplification can be introduced since it can be shown that the components are not independent but are related by

$$h_{ii} = \mu_i + \sum_{k \neq i} h_{ki} . \tag{3.18}$$

This simplifies the computations considerably.

Moreover,/...

Moreover, since ions cannot be introduced individually into solution, conditions of mass-charge balance simplifies the evaluation of μ_i. For example in a mixture of $CuSO_4$ and KCl it follows that $\mu_{Cu} = \mu_{SO_4}$, and $\mu_K = \mu_{Cl}$.

Using the sequence of operations defined by equations (3.10) to (3.18) it is possible to compute the desired value of a in equation (1.5). The method will be illustrated by first calculating the value of a for a simple electrolyte, NaCl, in order to compare the answer with that obtained in 3.1.1 above, and then for a 1:1 mixture of NaCl and $BaCl_2$.

For NaCl the data are as follows:

ion	molar concentration	equivalant conductivity |109|
Na^+	c_1	50,9
Cl^-	c_2	75,5

Clearly $c_1 = c_2$, $\Gamma_1 = c_1$, $\Gamma_2 = c_2$ and

$\Gamma = 2c_1$.

Thus from equation (3.10) $\mu_1 = \mu_2 = 0,5$

From equation (3.13)

$$\overline{(z/\Lambda)} = |\ c_1 \times 1/50,9 + c_1 \times 1/75,5\ |/2c_1$$

$$= 0,016\ 445\ 7 \quad .$$

Similarly from equation (3.15)

$$\overline{(z/\Lambda)^2} = 0,000\ 280\ 7 \quad .$$

From/...

From equation (3.12) the components of $\underline{\underline{r}}$ can now be calculated:

$$r_1 = 1 - (1/50{,}9)/0{,}016\ 445\ 7$$

$$= -\ 0{,}194\ 620\ 2$$

$$r_2 = +\ 0{,}194\ 620\ 3$$

From equation (3.14) the components of $\underline{\underline{s}}^{(o)}$ can be calculated.

$$s_1^{(o)} = 0{,}5|1/50{,}9 - 0{,}000\ 280\ 7/0{,}016\ 445\ 7\ |$$

$$= +\ 0{,}001\ 289\ 0$$

$$s_2^{(o)} = -\ 0{,}001\ 911\ 6$$

To obtain the values of $s_i^{(n)}(n \geqq 1)$ through the recursion formula (3.16) the components of the matrix H have to be calculated first. To do this first calculate elements for which $i \neq j$ using equation (3.17).

$$h_{21} = (0{,}5)(75{,}5/1)/|(50{,}9/1) + (75{,}5/1)|$$

$$= 0{,}298\ 655$$

$$h_{12} = 0{,}201\ 345$$

Now using equation (3.18)

$$h_{11} = 0{,}5 + 0{,}298\ 655$$

$$= 0{,}798\ 655$$

$$h_{22} = 0{,}701\ 345$$

So $H = \begin{vmatrix} 0{,}798\ 655 & 0{,}201\ 345 \\ 0{,}298\ 655 & 0{,}701\ 345 \end{vmatrix}$

and

$2H - E = \begin{vmatrix} 0{,}597\ 310 & 0{,}402\ 690 \\ 0{,}597\ 310 & 0{,}402\ 690 \end{vmatrix}$

Using/...

Using equation (3.16) we obtain

$$s_1^{(1)} = 1{,}5 \times 10^{-7} = s_1^{(2)} = s_1^{(3)} \text{ etc.}$$
$$s_2^{(1)} = 1{,}5 \times 10^{-7} = s_2^{(2)} \qquad s_2^{(3)}$$

We are now able to compute the second term in brackets of equation (3.9).

$$4\alpha_o\underline{\underline{rs}}^{(o)} = 4(-0{,}171\ 572\ 9)\begin{vmatrix}-0{,}194\ 620\ 2 & 0{,}194\ 620\ 3\end{vmatrix}\begin{vmatrix}+\ 0{,}001\ 289\ 0\\ -\ 0{,}001\ 911\ 6\end{vmatrix}$$
$$= 0{,}000\ 427$$
$$4\alpha_1\underline{\underline{rs}}^{(1)} = 1{,}46\times10^{-14} = 4\alpha_2\underline{\underline{rs}}^{(2)} \text{ etc.}$$

Therefore

$$4\underline{\underline{r}}\sum_{n=0}^{\infty}\alpha_n\underline{\underline{s}}^{(n)} \cong 0{,}000\ 427$$

$$\left|\sum_i \mu_i z_i/\Lambda_i - 4\underline{\underline{r}}\sum_{n=0}^{\infty}\alpha_n\underline{\underline{s}}^{(n)}\right| = 0{,}016\ 446 - 0{,}000\ 427$$
$$= 0{,}016\ 019$$

It follows that

$$a = (0{,}362/\eta_o\sqrt{DT})0{,}016\ 019$$
$$= 0{,}004\ 262$$

(using T = 298,15 K, η_o = 0,008 904 poise, D = 78,3)

For a single electrolyte

$$A\sqrt{c} = a\sqrt{\Gamma}$$

thus

$$A = a\sqrt{\nu_1 z_1^2 + \nu_2 z_2^2}$$
$$= a\sqrt{2}$$
$$= 0{,}0006\ 0$$

This agrees well with the value A = 0,006 1 calculated in 3.1.1

above/...

above using the Falkenhagen and Vernon equation (3.8) and with the experimental value A = 0,006 2

To show how equation (3.9) can be used for mixtures, *a* will now be computed for a 1:1 mixture of NaCl and $BaCl_2$ at 35°C. This system is chosen because work published by Chakravarti and Prasad |17| on $NaCl/BaCl_2$ mixtures will be discussed further on.

The equivalent conductivities at 35°C were obtained by graphical interpolation, using values at temperatures between 0° and 100°C as published in the International Critical Tables |106|. The data are as follows.

ion	molar concentration	equivalent conductivity
Na^+	c_1	63
Cl^-	c_2	91
Ba^{2+}	c_3	80

Clearly $c_1 = c_3$ and $c_2 = 3c_1$.

Therefore $\Gamma = c_1 \times 1^2 + 3c_1 + 1^2 + c_1 \times 2^2 = 8c_1$ and

$$\mu_1 = 0{,}125, \quad \mu_2 = 0{,}375, \quad \text{and } \mu_3 = 0{,}5$$

From equation (3.13)

$$(\overline{z/\Lambda}) = \sum_i \mu_i z_i/\Lambda_i = 0{,}018\ 605\ 0$$

Similarly from equation (3.15)

$$\overline{(z/\Lambda)^2} = 0{,}000\ 389\ 3$$

From equations (3.12) and (3.15) the components of the vectors $\underline{r}$ and $\underline{\underline{s}}^{(o)}$ can be calculated.

$r_1 = +0{,}146\ 841\ 4$ $\qquad s_1^{(o)} = -0{,}000\ 631\ 4$

$r_2 = +0{,}409\ 351\ 7$ $\qquad s_2^{(o)} = -0{,}003\ 725\ 8$

$r_3 = -0{,}343\ 724\ 8$ $\qquad s_3^{(o)} = +0{,}002\ 037\ 8$

Using equations (3.17) and (3.18) the terms of the matrix H can now be calculated. Since there are three ionic species present in the system, H is a 3 x 3 matrix.

$$H = \begin{vmatrix} 0{,}540\ 76 & 0{,}051\ 14 & 0{,}076\ 46 \\ 0{,}221\ 59 & 0{,}578\ 81 & 0{,}260\ 50 \\ 0{,}194\ 17 & 0{,}152\ 67 & 0{,}836\ 96 \end{vmatrix}$$

$$2H - E = \begin{vmatrix} -0{,}081\ 52 & 0{,}102\ 28 & 0{,}152\ 92 \\ 0{,}443\ 18 & 0{,}157\ 62 & 0{,}521\ 00 \\ 0{,}388\ 34 & 0{,}305\ 34 & 0{,}673\ 92 \end{vmatrix}$$

$\underline{\underline{s}}^{(n)}$ $n \geqq 1$ can now be calculated using equation (3.16):

$$s_1^{(1)} = \begin{vmatrix} 0{,}081\ 52 & 0{,}102\ 28 & 0{,}152\ 92 \end{vmatrix} \begin{vmatrix} -0{,}000\ 631\ 4 \\ -0{,}003\ 725\ 8 \\ 0{,}002\ 037\ 8 \end{vmatrix}$$

$$= -0{,}000\ 120\ 9$$

$$s_2^{(1)} = \begin{vmatrix} 0{,}443\ 18 & 0{,}157\ 62 & 0{,}521\ 00 \end{vmatrix} \begin{vmatrix} -0{,}000\ 631\ 4 \\ -0{,}003\ 725\ 8 \\ 0{,}002\ 037\ 8 \end{vmatrix}$$

$$= +0{,}000\ 194\ 6$$

$$s_3^{(1)} = \begin{vmatrix} 0{,}388\ 34 & 0{,}305\ 34 & 0{,}673\ 92 \end{vmatrix} \begin{vmatrix} -0{,}000\ 631\ 4 \\ -0{,}003\ 725\ 8 \\ +0{,}002\ 037\ 8 \end{vmatrix}$$

$$= -0{,}000\ 009\ 5$$

and/...

and similarly

$$s_1^{(2)} = +0{,}000\ 008\ 5 \qquad s_1^{(3)} = -0{,}000\ 001\ 2$$

$$s_2^{(2)} = -0{,}000\ 027\ 9 \qquad s_2^{(3)} = +0{,}000\ 002\ 6$$

$$s_3^{(2)} = +0{,}000\ 006\ 1 \qquad s_3^{(3)} = -0{,}000\ 001\ 1$$

The scalar products can now be calculated.

$$4\alpha_o\underline{\underline{rs}}^{(o)} = 0{,}001\ 591\ 0$$

$$4\alpha_o\underline{\underline{rs}}^{(1)} = -0{,}000\ 063\ 3$$

$$4\alpha_o\underline{\underline{rs}}^{(2)} = 0{,}000\ 005\ 4$$

$$4\alpha_o\underline{\underline{rs}}^{(3)} = 0{,}000\ 000\ 3$$

Higher terms can be neglected.

$$4\underline{\underline{r}} \cdot \sum_{n=0}^{\infty} \alpha_n s^n \cong 0{,}001\ 660\ 0$$

If now follows that

$$a = (0{,}362/\eta_o\sqrt{DT})(0{,}018\ 605\ 0 - 0{,}001\ 660)$$

$$= 0{,}005\ 62$$

(using the values $T = 308{,}15$ K, $D = 74{,}83$, and $\eta_o = 0{,}007\ 194$ poise)

The value obtained experimentally by Chakravarti and Prasad is 0,005 5, which compares well with the calculated value. The agreement is particularly satisfying since $BaCl_2$ affords a rare case where the theoretical value of A does not agree so well with the experimental one.

A (calculated) = 0,015 2, using equation (3.8), as opposed to A (experimental) = 0,018 for $BaCl_2$ at 35°C |16|.

Since/...

Since the computation of a single value for *a* can be very time-consuming when using a hand calculator, a suitable computer program was prepared to facilitate matters. This FORTRAN program can be found in Appendix A.

The A-coefficients of several single electrolytes were computed for comparison with published experimental value. The results are tabulated in Table 3.1.1 below. All values are at 25°C. Values for equivalent conductivities were obtained from the CRC Handbook |107|.

TABLE 3.1.1

ionic species	A(calculated)	A(experimental)
$AgNO_3$	0,005 6	0,006 3
$BaCl_2$	0,014 7	
$CaCl_2$	0,015 4	
$Ca(OH)_2$	0,011 0	
CsI	0,004 9	0,003 9
$CuSO_4$	0,022 5	0,022 6
HCl	0,002 2	
H_2SO_4	0,007 5	0,007 8
KBr	0,004 9	
KCl	0,005 0	0,000 52
$K_3Fe(CN)_6$	0,022 1	
$KClO_4$	0,005 4	
$K_4Fe(CH)_6$	0,034 2	0,036 9
$KHCO_3$	0,006 5	
KI	0,005 0	
KIO_4	0,005 9	
KNO_3	0,005 2	0,005 0

Continued/...

TABLE 3.1.1 continued

ionic species	A(calculated)	A(experimental)
$KReO_4$	0,005 9	
K_2SO_4	0,013 1	0,014 1
$KBrO_3$	0,005 8	0,005 8
$KMnO_4$	0,005 5	0,005 8
$LaCl_3$	0,027 7	
$LiCl$	0,006 7	
$LiClO_4$	0,007 2	
Li_2SO_4	0,016 4	0,016 7
$MgCl_2$	0,016 6	
$MgSO_4$	0,022 8	0,023 0
NH_4Cl	0,005 0	0,005 2
$NaCl$	0,006 0	0,006 2
$NaClO_4$	0,006 4	
NaI	0,006 0	
$NaOH$	0,003 6	
Na_2SO_4	0,015 0	
$SrCl_2$	0,015 4	

In the above calculations the following values were used for the equivalent conductivities at infinite dilution (in units of ohm^- cm^2 $equiv.^-$): Ag^+ = 62,7, NO_3^- = 70,6, Ba^{2+} = 65, Cl^- = 75,5, OH^- = 192, Cu^{2+} = 55, SO_4^{2-} = 79, Cs^+ = 78,1, I^- = 75,9, H^+ = 350, K^+ = 74,5, Br^- = 77,4, $Fe(CN)_6^{3-}$ = 100, ClO_4^- = 65,5, $Fe(CN)_6^{4-}$ = 111, HCO_3^- = 43,5, IO_4^- = 53,4, ReO_4^- = 53,7, La^{3+} = 72, Li^+ = 39,5, Mg^{2+} = 53,9, NH_4^+ = 74,5, Na^+ = 50,9, Sr^{2+} = 60,3.

From table 3.1.1 it can be seen that the general equation (3.9) gives good agreement between calculated and experimental values for the special case of single electrolytes. Furthermore it has been tested extentively by Asmus on mixtures of $CuSO_4$ and KCl, as well as of $CuSO_4$ and H_2SO_4. Calculated values of a were found in good agreement with experimental values, and the validity of expression (3.9) can be regarded as established.

3.1.3 The additivity of the A-coefficient

Chakravarti *et al.* |17, 18, 19| found experimentally that a mixture of two electrolytes in a definite proportion behaves like a single electrolyte with respect to viscosity when the concentration is changed without affecting the proportion of the components of the mixture by diluting with water. The variation in viscosity was represented by an equation of the Jones-Dole type. $(\eta_{rel} - 1)/\sqrt{c}$ was plotted against $\sqrt{c}$ in the normal way, giving a straight line with intercept A* and a slope B*. Here c is now the <u>total</u> molar concentration of the solution, and the Jones-Dole equation becomes

$$\eta_{rel} = 1 + A^*\sqrt{c} + B^*c \qquad (1.7)$$

The conclusion reached was that if the electrolytes were of concentrations c_1 and c_2 and of individual electrostatic coefficients A_1 and A_2 respectively, A* can be calculated from

A*/...

$$A^* = A_1(c_1/(c_1 + c_2)) + A_2(c_2/(c_1 + c_2)) \tag{3.19}$$

Now Asmus has clearly shown that the a-coefficient of equation (1.5) does not vary linearly with composition. However it is not immediately obvious whether or not this implies linearity for A*. A general expression is easily derived for binary mixtures to relate A* to a so as to make theoretical computation of A* possible in order to test its linearity.

Clearly

$$A^*\sqrt{c} = a\sqrt{\Gamma} \quad . \tag{3.20}$$

Suppose we have two electrolytes A_nB_m and D_pE_q with $|A_nB_m| = c_1$ and $|D_pE_q| = c_2$.

Then the total concentration $= c = c_1 + c_2$ (3.21)

Let the valencies of the ionic species A, B, D, and E be z_1, z_2, z_3, z_4 respectively. The ionic concentrations are

$$|A| = nc_1 \qquad |B| = mc_1$$

$$|D| = pc_2 \qquad |E| = qc_2$$

and $\Gamma = (nc_1z_1^2 + mc_1z_2^2 + pc_2z_3^2 + qc_2z_4^2)$ (3.22)

Substituting (3.22) and (3.21) into (3.20) one obtains

$$A^* = a\sqrt{(nc_1z_1^2 + mc_1z_2^2 + pc_2z_3^2 + qc_2z_4^2)/(c_1 + c_2)} \tag{3.23}$$

Chakravarti/...

Chakravarti and Prasad worked on mixtures of $NaCl/MgCl_2$ and $NaCl/BaCl_2$ |17| when they postulated equation (3.19). Tables 3.1.2 and 3.1.3 below contain their experimental values of A* along with theoretical values of α and A* calculated from Asmus' formula (3.9) and equation (3.23). All values are at 35°C. The equivalent conductivity of Mg^{2+} was taken as 67,0, with those of Ba^{2+}, Na^+, and Cl^- as before.

TABLE 3.1.2

$\|NaCl\|:\|MgCl_2\|$	α(calc.)	A*(calc.)	A*(exptl.)
100:0	0,004 35	0,006 2	0,006
90:10	0,004 89	0,007 6	-
80:20	0,005 24	0,008 8	0,009
70:30	0,005 48	0,009 8	-
60:40	0,005 84	0,011 1	-
50:50	0,006 08	0,012 2	-
40:60	0,006 28	0,013 2	0,013
30:70	0,006 46	0,014 1	-
25:73	0,006 53	0,014 6	-
20:80	0,006 61	0,015 1	-
15:85	0,006 68	0,015 5	-
10:90	0,006 75	0,016 0	
5:95	0,006 81	0,016 4	-
0:100	0,006 87	0,016 8	0,017

Table 3.1.3/...

TABLE 3.1.3

$\lvert NaCl\rvert : \lvert BaCl_2\rvert$	a(calc.)	A*(calc.)	A*(exptl.)
100:0	0,004 35	0,006 2	0,006
90:10	0,004 73	0,007 3	-
80:20	0,005 02	0,008 4	-
75:25	0,005 14	0,008 9	0,009
70:30	0,005 23	0,009 4	-
60:40	0,005 45	0,010 3	-
50:50	0,005 61	0,011 2	0,011
40:60	0,005 76	0,012 1	-
30:70	0,005 89	0,012 9	-
25:75	0,005 93	0,013 3	0,015
20:80	0,005 98	0,013 6	-
15:85	0,006 03	0,014 0	-
10:90	0,006 07	0,014 4	-
5:95	0,006 114	0,014 7	-
0:100	0,006 15	0,015 1	0,018

In the NaCl/$MgCl_2$ case theoretical and experimental values of A* agree exactly. Figure 3.1.2 at the end of this section contains a plot of A* vs. molar % NaCl for this system. The plot is not linear but has a definite curvature. Figure 3.1.3 contains the same plot for the mixture of NaCl/$BaCl_2$. It should be noted that theoretical

and/...

and experimental values of A* agree up to 50 mol % NaCl, but deviate for higher concentrations of $BaCl_2$. The experimental data points do fall approximately on a straight line, but the scatter is so great that one would like to see the experiment repeated more accurately, and with more data points taken. Theory again predicts a curve. Figure 3.1.1 shows values of α for both these mixtures plotted against mol % NaCl. The curves have the same shape as those of A* vs percentage composition, with the curvature slightly more exaggerated.

For the sake of completeness values of A* were computed from the values of α reported for the $CuSO_4/KCl$ and $CuSO_4/H_2SO_4$ mixtures by Asmus |6|. These plots of A* vs mol % are found as figures 3.1.4 and 3.1.5. Again both have the same shape as plots of α vs molar percentage as shown in the Asmus paper. It is interesting to note that the plot for the $CuSO_4/H_2SO_4$ mixture has a negative curvature.

It can therefore be concluded that equation (3.19) does not hold good, and that the most accurate way of calculating the electrostatic contribution to the viscosity increment is through the Onsager and Fuoss theory.

FIGURE 3.1.1./...

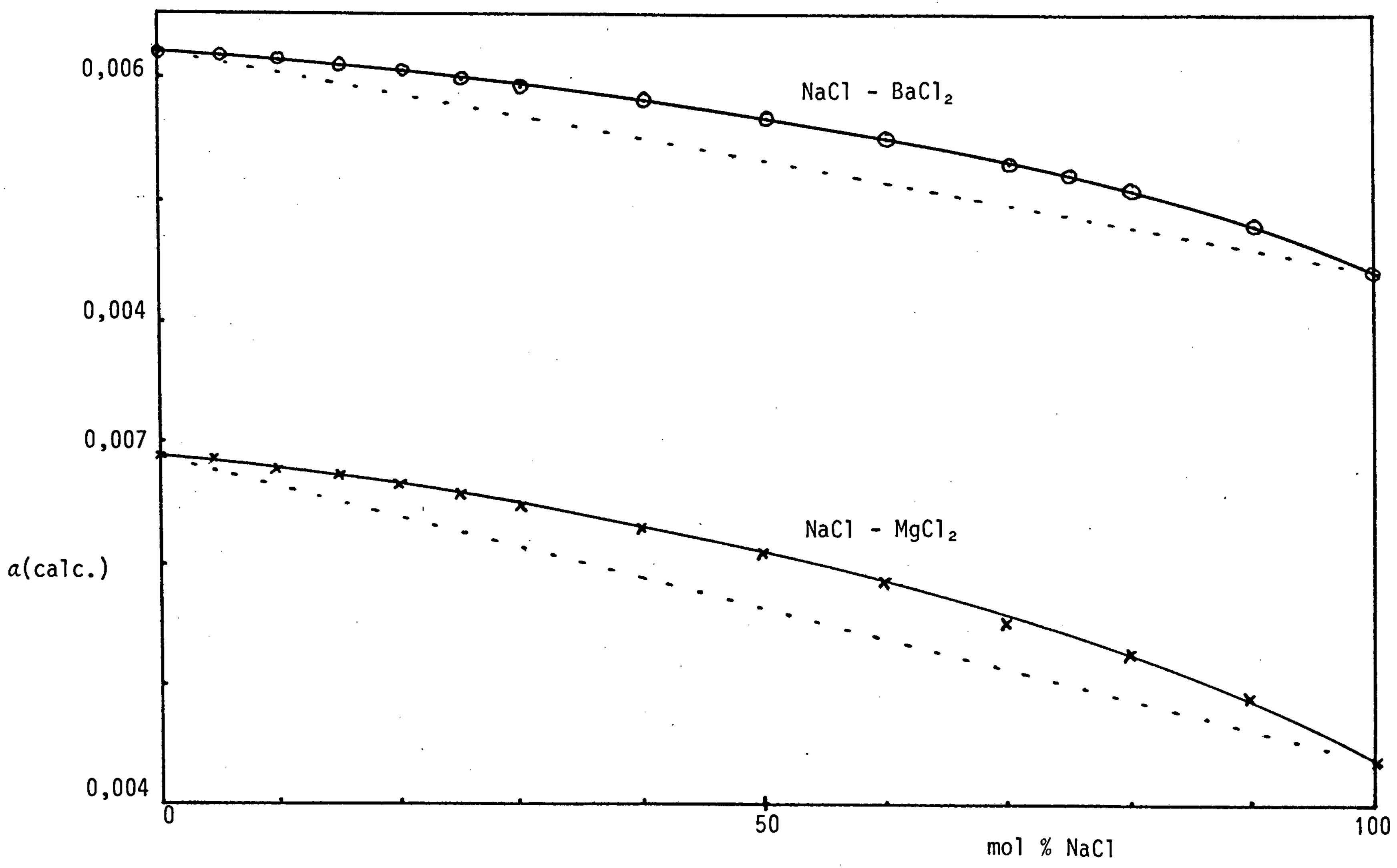


FIGURE 3.1.1: Plot of a(calc.) vs mol % NaCl for mixtures of NaCl - $BaCl_2$ and $MgCl_2$

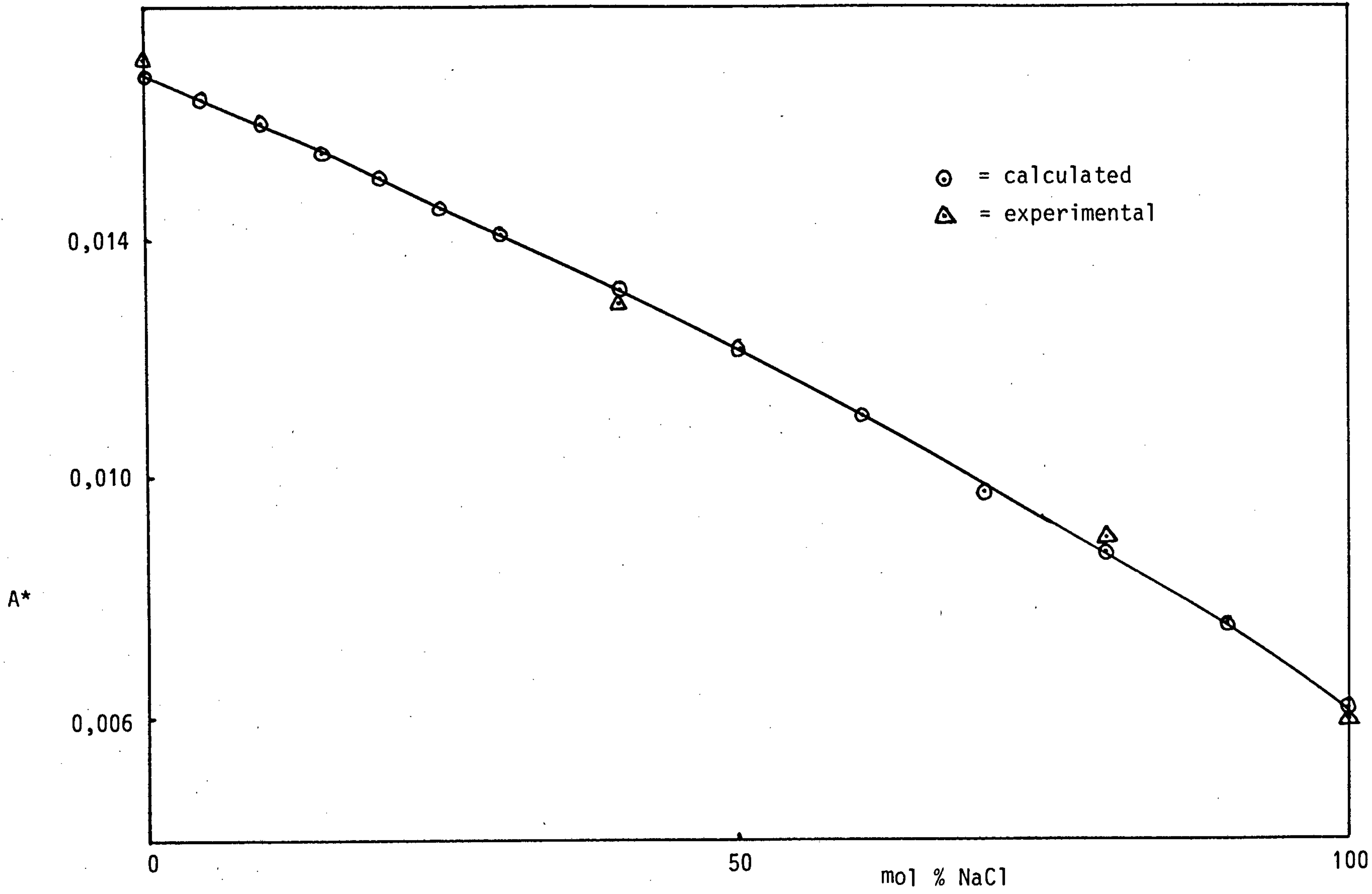


FIGURE 3.1.2: Plot of A* vs mol % NaCl for the mixture NaCl - $MgCl_2$

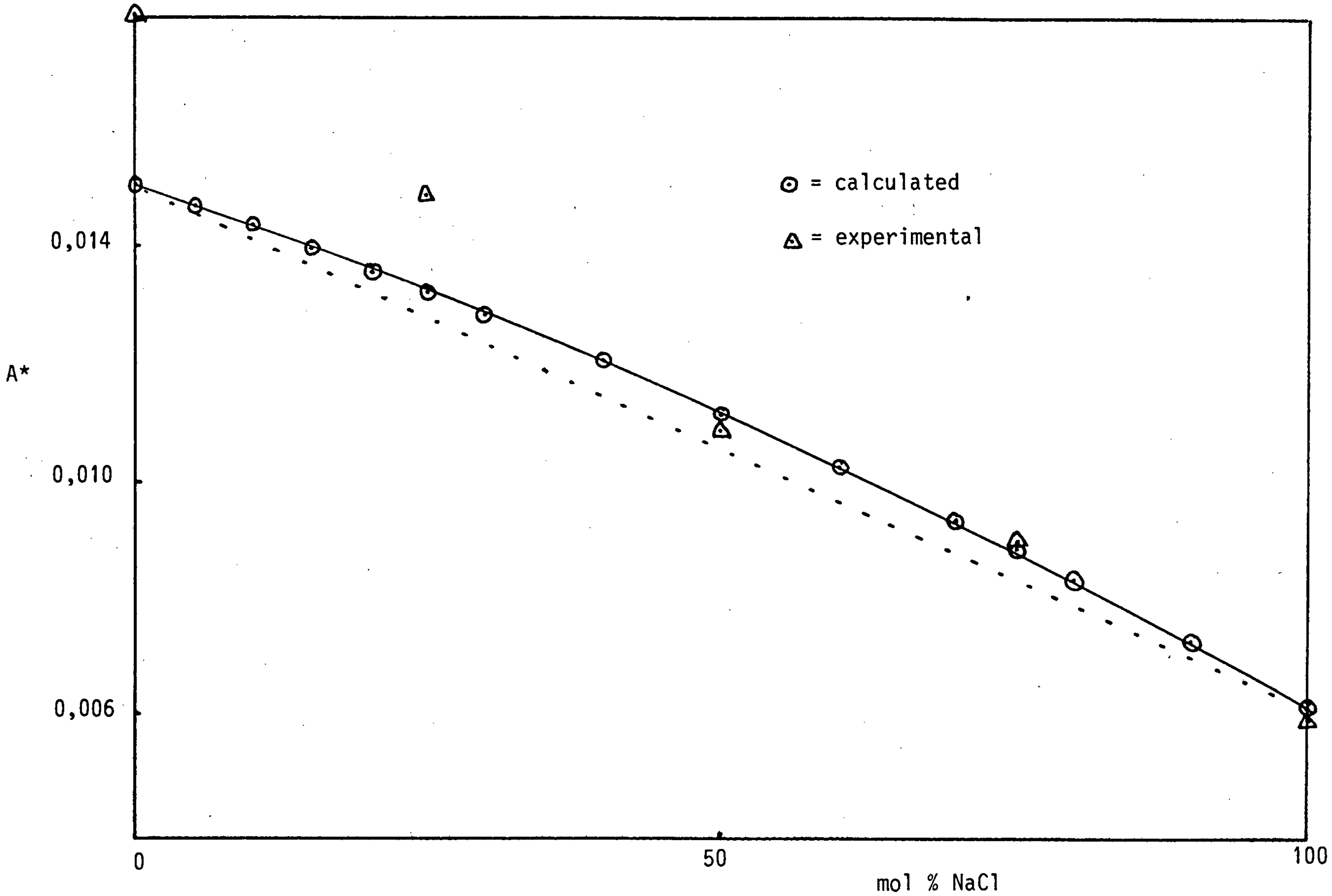
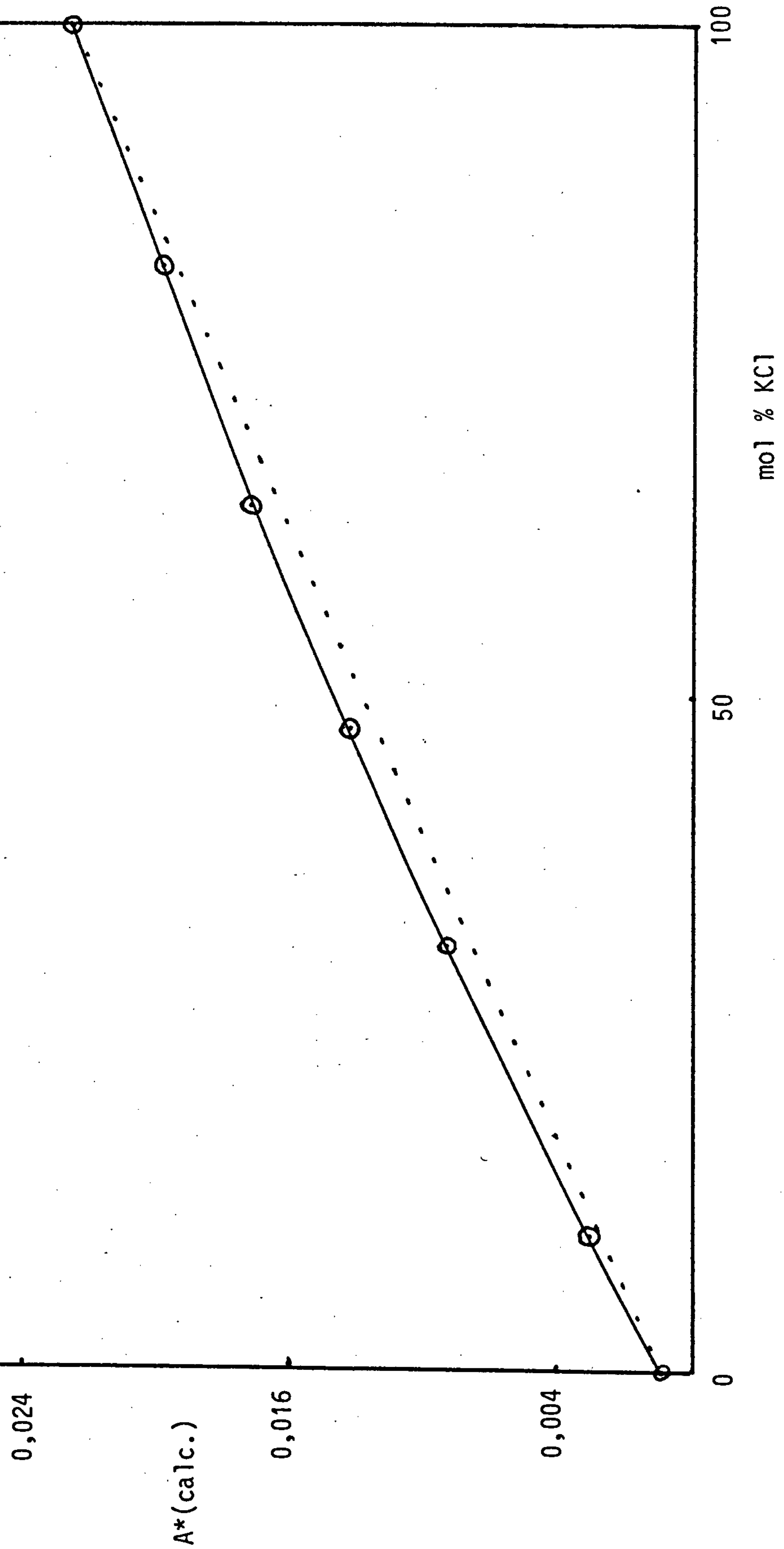


FIGURE 3.1.3: Plot of A* vs mol % NaCl for the mixture NaCl - $BaCl_2$

FIGURE 3.1.4: Plot of A* (calc.) vs mol % $CuSO_4$ for the mixture $CuSO_4$ - KCl



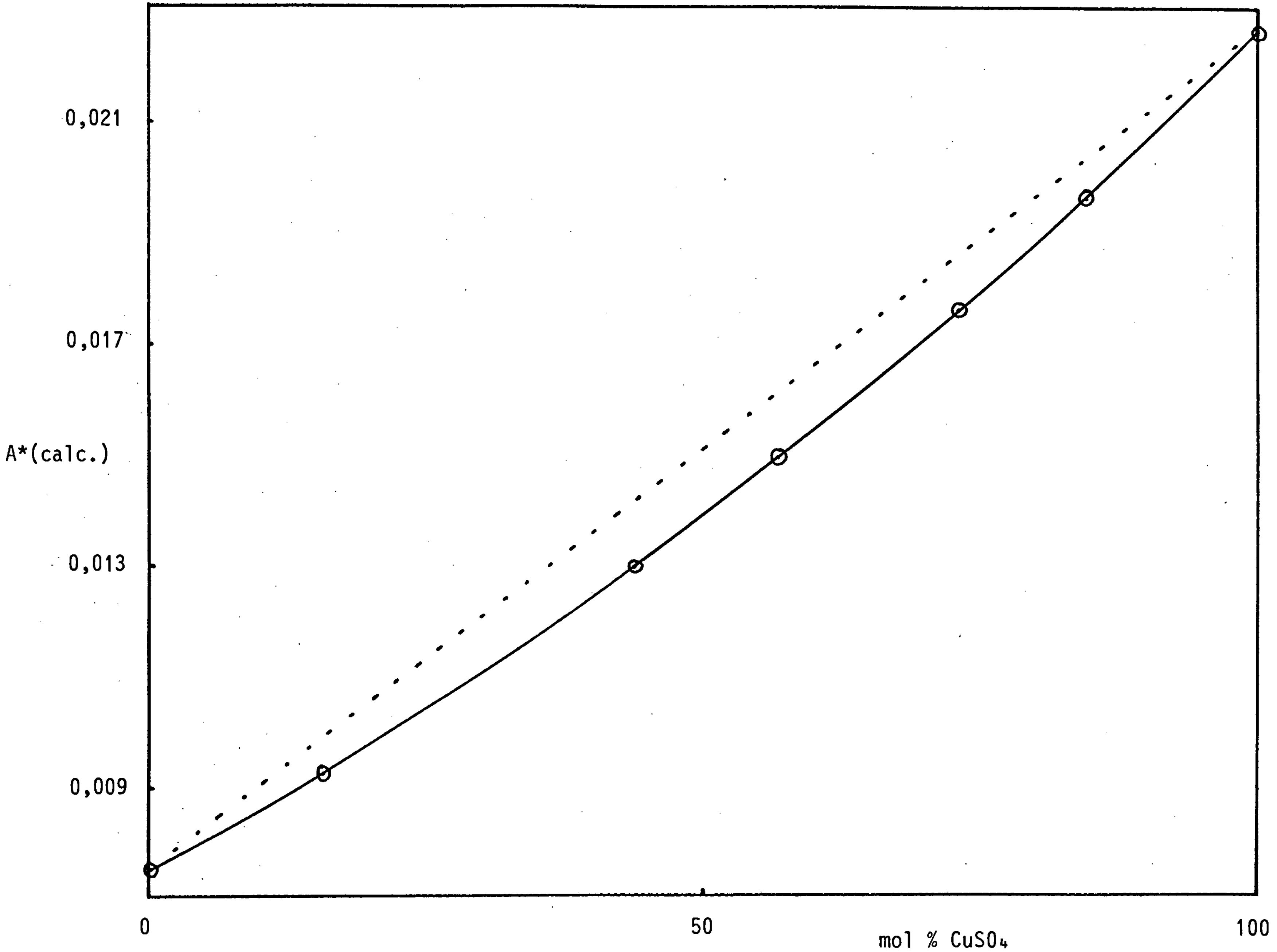


FIGURE 3.1.5: Plot of A*(calc.) vs mol % $CuSO_4$ for the mixture $CuSO_4$ - H_2SO_4

3.2 ION-SOLVENT INTERACTION

In aqueous solutions of strong electrolytes the variation of viscosity with concentration is markedly linear in the dilution range 0,002 M - 0,1 M. The reason for this is that the linear term, Bc, here predominates over the electrostatic square root term in the Jones-Dole equation (1.4). Unlike A which is a computable constant and always positive, B is purely empirical and can be either positive or negative.

There are several interesting qualitative correlations between values of B and other solution properties, e.g. the effective radii of hydrated ions and entropies of hydration. However, a successful quantitative theory for B still has to be developed. In general it is accepted though, that the B-coefficients are a measure of ion-solvent interaction.

3.2.1 Determination of ionic contributions to B

Table 3.2.1 below contains some typical values of B-coefficients of salts in aqueous solution.

TABLE 3.2.1

B-Coefficients of Salts in Aqueous Solution at 25°C

Electrolyte	B/mol^{-1} litre	Electrolyte	B/mol^{-1}litre
LiCl	0,139	KCl	-0,014 0
NaCl	0,079 3	RbCl	-0,037
Li_2SO_4	0,507 6	KI	-0,075 5

Continued/...

TABLE 3.2.1 continue

Electrolyte	B/mol^{-1}litre	Electrolyte	B/mol^{-1}litre
Na_2SO_4	0,382	RbI	-0,099
LiI	0,081	CsCl	-0,052
NaI	0,018	CsI	-0,114

The immediate striking feature is the constant difference between values of B for pairs of salts with the same anion but different cations. For example, the difference in the value of B for the chlorides and iodides of potassium and rubidium are 0,023 and 0,023 5 respectively. The chlorides, iodides, and sulphates of sodium and lithium show a difference of 0,062 ± 0,002. This constant difference is shown by all cases cited in the literature and is strong evidence supporting the additivity of B.

It is useful to split the B-coefficient into ionic contributions in order to predict values for new cases, as well as for work on mixtures. However, since there is no quantity analogous to the transport number, this cannot be done in the same way as the division of equivalent conductivities.

The first attempt at a division was carried out by Cox and Wolfenden |20|. They made the assumption that the ionic values of B for Li^+ and IO_3^- in $LiIO_3$ are proportional to the ionic volumes and that these, in turn, are inversely proportional to the third power of the ionic mobilities. Their calculations indicated that the volume of the hydrated Li^+ ion is 10% greater than that of the IO_3^- ion, and hence the value of B for the salt, which is 0,283 at 18°C, was split into two ionic contributions, $B_{Li^+} = 0{,}147$ and $B_{IO_3^-} = 0{,}136$. The values of B ascribed to other ions at 18°C followed at once.

Gurney |44|, and later Kaminsky |63|, used an alternative method to assign ionic values of B, based on the assumption that at every temperature $B_{K^+} = B_{Cl^-}$. This assumption was motivated by the fact that the mobilities of K^+ and Cl^- ions differ by less than 3% over a wide temperature range. Furthermore, the relationships which exist between values of B and other quantities, such as entropies of hydration, which is discussed in great detail by Asmus |9|, support this manner of division, since K^+ and Cl^- ions show a similar behaviour. Excellent agreement was obtained between the values reported by Cox and Wolfenden on the one hand, and Gurney and Kaminsky on the other.

More recently Sacco *et al.* |88| introduced a new method for obtaining ionic B-coefficients based on $B_{BPh_4^+} = B_{PPh_4^-}$. Since BPH_4PPh_4 is scarcely soluble in water, the value of the B-coefficient was obtained from

$$B_{NaBPh_4} + B_{PPh_4Br} - B_{NaBr} = B_{BPh_4PPh_4}$$

Values obtained in this manner were in good agreement with previously cited ones. Numerous tables of ionic B-coefficients at different temperatues are found in the literature |e.g. 44, 97|. Table 3.2.2 below contains a sample of such values.

TABLE 3.2.2/...

TABLE 3.2.2

T/°C	Li^+	Na^+	K^+	Cl^-	I^-
5	0,161 5	0,086 0	-0,020 0	-0,020 0	-
25	0,149 5	0,086 3	-0,007 0	-0,007 0	-0,068 5
35	0,138 5	0,085 1	+0,004 9	+0,004 9	-0,053 6
42.5	0,131 0	0,086 1	+0,012 1	+0,012 1	-

3.2.2 Qualitative discussion of B

Kaminsky |61| formulated two general rules concerning the B-coefficient. The first states that at constant temperatures the values of B_{ion} decrease within a group of the periodic table as the crystal ionic radii increase. The second rule states that within a group of the periodic system, the temperature coefficient, dB/dT, increases as the crystal ionic radius increases.

These rules are reflected in the values tabulated in Table 4.2. $B_{Li^+} > B_{Na^+} > B_{K^+}$ at all temperatures satisfying rule 1. A noted exception to this rule is the Be^{2+} ion at temperatures above 26,5°C, where $B_{Be^{2+}} < B_{Mg^{2+}}$. This anomaly also appears in the apparent partial molar volumes, and may be attributed to hydrolysis.

Rule 2 satisfies all available ionic values of B. In Table 4.2 B_{Li^+} is seen to decrease with increasing temperature, giving a negative

value/...

value for dB/dT. Down the group dB/dT for sodium is approximately zero, while that of potassium is positive. It should be noted that negative temperature coefficients have so far only been found for cations. If the temperature dependence of the ionic values of B are known, one can predict negative temperature coefficients for some salts, e.g. $BeCl_2$, since $dB_{Be^{2+}}/dT + 2dB_{Cl^-}/dT < 0$ |61|.

All these features can be explained in terms of the analysis presented in their monograph on the viscosity of electrolytes by Stokes and Mills |97|.

The increment in the relative viscosity due to the term, Bc, can be represented as the sum of three specialized viscosity effects. Concisely

$$Bc = (\eta^E + \eta^A + \eta^D)/\eta_0. \qquad (3.24)$$

η^E is the viscosity increment arising from the size and shape of an ion, and is closely related to the Einstein effect (mentioned in section 2). It will always be positive and normally increases with increasing ion size. η^A is the increment due to the alignment or orientation of polar molecules by the ionic field. The freedom of movement of these molecules are restricted and the viscosity of the solution increases. η^D is the viscosity change associated with distortion of the solvent structure leading to lowered viscosity. This distortion can be thought of as due to competing forces from the solvent structure in the bulk and from the ionic field and/or the

oriented/...

oriented molecules associated with the ion. At any given concentration and temperature, the magnitude of the B-coefficient can be interpreted in terms of these three competing viscosity effects.

Small and highly charged cations such as Li^+ and Mg^{2+} strongly orient water molecules and are believed to have a firmly attached sheath of molecules which move with them as a kinetic entity. The ion plus its primary solvent sheath can be visualized as a single particle and η^E will therefore be large. At room temperature water molecules beyond this minor layer are also oriented to some extent, giving a positive η^A. The sum of $\eta^E + \eta^A$ will far outweigh η^D, especially since the outward pointing hydrogen atoms fit reasonably well into the tetrahedral water structure, distorting the solvent structure minimally. B is thus large and positive since $\eta^E + \eta^A >> \eta^D$

The negative temperature coefficient of this class of ion can be explained in terms of the secondary layer of water molecules mentioned above. Although the primary sheath of water molecules will remain largely unmoved, the secondary layer will be held less rigidly with increasing temperature. η^A will decrease significantly, yet the sum of $\eta^E + \eta^A$ will still be larger than η^D and B will remain positive.

At the opposite end of the scale we have the class of ion with $\eta^E + \eta^A < \eta^D$ and B negative. Examples are Cs^+ and I^-. They have small charge to surface ratios and thus only a weak orienting effect in the primary solvent layer. η^E is therefore approximately equivalent to that for the bare ion and very small, while η^A is also small. However, η^D is now large since there is considerable distortion in the immediate neighbourhood of the ion due to competition between the ionic field and the bulk structure.

With increasing temperature η^D will decrease because there will be less competition between the ionic field and the solvent structure. Since η^E will remain fairly constant and η^A will decrease slowly with increased temperature, $\eta^E + \eta^A$ will eventually outweigh η^D, and B will become positive.

In between these two extremes we have ions such as K^+ and Cl^- with a close belance of viscous forces such that $\eta^E + \eta^A \cong \eta^D$ and B is close to zero. The ammonium ion also falls into this category in both aqueous and sulphuric acid solutions, since on the one hand, its tetrahedral structure allows it to fit into the solvent structure with minimum disturbance while on the other hand it has little polarizing power. The consequence is that $B_{NH_4^+}$ stays close to zero over a wide range of temperatures.

Finally, one would expect η^E in large molecular ions, such as the tetra-alkyl-ammonium ions, to far outweigh other effects because of their size. The values of B for these ions are large and positive, fulfilling expectations.

3.2.3/...

3.2.3 The additivity of B in Mixtures of electrolytes

Up to this point only single electrolytes have been discussed. However, since it is clear that the individual ions in solution make their contributions to the viscosity increment attributed to ion-solvent interaction independently of one another, it follows that in mixtures of more than two ionic species this change in viscosity can be represented as the sum of the individual terms for each ion,

i.e. $\sum_{i=1}^{n} B_i c_i$.

Simpson used this expression, in conjunction with the Onsager and Fuoss theory, to predict the course of viscometric titrations |92|. His overall equation for the relative viscosity of mixtures is

$$\eta_{rel} = 1 + a \cdot \sqrt{\Gamma} + \sum_{i=1}^{n} B_i c_i \quad . \qquad (3.25)$$

It has already been mentioned that Chakravarti and Prasad found that a mixture of electrolytes behave like a single salt if its composition is kept constant | 17, 18, 19 |, and that it obeys the Jones-Dole equation which can be rewritten as

$$\eta_{rel} = 1 + A^* \sqrt{c}_{total} + B^* c_{total} \qquad (1.7)$$

In/...

In mixtures of $NaCl/MgCl_2$, K_2SO_4/KCl, and $NaNO_3/NaCl$, B* was found to obey the equation

$$B^* = B_1c_1/c_{\text{total}} + B_2c_2/c_{\text{total}} \tag{3.26}$$

where B_1, B_2, c_1 and c_2 are the values of B and the concentrations of the two salts, and, of course, $c_{\text{total}} = c_1 + c_2$. Equation (3.26) can be rearranged to give

$$B^*c_{\text{total}} = B_1c_1 + B_2c_2. \tag{3.27}$$

B_1 and B_2 can now be divided into their ionic components and since all three systems have either a common cation or anion, equation (3.26) turns out to be a reformulation of Simpson's expression with n = 3,

$$\text{i.e. } B^*c_{\text{total}} = \sum_{i=1}^{3} B_ic_i \tag{3.28}$$

where B_i are the ionic B-coefficients.

Chakravarti and Prasad found that mixtures of NaCl and $BaCl_2$ did not obey equation (3.26). However, for reasons mentioned in section 3.1 their results are not above suspicion, and one would like to see further experimentation on this system since there is no obvious reason why B should not be additive in this particular mixture.

Asmus, wanting to see whether calculated values of a correlated with experimental values, plotted $(\eta_{\text{rel}} - 1)/\sqrt{\Gamma}$ against $\sqrt{\Gamma}$ for mixtures of $CuSO_4$ and KCl, as well as of $CuSO_4$ and H_2SO_4 |6|. The Jones-Dole equation (1.4) now takes the form

η_{rel}/...

$$\eta_{rel} = 1 + a\sqrt{\Gamma} + b\Gamma \tag{1.11}$$

It should be re-emphasised that a and b are general constants, both holding for mixtures as well as for single electrolytes. In addition ionic values of b can be calculated. For example, for an ionic species $A^{z\pm}$, $\Gamma_A = c_A z_A^2$, and since $b_A\Gamma_A = B_A c_A$, it follows that

$$b_A z_A^2 = B_A. \tag{3.29}$$

Clearly

$$\sum_i B_i c_i = b\Gamma \tag{3.30}$$

since both represent the total viscosity increment due to ion-solvent interaction.

It follows that

$$b = \frac{1}{\Gamma}\sum_i B_i c_i \ . \tag{3.31}$$

Substituting $B_i c_i = b_i\Gamma_i$ into equation (3.31) one obtains

$$b = \frac{1}{\Gamma}\sum_i b_i\Gamma_i \tag{3.32}$$

It should be obvious that equations (3.26), (3.28) and (3.32) are simply restating the fact that the B-coefficient is additive.

Table 3.2.3 gives calculated and experimental values of b (as reported by Asmus) for mixtures of $CuSO_4$ and KCl. The values of B_{ion} which were used, are SO_4^2 = 0,2085, Cu^{2+} = 0,3315, and $K^+ = Cl^-$ = -0,007.

Table 3.2.3/...

TABLE 3.2.3

b Values for $CuSO_4$ - KCl Mixtures

mol % $CuSO_4$	*b*(experimental)	*b*(calculated)
100	0,068	0,067 5
82,3	0,064	0,063 7
64,8	0,060	0,058 5
47,9	0,054	0,051 6
31,9	0,045	0,041 6
21,0	0,036	0,031 4
10,3	0,019	0,017
4,3	0,010	0,004 3
0	0,000	-0,007

Figure 3.2.1 contains plots of both *b*(calc.) and *b*(exptl.) vs mol % $CuSO_4$. The correlation is excellent. If we accept the validity of equation (3.32) as a means of calculating *b* from published values of B_i the discrepancies between these calculated values and those derived from Asmus' data (which are always lower) may originate from uncertainties or errors in the tabulated values of the ionic B-coefficients themselves. It will be recalled that values of B_i have been estimated from experimental values of B-coefficients by various arbitrary assumptions (section 3.2.2) and these also represent a compromise based upon experimental values of B for different salts. An exactly comparable situation occurs in calculating (unique) values of "ionic-radii" from the experimental interionic distances reported for a great number of salts.

For example the literature value for pure KCl gives $B_{KCl} = -0{,}014$ whereas Asmus reports $B_{KCl} = 0$ (whence $b_{K^+} = b_{Cl^-} = 0$). If these values are adopted there is almost precise agreement between calculated and theoretical values.

If equation (3.32) holds good then a plot of b vs the fractional contribution to the total ional strength of one constituent of a binary system should be linear. To illustrate this point consider an aqueous solution containing both $CuSO_4$ and KCl.

Let $|CuSO_4| = c_1$ and $|KCl| = c_2$.

It follows that $\Gamma = 8c_1 + 2c_2$.

$$\Gamma_{Cu^{2+}}/\Gamma = \Gamma_{SO_4{}^{2-}}/\Gamma = 4c_1/(8c_1 + 2c_2) \qquad (3.33)$$

$$\text{Let } \Gamma_{Cu^{2+}}/\Gamma = x \qquad (3{,}34)$$

then

$$\Gamma_{K^+} = (1-2x)/2 \qquad (3.35)$$

Substituting equations (3.34) and (3.35) into (3.32) one obtains

$$b = b_{Cu^{2+}}\,x + b_{SO_4{}^{2-}}\,x + b_{K^+}\left(\frac{1-2x}{2}\right) + b_{Cl^-}\left(\frac{1-2x}{2}\right).$$

Rearrangement gives

$$b = \tfrac{1}{2}(b_{K^+} + b_{Cl^-}) + (b_{Cu^{2+}} + b_{SO_4{}^{2-}} - b_{K^+} - b_{Cl^-})x \qquad (3.36)$$

and b is thus clearly linearly dependent upon $\Gamma_{Cu^{2+}}/\Gamma$.

In/...

In order to see in what manner b is dependent upon the fractional contribution to the total molar concentration, $Y = c_1/(2c_1 + 2c_2)$, we can multiply and divide the last term of the right hand side of equation (3.36) by $(2c_1 + 2c_2)$ to give

$$b = \tfrac{1}{2}(b_{K^+} + b_{Cl^-}) + (b_{Cu^{2+}} + b_{SO_4{}^{2-}} - b_{K^+} - b_{Cl^-}) \frac{4(2c_1 + 2c_2)}{(8c_1 + 2c_2)} . y \quad . \quad (3.37)$$

b is thus not linearly dependent upon y.

The above can be shown for any single ionic component in any binary mixture of two salts.

Figure 3.2.3 contains a plot of b(exptl.) vs % contribution made by $CuSO_4$ to the total ional strength in a mixture of $CuSO_4$ and KCl. The values are those reported by Asmus |6|. As expected, the plot is a straight line. On the other hand, in figure 3.2.1 where b (exptl) and b(calc.) are plotted against % contribution to the total concentration the curves are very clearly not linear.

Figure 3.2.2 contains plots of b(calc.) and b(exptl) vs mol % $CuSO_4$ for mixtures of $CuSO_4$ for mixtures of $CuSO_4$ and H_2SO_4. There is a big discrepancy between the two values in every case. b was calculated from equation (3.32) assuming that H_2SO_4 dissociates completely. A plot of b(exptl) vs % contribution to the total ional strength made by $CuSO_4$ also does not yield a straight line for this system (figure 3.2.3). Asmus thus concluded that there is no general method for calculating b from known B_{ion} values.

It/...

It should be born in mind, however, that at finite dilution H_2SO_4 does not dissociate completely. As the concentration tends toward zero, the molecules tend toward complete dissociation, and since a is obtained by extrapolating to zero, calculated and experimental values of a agree. However, as the concentration increases, the proportion of HSO_4^- molecules in solution increases as well, making the value obtained for b meaningless. It is not surprising that the plot of $(\eta_{rel}-1)/\sqrt{\Gamma}$ vs $\sqrt{\Gamma}$ for H_2SO_4 alone starts showing a curvature at the low concentration of 0,008 M, since both a and b vary at each point along the curve with the changing proportions of ionic species in solution. Since the hydrogen sulphate ion is a weak electrolyte, this problem will be examined in more detail in section 4 and it will be shown that equations (1.11) and (3.32) apply to weak electrolytes as well, provided every species in solution is known.

It can thus be concluded that for dilute solutions the relative viscosity of mixtures can be expressed as a function of Γ, the total ional strength, in the equation

$$\eta_{rel} = 1 + a\sqrt{\Gamma} + b\Gamma \qquad (1.11)$$

where both a and b are constants independent of Γ but dependent upon the composition of the solution. a is computable from first principles as discussed in section 3.1, while b can be obtained from individual ionic B-coefficients using equations (3.29) and (3.32).

In order to predict the course of a viscometric titration involving dilute solutions of strong electrolytes it only remains to determine the concentrations of the various ionic species present at each point along the curve and then from equation (1.11) obtain the viscosity at each data point.

FIGURE 3.2.1./...

FIGURE 3.2.1: Plot of *b* vs mol % $CuSO_4$ for the mixture $CuSO_4$ - KCl. (*b*(calc.) obtained using $B_{Cu^{2+}} = 0{,}331\,5$, $B_{SO_4{}^{2-}} = 0{,}208\,5$ and $B_{K^+} = B_{Cl^-} = -\,0{,}007$)

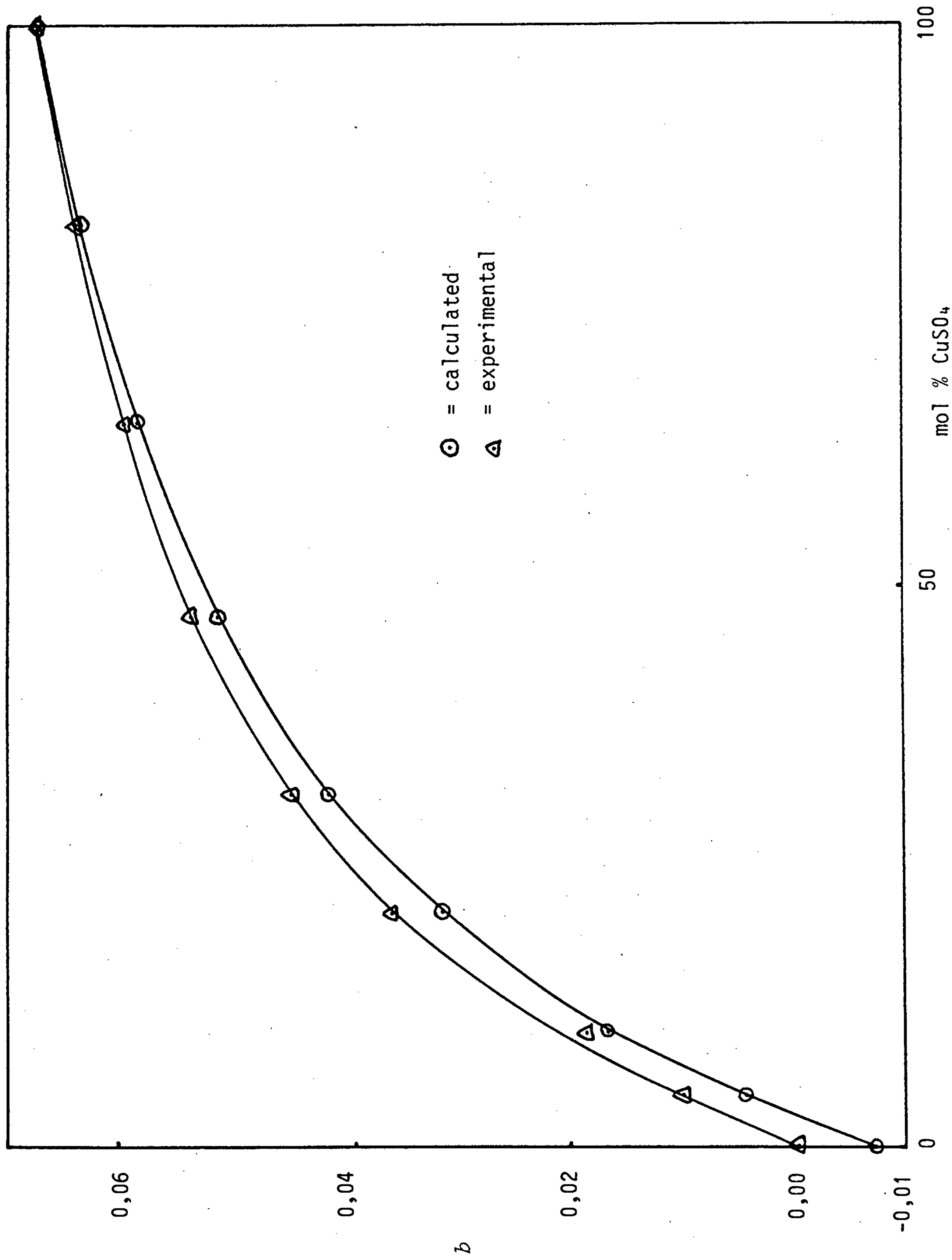
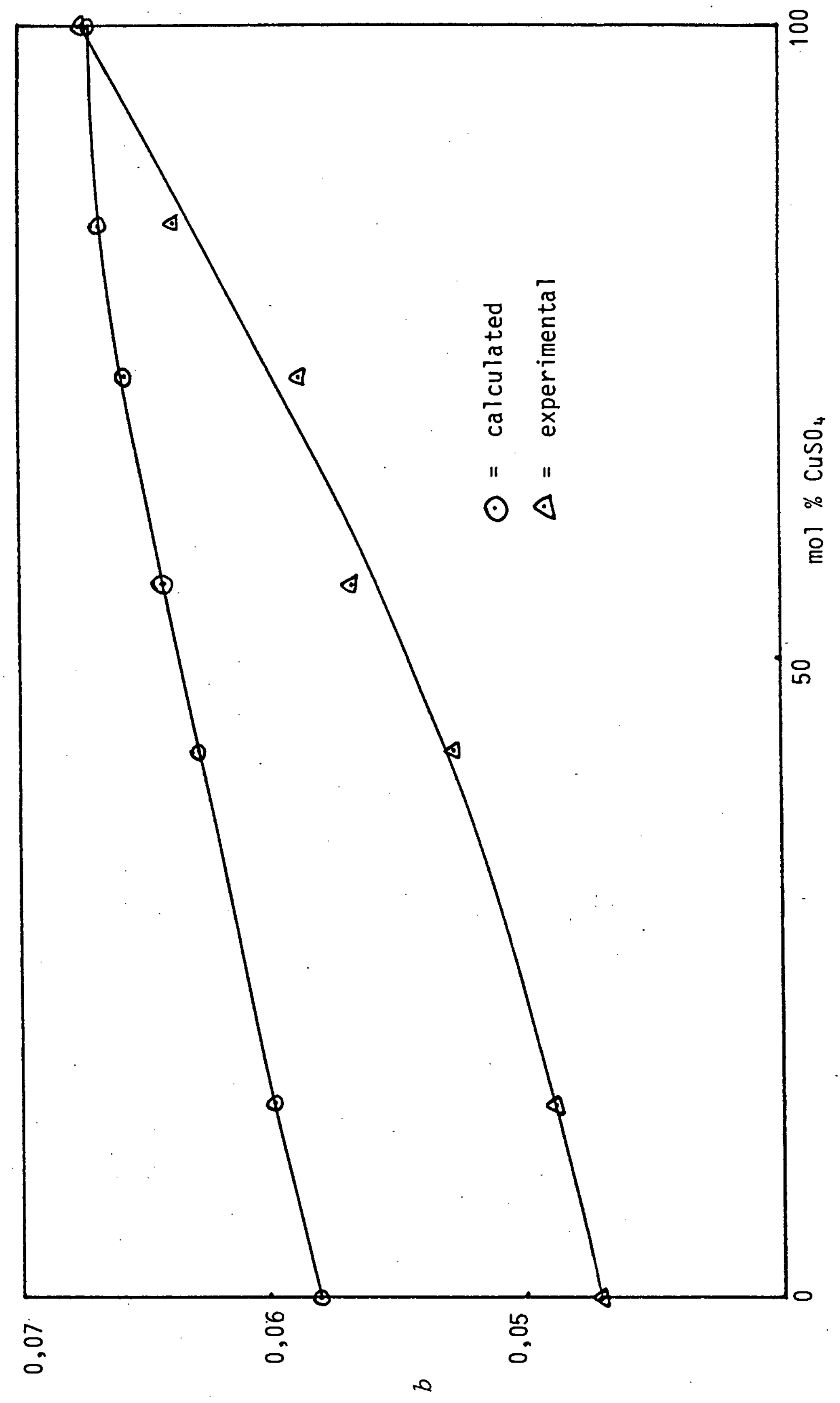


FIGURE 3.2.2: Plot of *b* vs mol % $CuSO_4$ for the mixture $CuSO_4$ - H_2SO_4. (*b* (calc.) obtained using $B_{H^+} = 0{,}072$, $B_{SO_4{}^{2-}} = 0{,}208\ 5$, $B_{Cu^{2+}} = 0{,}331\ 5$)



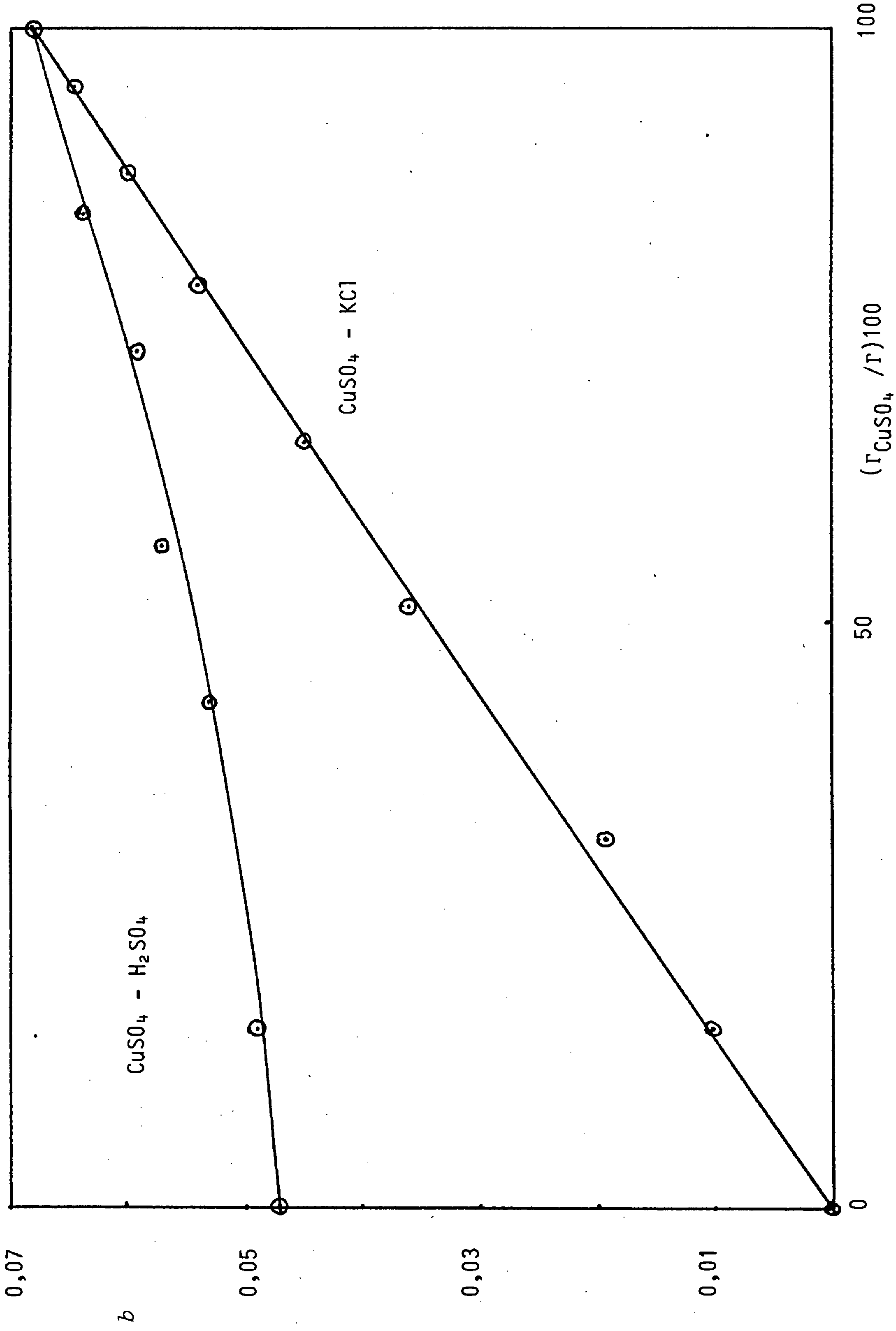


FIGURE 3.2.3: Plots of *b* (exptl) vs % contribution to the total ionic strength made by $CuSO_4$ in the mixtures $CuSO_4$ - KCl and $CuSO_4$ - H_2SO_4.

4. THE VISCOSITY OF DILUTE SOLUTIONS OF WEAK ELECTROLYTES

Provided the concentrations of every ionic species in solution is known the theory discussed so far should apply to weak electrolytes as well. In this section it is shown to be valid for both sulphuric and acetic acid. A different approach is used in each case.

As has already been mentioned Asmus |6| measured the viscosity of mixtures of $CuSO_4$ - KCl and $CuSO_4$ - H_2SO_4 at 25°C. For each mixture a series of relative viscosity measurements were carried out at six or more constant proportions. In each case the *a* and *b*-coefficients were obtained from the intercept and slope of a plot of $(\eta_{rel}-1)/\sqrt{\Gamma}$ vs $\sqrt{\Gamma}$. In every case the experimental and calculated values for *a* agreed. For the $CuSO_4$ - KCl system the *b*-coefficient was found to vary linearly with the percentage contribution to the total ional strength of any single species in solution (Figure 3.2.3), which means that the *b*-coefficient could be calculated from

$$b = \sum_{i=1}^{n} b_i \Gamma_i / \Gamma \qquad (3.32)$$

For the $CuSO_4$ - H_2SO_4 system equation (3.32) does not hold however. What is more, from approximately a 50:50 mixture to pure H_2SO_4 the $(\eta_{rel}-1)/\sqrt{\Gamma}$ vs $\sqrt{\Gamma}$ curve deviates progressively more from linearity as Γ increases.

All this is explainable in terms of the incomplete dissociation of the hydrogen sulphate ion. As the proportion of sulphuric acid

in/...

in solution increases, and as the concentration of sulphuric acid increases, so does the proportion of HSO_4^- increase. Since *a* and *b* are constant only for constant proportions of ionic species it is to be expected that the slope of $(\eta_{rel}-1)/\sqrt{\Gamma}$ vs $\sqrt{\Gamma}$ will change if the contribution to *b* made by SO_4^{2-} and HSO_4^- differ. It remains then to show that $B_{SO_4^{2-}}$ and $B_{HSO_4^-}$ do in fact differ.

4.1 CALCULATION OF THE B-COEFFICIENT FOR HYDROGEN SULPHATE

In order to arrive at a value for $B_{HSO_4^-}$ it is necessary to calculate the concentration of each significant ionic species present in solution at each viscosity data point. Then from equation (3.32) and known values of B for the other species present $B_{HSO_4^-}$ can be computed at each data point and an average value taken. One assumes $B_{HSO_4^-}$ to have a reasonably constant value at each point.

Knowing $|H_2SO_4|_0 = c$ from analytical data we need to be able to calculate values of $|H^+|$, $|HSO_4^-|$, and $|SO_4^{2-}|$ in solutions of different ionic strength, I. This implies a knowledge of

$$K_2 = |H^+|\,.|SO_4^{2-}|/|HSO_4^-|$$

for a series of ionic strengths. It is assumed that the first stage of ionisation

$$H_2SO_4 \rightarrow HSO_4^- + H^+$$

is/...

is complete under the experimental conditions used.

After the second dissociation the equilibrium

$$HSO_4^- \underset{}{\overset{K_2}{\rightleftharpoons}} H^+ + SO_4^{2-}$$

is established. The concentrations will now be

$$|HSO_4^-| = c - x$$
$$|H^+| = c + x$$
$$|SO_4^{2-}| = x$$

where x is unknown. We can therefore write

$$K_2 \frac{(c + x)x}{c - x}$$

i.e. $x^2 + (c + K_2)x - K_2c = 0$ (4.1)

Now K_2 applies to a specific ionic strength, I, only and in this case, by definition

$$I = \tfrac{1}{2}\left|1^2(c - x) + 1^2(c + x) + 2^2x\right|$$

i.e. $I = c + 2x$. (4.2)

Substituting (4.2) into (4.1) one gets

$$x^2 - (I + 3K_2)x + K_2I = 0 \qquad (4.3)$$

The next step is to calculate a number of values for K_2 at a series of ionic strengths. For this purpose the method proposed by Linder and Murray |68|, and the values for K_2 for H_2SO_4 (table 4.1) obtained from Martell and Smith |69| will be employed.

TABLE 4.1/...

TABLE 4.1

$-\log K_2$*	I
1,99 ($-\log K_2^T$)	0
1,55	0,1
1,32	0,5

(* or $\log K_1$ for the reaction $H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$)

The expression for the activity coefficient is:

$$-\log\gamma_i = \frac{Az_i^2\, I^{\frac{1}{2}}}{1 + B\mathring{a}_i I^{\frac{1}{2}}} + cI \tag{4.4}$$

where A and B are constants characteristic of the solvent (A = 0,509 and B = 0,328 for water at 25°C), z_i and γ_i are the charge and the activity coefficient respectively of the i-th ion, and $\mathring{a}_i$ is an ionic size parameter, estimates of which are taken from Kielland |64|. c is constant (normally negative) for a given system. A method for calculating c is given below.

For the reaction between two ionic species, M^{Z_M} and L^{Z_L},

$$pM^{Z_M} + q\,L^{Z_L} \rightleftharpoons (M_pL_q)^{(pZ_M + qZ_L)} \tag{4.5}$$

the equilibrium constant, K' and K'', at ionic strengths, I' and I'', are related by

$$K'' = G''(G')^{-1}\,K' \tag{4.6}$$

where/...

where each G is a quotient, expressed generally by

$$G = \frac{(\gamma_M)^p(\gamma_L)^q}{\gamma_{M_pL_q}} \quad . \tag{4.7}$$

The γ's are activity coefficients of the respective species, as indicated by individual subscripts. The activity coefficients can be calculated from equation (4.4) provided the values for $\mathring{a}_i$ and c are available. Combining the assumption that c has the same value for each ion in any given equilibrium, (4.5), with equations (4.4), (4.6) and (4.7) the following expression is obtained:

$$\log K'' = \log K' + AF(\mathring{a}_i, I^{\frac{1}{2}}) + c(I'' - I')(1 - p - q) \tag{4.8}$$

where

$$F(\mathring{a}_i, I^{\frac{1}{2}}) = (pZ_M + qZ_L)^2 \left[\frac{(I'')^{\frac{1}{2}}}{1 + B\mathring{a}_{M_pL_q}(I'')^{\frac{1}{2}}} - \frac{(I')^{\frac{1}{2}}}{1 + B\mathring{a}_{M_pL_q}(I')^{\frac{1}{2}}} \right]$$

$$- p\,Z_M^2 \left[\frac{(I'')^{\frac{1}{2}}}{1 + B\mathring{a}_M(I'')^{\frac{1}{2}}} - \frac{(I')^{\frac{1}{2}}}{1 + B\mathring{a}_M(I')^{\frac{1}{2}}} \right]$$

$$- q\,Z_L^2 \left[\frac{(I'')^{\frac{1}{2}}}{1 + B\mathring{a}_L(I'')^{\frac{1}{2}}} - \frac{(I')^{\frac{1}{2}}}{1 + B\mathring{a}_L(I')^{\frac{1}{2}}} \right]$$

The overall value of c for a given system may be calculated from equation (4.8) and used in equation (4.4) for predicting values for the activity coefficients for the ionic species present at the ionic strength required. Equation (4.6) can now be used to calculate the appropriate stoicheiometric equilibrium constant.

For/...

For convenience of calculation the equilibrium will be reversed to

$$H^+ + SO_4{}^{2-} \overset{K_1}{\rightleftharpoons} HSO_4{}^-.$$

Taking the values $\mathring{a}_{H^+} = q$, $\mathring{a}_{SO_4{}^{2-}} = 4$ from Kielland |64|, making the approximation $\mathring{a}_i = 2Z_i + 2 = 4$ for $HSO_4{}^-$, and using the values for $K_1{}^T$ and K_1 at I = 0,5 from table 4.1 the value $c = -0{,}013\,4$ is obtained.

Values for log K_1 at ionic strengths between 0,0 and 0,8 can now be calculated by interpolating and extrapolating within this range using the thermodynamic value, $K_1{}^T$ and the stoicheiometric formation constant, K_1, at I = 0,5 in equation (4.6). These calculated values, along with the appropriate activity coefficients obtained from equation (4.4) are given in table 4.2 below.

TABLE 4.2

I	$\gamma_{HSO_4{}^-}$	γ_{H^+}	$\gamma_{SO_4{}^{2-}}$	Γ	log K_1
0,00	1	1	1	1	1,99
0,001	0,965 1	0,966 7	0,086 74	0,868 8	1,929
0,005	0,927 1	0,933 9	0,720 2	0,725 5	1,851
0,01	0,901 9	0,913 8	0,660 9	0,669 6	1,816
0,02	0,870 1	0,890 2	0,572 0	0,585 2	1,775 7
0,04	0,831 6	0,864 0	0,476 4	0,475 0	1,685
0,06	0,806 2	0,848 1	0,420 2	0,442 0	1,635

TABLE 4.2 Continued/...

TABLE 4.2 Continued

I	$\gamma_{HSO_4^-}$	γ_{H^+}	$\gamma_{SO_4^{2-}}$	Γ	$\log K_1$
0,08	0,787 2	0,836 8	0,381 2	0,405 2	1,597
0,10	0,771 9	0,828 1	0,351 8	0,377 4	1,567
0,15	0,743 5	0,812 9	0,301 4	0,329 5	1,507
0,20	0,723 1	0,802 7	0,268 4	0,297 9	1,464
0,25	0,707 4	0,795 3	0,244 7	0,275 1	1,429
0,30	0,694 7	0,789 7	0,226 5	0,257 5	1,401
0,35	0,684 2	0,785 7	0,212 1	0,243 6	1,377
0,40	0,675 2	0,781 7	0,200 3	0,231 9	1,355
0,45	0,667 5	0,778 9	0,190 4	0,222 2	1,337
0,50	0,660 7	0,776 4	0,181 9	0,213 75	1,32
0,60	0,649 4	0,772 8	0,168 2	0,200 2	1,291
0,70	0,640 2	0,770 3	0,157 5	0,189 5	1,268
0,80	0,632 8	0,768 5	0,148 9	0,180 8	1,247

By substituting pairs of values for I and K_2 equation (4.3) and solving for x the exact concentration of each ionic species present at each ionic strength can be calculated. These values are tabulated in table 4.3 below.

TABLE 4.3/...

TABLE 4.3

I	K_2	$\|H_2SO_4\|_0$	$\|SO_4^{2-}\|$	$\|H^+\|$	$\|HSO_4^-\|$	$\%\|HSO_4^-\|$
0,000 25	0,010 99	0,000 084	0,000 083	0,000 167	0,000 001	0,4
0,001	0,011 78	0,000 346	0,000 327	0,000 673	0,000 019	1,9
0,003	0,012 94	0,001 100	0,000 950	0,002 050	0,000 151	4,8
0,005	0,014 09	0,001 918	0,001 541	0,003 459	0,000 377	7,0
0,008	0,014 72	0,003 270	0,002 365	0,005 635	0,000 906	10,2
0,010	0,015 28	0,004 228	0,002 886	0,007 114	0,001 342	11,8
0,013	0,016 03	0,005 747	0,003 626	0,009 374	0,002 121	14,0
0,018	0,017 10	0,008 460	0,004 767	0,013 230	0,003 691	17,0
0,020	0,017 50	0,009 598	0,005 201	0,014 799	0,004 397	18,0
0,025	0,018 37	0,012 570	0,006 215	0,018 785	0,006 355	20,3
0,035	0,019 97	0,018 907	0,008 047	0,026 954	0,010 861	23,7
0,04	0,020 65	0,022 250	0,008 875	0,031 125	0,013 375	25,1
0,06	0,023 17	0,036 377	0,011 815	0,048 189	0,024 566	29,05
0,08	0,025 79	0,051 420	0,014 290	0,065 710	0,037 130	31,7
0,10	0,027 10	0,067 124	0,016 438	0,083 562	0,050 686	33,6
0,15	0,031 12	0,108 016	0,020 992	0,129 008	0,087 024	36,7
0,20	0,034 36	0,150 632	0,024 684	0,175 316	0,125 948	38,6
0,25	0,037 24	0,194 224	0,027 888	0,222 112	0,166 336	40,0
0,30	0,039 72	0,238 654	0,030 673	0,269 327	0,207 982	40,9
0,35	0,041 98	0,283 629	0,033 185	0,316 815	0,250 444	41,7
0,40	0,044 16	0,328 908	0,035 546	0,364 454	0,293 362	42,3
0,45	0,046 03	0,374 741	0,037 629	0,412 371	0,337 112	42,8
0,50	0,047 86	0,420 756	0,039 622	0,460 378	0,381 134	43,3
0,60	0,051 17	0,513 550	0,043 225	0,556 775	0,470 325	43,9
0,70	0,053 95	0,607 387	0,046 307	0,653 694	0,561 081	44,5
0,80	0,056 62	0,701 583	0,049 209	0,750 791	0,652 374	44,9

(*$\%|HSO_4^-|$ is $|HSO_4^-|$ as percentage of total concentration)

$|H_2SO_4|_0$ / ...

$|H_2SO_4|_0$ was now plotted against $|SO_4^-|$(figure 4.3). The values for Γ given by Asmus at each data point are calculated assuming complete dissociation for sulphuric acid. From these values $|H_2SO_4|_0$ can be calculated at each point, the actual sulphate ion concentration in solution can be read off from the graph, and $|H^+|$ and $|HSO_4^-|$ can be determined.

Since $|H^+|$, $|HSO_4^-|$ and $|SO_4^{2-}|$ are now known, the true ional strength, as well as the value of the a-coefficient at each data point can be computed. The contribution to the viscosity increment due to ion-solvent interaction, $b\Gamma$, and hence b at every point can also then be calculated. $B_{HSO_4^-}$ at each point can then be obtained from known values of B for H^+ and SO_4^{2-} and equation (3.32). All calculated values are listed in tables 4.4 and 4.5 below. The literature values used in the computations are:

$B_{SO_4^{2-}} = 0{,}2085$, $B_{H+} = 0{,}072$ (101) and $\lambda_{H+} = 349{,}82$, $\lambda_{SO_4^{2-}} = 79{,}8$, and $\lambda_{HSO_4^-} = 50$ (21).

TABLE 4.4

Γ(Asmus)	$\|H_2SO_4\|_0$	$\|SO_4^{2-}\|$	$\|H^+\|$	$\|HSO_4^-\|$	$\%\|HSO_4^-\|$
0,003 15	0,000 525	0,000 45	0,000 975	0,000 075	5,0
0,006 64	0,001 107	0,000 90	0,002 007	0,000 207	6,6
0,011 42	0,001 903	0,001 52	0,003 423	0,000 383	7,2
0,012 36	0,002 060	0,001 62	0,003 680	0,000 44	7,6

TABLE 4.4 Continued/...

TABLE 4.4 Continued

Γ(Asmus)	$\|H_2SO_4\|_0$	$\|SO_4^{2-}\|$	$\|H^+\|$	$\|HSO_4^-\|$	$\%\|HSO_4^-\|$
0,019 76	0,003 293	0,002 41	0,005 703	0,000 88	9,8
0,029 27	0,004 878	0,003 20	0,008 078	0,001 68	13,0
0,042 83	0,007 138	0,004 23	0,011 368	0,002 91	15,7
0,052 31	0,008 718	0,004 81	0,013 528	0,003 91	17,6
0,055 77	0,009 295	0,005 06	0,014 355	0,004 24	17,9
0,057 59	0,009 598	0,005 201	0,014 799	0,004 40	18,0
0,067 64	0,011 273	0,005 79	0,017 063	0,005 48	19,3

TABLE 4.5

True Γ	a	η_{rel}	bΓ	$B_{HSO_4^-}$
0,002 85	0,002 98	1,000 339	0,000 180	0,213 0*
0,005 814	0,002 95	1,000 581	0,000 356	0,115 2
0,009 886	0,002 94	1,000 847	0,000 555	0,166 1
0,010 60	0,002 93	1,000 943	0,000 641	0,087 0*
0,016 226	0,002 89	1,001 367	0,000 999	0,097 3*
0,022 566	0,002 84	1,001 956	0,001 529	0,167 0
0,031 196	0,002 78	1,002 635	0,002 144	0,152 5
0,036 676	0,002 76	1,003 058	0,002 529	0,141 3
0,038 830	0,002 74	1,003 124	0,002 584	0,117 0
0,040 000	0,002 74	1,003 260	0,002 712	0,127 8
0,045 706	0,002 71	1,003 723	0,003 144	0,128 4

(* omitted in calculating the mean $B_{HSO_4^-}$ value)

A/...

A mean value of $B_{HSO_4^-}$ = 0,136 ± 0,023 is thus obtained.

Since the standard deviation obtained is rather large it was decided to do a series of independent viscosity measurements for sulphuric acid in order to arrive at a more consistent B-value. A possible reason for the scatter in values obtained for $B_{HSO_4^-}$ is the high dilution at which the measurements were done. The contribution of hydrogen sulphate to bΓ is consequently very small, approaching the order of magnitude of the experimental error, leading to scattered results. Furthermore, as has been mentioned in section 3, the sensitivity of the equipment used by Asmus is not above suspicion, since his value for A for KCl is zero, as opposed to the normal literature value of -0,014. The experimental results and calculated values are listed in Tables 4.6 and 4.7 below.

Asmus' density measurements were used to obtain the relationship, $d_{rel} = 1 + 0{,}07685\, c_0$, for pure sulphuric acid.

TABLE 4.6

Ionic Composition of Sulphuric Acid at varying concentration.

$\lvert H_2SO_4\rvert_0$	$\lvert SO_4^{2-}\rvert$	$\lvert H^+\rvert$	$\lvert HSO_4^-\rvert$	$\%\lvert HSO_4^-\rvert$	Γ
0,092 95	0,019 30	0,112 25	0,073 65	35,8	0,263 10
0,107 53	0,020 62	0,128 15	0,086 91	36,9	0,297 54
0,120 63	0,022 30	0,142 93	0,098 33	37,3	0,330 46
0,137 94	0,023 35	0,161 29	0,114 59	38,3	0,369 28
0,155 36	0,024 95	0,180 31	0,130 41	38,9	0,410 52
0,169 99	0,026 00	0,195 99	0,143 99	39,3	0,443 98
0,183 89	0,027 15	0,211 04	0,156 74	39,7	0,476 38

TABLE 4.7

Calculation of $B_{HSO_4^-}$ from viscosity data determined in this work.

Γ	d_{rel}	η_{rel}	a	$b\Gamma$	$B_{HSO_4^-}$
0,263 10	1,007 14	1,021 59	0,002 31	0,020 41	0,112 8
0,297 54	1,008 26	1,024 64	0,002 28	0,023 40	0,113 6
0,330 46	1,009 27	1,027 24	0,002 27	0,025 94	0,111 9
0,369 28	1,010 60	1,030 93	0,002 24	0,029 57	0,114 2
0,410 52	1,011 94	1,034 61	0,002 22	0,033 19	0,115 1
0,443 98	1,013 06	1,037 66	0,002 21	0,036 19	0,115 7
0,476 38	1,014 13	1,040 44	0,002 20	0,038 92	0,115 3

The average value obtained is thus

$$B_{HSO_4^-} = 0{,}114 \pm 0{,}001$$

The standard deviation is ± 0,9%, as apposed to ± 16,9% obtained for the calculation using Asmus' data.

4.1.2 Discussion

The difference in the values of B for sulphate, (0,208 5), and bisulphate, (0,102 2), makes sense in terms of the analysis presented in section 3.2.2. In comparison to other B_{ion} values, $B_{HSO_4^-}$ is high. HSO_4^- is a big molecule, which will have a large η^E. Although the charge to

surface/...

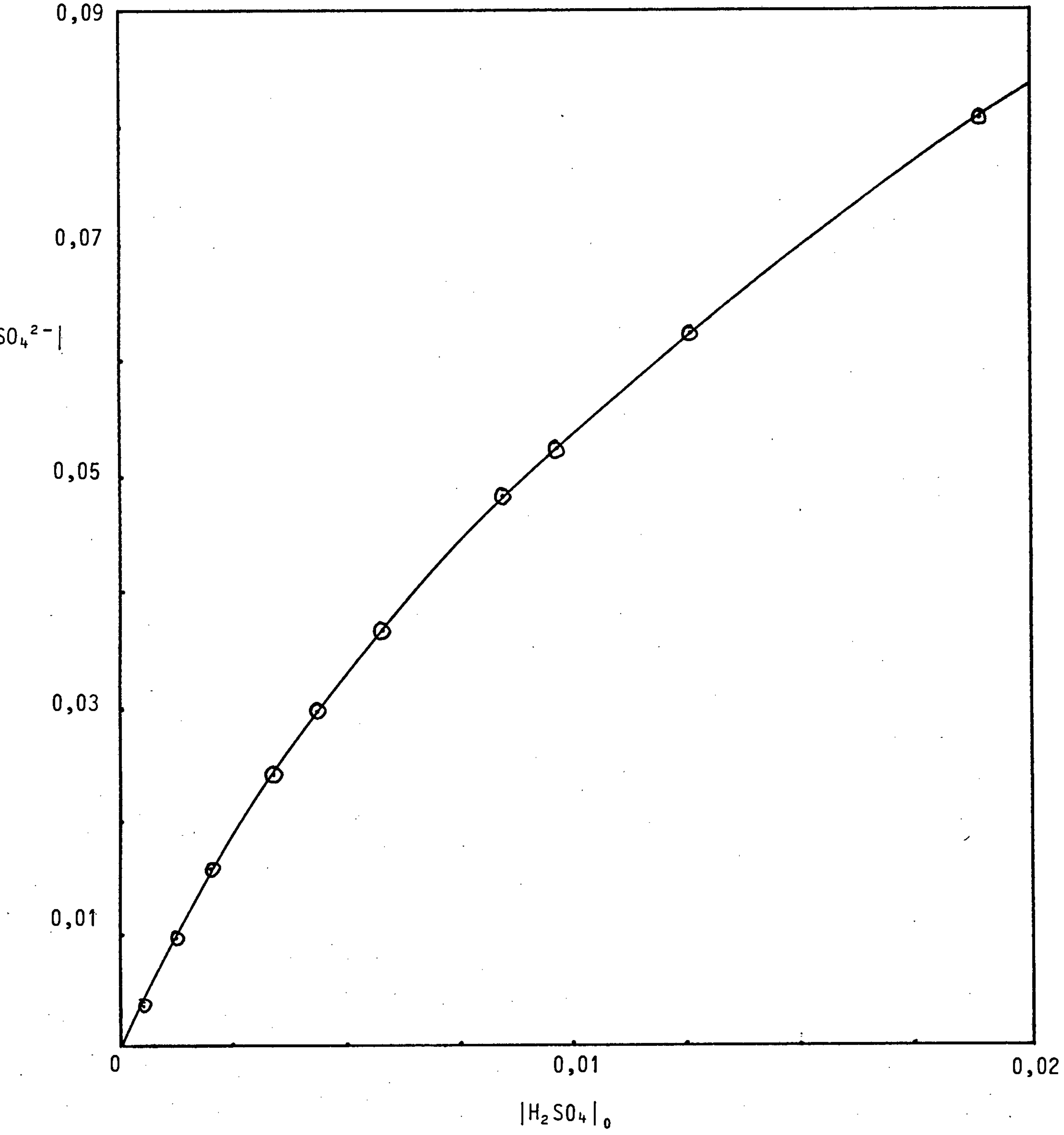
surface ratio is small and therefore solvent orientation due to the ionic field minimal, one would expect hydrogen bonding of the water molecules to the outward pointing oxygen atoms, making for a large kinetic entity, and thus expect $\eta^E + \eta^A >> \eta^A$.

The effect of the increase in charge on the size of the molecule will outweigh the effect of the loss of a hydrogen atom, and dissociation will lead to an increase in size and a larger η^E. We would expect the size of the molecule to increase, but not to double, thus we can reasonably expect an increase in the charge to surface ratio which will lead to an increase in solvent molecule orientation. Furthermore, the loss of the hydrogen atom will give an extra site for hydrogen bonding for a water molecule. In all, it would be reasonable to expect $B_{SO_4^{2-}}$ to be substantially higher than $B_{HSO_4^-}$. This is indeed the case.

It has been mentioned that Asmus observed deviation from linearity for plots of $(\eta_{rel} - 1)/\sqrt{\Gamma}$ vs $\sqrt{\Gamma}$ in mixtures of $CuSO_4$ and H_2SO_4. The deviation, which is a downward bend at higher values of $\sqrt{\Gamma}$, can be explained now in terms of the value determined for $B_{HSO_4^-}$. As the concentration increases, so does the proportion of hydrogen sulphate. The combined effect of a dissociated proton and a sulphate ion ($B_{SO_4^{2-}} + B_{H^+} = 0{,}280\ 5$) on $b\Gamma$ is nearly three times that of a hydrogen sulphate molecule. Thus as the concentration increases there will be an increased negative deviation from what the relative viscosity would have been, had dissociation been complete, and hence the downward curvature of the plot.

FIGURE 4.1/...

FIGURE 4.1: Plot of $|H_2SO_4|_0$ vs $|SO_4^{2-}|$



4.2 THE VISCOSITY COEFFICIENTS OF ACETIC ACID AND ACETATE

At least two papers dealing with this subject have been published. Laurence and Wolfenden |67| simply ignored possible effects due to hydrolysis and dissociation when they determined the coefficients for potassium and lithium acetate, and for acetic acid. Their experimental values, along with calculated values for A are tabulated below in Table 4.8. All values are at 25°C.

TABLE 4.8

Species	A(exptl)	A(calc.)	B
Lithium Acetate	0,006 6	0,009 4	0,397
Potassium Acetate	0,003 8	0,006 8	0,238
Acetic acid	0,000 6	0	0,117

The values for A were calculated from $\Lambda(CH_3CO_2^-) = 40,8$ $\Lambda(Li^+) = 39,5$ and $\Lambda(K^+) = 74,5$. Laurence and Wolfenden give A(calc.) for potassium acetate incorrectly as 0,003 0. Since acetic acid is uncharged we should have A = 0.

Using the values $B_{Li^+} = 0,149\ 5$ and $B_{K^+} = -0,007$ |97| values of 0,247 and 0,245 for $B_{acetate}$ result in good agreement. The mean value $B_{acetate} = 0,246$ has been adopted. Laurence and Wolfenden's viscosity coefficient values will be discussed and compared with the values obtained in this work in sections 4.2.1 and 4.2.2.

In contrast Srinivasan and Prasad |96| did take the dissociation of acetic acid into account in their work. They argued that the increase in relative viscosity due to the dissociated part may be represented as

$$\frac{\Delta_1}{\eta_0} = A\sqrt{\alpha c} + B\alpha c \; . \qquad (4.9)$$

Since the degree of dissociation, α, is small, the second term on the right hand side may be neglected for small values of c. The increase in viscosity due to the undissociated part, which is really a non-electrolyte, may be represented as

$$\frac{\Delta_2}{\eta_0} = \beta(1 - \alpha)c. \qquad (4.10)$$

β is identifiable with B. The total increase in relative viscosity is thus

$$\frac{\eta - \eta_0}{\eta_0} = A\sqrt{\alpha c} + \beta(1 - \alpha)c. \qquad (4.11)$$

They obtained the values A = 0,020 and β = 0,104. The value of A calculated from the conductivities of acetate and H^+, assuming complete dissociation, is 0,003 1.

However/...

However, if their experimental data are used simply to plot $(\eta_{rel}-1)/\sqrt{c}$ against $\sqrt{c}$ in the usual way, the intercept and slope give A = 0,000 8 and B = 0,105. Equation (4.11) thus does not alter matters much. B hardly changes at all, while the value for A is closer to the theoretical one if the normal Jones-Dole equation is used.

Srinivasan and Prasad report an experimental uncertainty of ± 0,2 seconds in their flow times. This is reflected in an unacceptable amount of scatter in their data. Their coefficient values will hence be neglected in the comparison of results which follows in section 4.2.3.

The approach for determining the B-coefficient of acetic acid taken in this work was to suppress the dissociation of acetic acid by the addition of hydrochloric acid to the experimental solution. Similarly for finding $B_{acetate}$ a mixture of acetic acid and sodium hydroxide, in slight excess, was used. The presence of hydroxyl ions in the solution would effectly prevent any possible hydrolysis. Furthermore, since we have a mixture of ions in each case, the results could at once be used to test the validity of equations (1.11) and (3.32).

4.2.1 The B-coefficient of acetic acid

From uncharged species the relative viscosity is normally represented as

$$\eta_{rel} = 1 + S_0(x_2) + S_1(x_2)^2 \qquad (4.12)$$

where/...

where S_0 and S_1 are constants and x_2 is the mole fraction of the solute. The acetic acid molecule will thus definitely make a contribution to the B-coefficient, although strictly speaking we cannot use the expression

$$\eta_{\text{rel}} = 1 + a\sqrt{\Gamma} + b\sqrt{\Gamma} \qquad (1.11)$$

since acetic acid is uncharged. For this work the expression

$$\eta_{\text{rel}} = 1 + \text{a}\sqrt{\Gamma} + \text{B}^{*}c_{\text{Total}} \qquad (4.13)$$

will be used, where c_{Total} is the sum of the concentrations of every species present, and B* is defined by equation (3.26). The intercept and slope of a plot of $(\eta_{\text{rel}}-1)/\sqrt{\Gamma}$ against $c_{\text{Total}}/\sqrt{\Gamma}$ give the values of a and B*.

A 50:50 mixture of 0,504 00<u>M</u> HCl and 0,483 2<u>M</u> acetic acid was used in this experiment. The titrating solution thus had the concentration values of

$$\Gamma = 0{,}504\ 0 \text{ and } c_{\text{Total}} = 0{,}745\ 86.$$

The density and viscosity data are tabulated below in Tables 4.9 - 4.11.

Table 4.9 Continued/...

TABLE 4.9

Density Measurements for a 1:0,959 8 mixture of HCl and acetic acid at 25°C

Γ	d_{rel}
0,028 00	1,000 239
0,031 50	1,000 395
0,063 00	1,001 00
0,094 50	1,001 376
0,126 00	1,001 840
0,144 00	1,002 025
0,252 00	1,003 42

A least squares analysis yields

$$\eta_{rel} = 1 + 0{,}013\ 92\ \Gamma \qquad (4.14)$$

Table 4.10 Continued/...

TABLE 4.10

Viscosity measurements of a 1:0,959 8 mixture of HCl and Acetic Acid at 25°C

c_{Total}	Γ	Flow time	d_{rel}	η_{rel}
0	0	155,807	1	1
0,003 73	0,005 04	155,856	1,000 07	1,000 38
0,018 65	0,012 60	155,945	1,000 18	1,001 07
0,024 86	0,016 80	156,021	1,000 23	1,001 60
0,041 44	0,028 00	156,169	1,000 39	1,002 71
0,046 62	0,031 50	156,187	1,000 44	1,002 88
0,062 16	0,042 00	156,300	1,000 58	1,003 75
0,093 23	0,063 00	156,678	1,000 88	1,006 48
0,139 85	0,094 50	156,958	1,001 32	1,008 72
0,186 47	0,126 00	157,250	1,001 75	1,011 03
0,213 10	0,144 0	157,493	1,002 00	1,012 84
0,372 93	0,252 00	158,684	1,003 51	1,022 04

TABLE 4.11

Values used in plot for obtaining *a* and B* for the HCl-acetic acid mixture

$(\eta_{rel}-1)/\sqrt{\Gamma}$	$c_{Total}/\sqrt{\Gamma}$
0,005 35	0,052 54
0,009 53	0,166 15
0,012 34	0,191 80
0,016 20	0,247 65
0,016 23	0,262 67

Table 4.11 Continued/...

TABLE 4.11 Continued

$(\eta_{rel}-1)/\sqrt{\Gamma}$	$c_{Total}/\sqrt{\Gamma}$
0,018 30	0,303 31
0,025 82	0,371 44
0,028 36	0,454 93
0,031 07	0,525 33
0,033 84	0,561 57
0,043 90	0,742 89

A least squares analysis gives

$$\eta_{rel} = 1 + 0{,}001\ 6\sqrt{\Gamma} + 0{,}057\ 47\ c_{Total} \tag{4.15}$$

The calculated value for a is 0,001 5, which is the a-coefficient for pure HCl. Agreement is excellent.

Using $B_{H^+} = 0{,}072$ and $B_{Cl} = -0{,}007$ |101| equation (3.26) gives $B_{acetic\ acid} = 0{,}109\ 5$.

4.2.2 The B-coefficient of Acetate

For this experiment 0,997 8M NaOH was added to a 1,008 8M acetic acid solution in a 49,96:40,04 proportion. It follows that the concentrations of ionic species in the experimental solution were:

$|\text{acetate}| = 0{,}448\ 80\ \underline{M}$

$|Na^+| = 0{,}553\ 88\ \underline{M}$

$|OH^-| = 0{,}105\ 08\ \underline{M}$

and $\Gamma = 1{,}107\ 76.$

The results are tabulated in Tables 4.12 - 4.14 below.

TABLE 4.12

Density measurements for a solution containing Na^+, acetate and OH^- ions in the proportion 1:0,810 3:0,189 7

d_{rel}	Γ
1,011 86	0,553 88
1,008 25	0,383 24
1,006 28	0,293 02
1,005 06	0,237 18
1,002 35	0,110 80
1,001 94	0,092 31

A least squares analysis gives the relationship

$$d_{rel} = 1 + 0{,}021\ 43\ \Gamma \qquad (4.16)$$

TABLE 4.13/...

TABLE 4.13

Viscosity measurement of the NaOH-acetic acid mixture at 25°C

Γ	d_{rel}	Flow time	η/η_0
0	1	155,817	1
0,005 49	1,000 12	155,981	1,001 17
0,030 67	1,000 66	156,609	1,005 75
0,036 87	1,000 79	156,692	1,006 41
0,055 25	1,001 19	157,087	1,009 35
0,061 54	1,001 32	157,164	1,009 98
0,009 24	1,001 48	157,403	1,011 67
0,076 63	1,001 64	157,570	1,012 91
0,079 13	1,001 70	157,630	1,013 36
0,093 10	1,001 98	157,827	1,014 91
0,110 80	1,002 37	158,256	1,018 06
0,237 18	1,005 08	160,860	1,037 61
0,293 02	1,006 28	162,048	1,046 52
0,383 24	1,008 21	163,821	1,060 00
0,543 88	1,011 66	167,386	1,086 77

TABLE 4.14/...

TABLE 4.14

Values plotted to obtain *a* and *b* for the NaOH-acetic acid mixture

$(\eta_{rel}-1)/\sqrt{\Gamma}$	$\sqrt{\Gamma}$
0,074 09	0,015 79
0,175 13	0,032 83
0,192 02	0,033 38
0,235 27	0,039 74
0,248 07	0,040 23
0,263 13	0,044 35
0,276 82	0,046 64
0,281 29	0,047 50
0,303 83	0,049 07
0,332 86	0,054 26
0,487 01	0,077 23
0,541 32	0,085 94
0,619 06	0,096 92
0,737 48	0,117 66

A least squares analysis gives

$$\eta_{rel} = 1 + 0{,}004\ 3\ \sqrt{\Gamma} + 0{,}151\ 22\ \Gamma. \qquad (4.17)$$

The value calculated for *a* is 0,004 9. Once again the agreement is excellent.

Substituting the values $B_{OH^-} = 0{,}118\ 8$ $B_{Na^+} = 0{,}086\ 3$ and the appropriate Γ's into equation (3.32) one gets $B_{acetate} = 0{,}239$.

4.2.3/...

4.2.3 Discussion

In order to make a comparison between the B-values obtained in this work and those of Laurence and Wolfenden more meaningful, it is necessary to calculate the extent of hydrolysis of acetate, as well as the extent of dissociation of acetic acid in the concentration range 0,01 M to 0,10 M - this being the approximate range in which their measurements were done.

Using the values given by Martell and Smith |69| for log K for the equilibrium

$$H^+ + CH_3COO^- \rightleftharpoons CH_3COOH, \qquad (4.18)$$

(log K = 4,757 at I = 0 and log K = 4,56 at I = 0,1), the constant, c, in the expression for evaluating the individual activity coefficients, equation (4.4), is calculated to be 0,040 1.

It can then be shown, using a technique similar to that discussed in the case of hydrogen sulphate, that at 0,0100 0 M initial acetic acid concentration the extent of dissociation is 4,2% while at 0,090 1 M it is 1,3%.

Now Laurence and Wolfenden plotted $(\eta_{rel}-1)/\sqrt{c}$ against $\sqrt{c}$ in the normal way, assuming that dissociation will not cause observable changes in viscosity. However, from the values of the B-coefficients arrived at in section 4.22 above, one can see that the difference between the contributions to the relative viscosity of acetic acid and acetate is very marked. Furthermore, every acetate ion and proton which dissociate contribute to the term, $a\sqrt{\Gamma}$, while acetic acid, being uncharged, does not. The difference in the actual relative viscosity and what η_{rel} would have been, had no dissociation taken place, $\Delta\eta_{rel}$, can easily be calculated:

$$\Delta\eta_{rel} = A_{(CH_3CO_2^- + H^+)}(\sqrt{x}) + B_{CH_3CO_2^-}(x) + B_{H^+}(x) - B_{CH_3CO_2H}(x) \qquad (4.19)$$

where $|CH_3CO_2^-| = |H^+| = x$

Using the B-values arrived at in sections 4.2.1 and 4.2.2, the calculated value for A for equal proportions of acetate and hydronium ions (0,003 1), and $B_{H^+} = 0{,}072$, gives $\Delta\eta_{rel} = 0{,}000\ 148$ at 0,01 M, while at 0,1 M $\Delta\eta_{rel} = 0{,}000\ 374$.

From these values it can be seen that the increment in relative viscosity due to dissociation increases with increasing concentration. This will result in a slight increase in the slope of the plot of $(\eta_{rel}-1)/\sqrt{c}$ vs. $\sqrt{c}$, giving $B_{\text{acetic acid}}$ a slightly exaggerated value. This is reflected in the value of $B_{\text{acetic acid}}$ of Laurence and Wolfenden, which is 6% greater than the one arrived at in this work.

On/...

On the other hand hydrolysis has very little effect on the determination of $B_{acetate}$ if a solution of only potassium or lithium acetate is used.

Hydrolysis does not alter the ionic strength of an acetate solution, since for every molecule of acetic acid formed an hydroxyl ion is released. The ionic strength will thus be equal to the analytical concentration of the solution, provided no other electrolytes are present. Using the values of log K_b already quoted, log K_b at $I = 0{,}01$ is calculated to be 4,673.

At 0,01 M and 0,1 M the degrees of hydrolysis of sodium, and of course lithium, acetate are 0,217 0% and 0,019 1% respectively. This means $|OH^-| = |\text{acetic acid}| = 0{,}000\ 022$ M in a solution with an initial acetate concentration of 0,01 M, and $|OH^-| = 0{,}000\ 019$ M in a 0,1 M solution.

The minimal change in the composition of the solution results in a change in a of less than 0,000 01 at each concentration. Since the ionic strength does not change, hydrolysis will have no observable effect on the term, $a\sqrt{\Gamma}$.

Furthermore, the combined effect of an acetic acid molecule and an hydroxyl ion ($B_{\text{acetic acid}} + B_{OH^-} = 0{,}110 + 0{,}119 = 0{,}229$) is very close to that of the acetate ion which is removed from solution during hydrolysis ($B_{acetate} = 0{,}239$). In the same way as for acetic acid above $\Delta\eta_{rel}$ for 0,1 M sodium acetate is calculated to be $-3{,}4 \times 10^{-6}$

and/...

and less at 0,01 M. Since this is very well within experimental error hydrolysis will not cause any detectable deviation in the viscosity of an acetate solution at low concentration.

The excellent agreement between a(calc.) and a(exptl) for the acetic acid-sodium hydroxide mixture as opposed to the less good correspondence between the calculated and experimental values for A for both lithium and potassium acetate achieved by Laurence and Wolfenden, leads one to accept the 2,8% difference between the two values for $B_{acetate}$ (0,246 (Laurence and Wolfenden) and 0,239 (present work)) as due to experimental error. This is especially so since they quote a standard deviation of ± 0,1 seconds for their flow times.

In view of the calculations for acetic acid it should be added that the obvious flaw in the Srinivasan and Prasad equation (4.11) is that the term, $B\alpha c$, due to the dissociated part cannot be neglected. Dissociation, in fact, has a greater effect on the term, $b\Gamma$, than on $a\sqrt{\Gamma}$.

Another point of interest is that, as in the case of sulphate and hydrogen sulphate, the value of B approximately doubles with an increase in charge.

Finally, the experimental results achieved certainly lend support to equations (1.11) and (3.32) discussed in section 3.

4.3/...

4.3 VISCOMETRIC TITRATIONS OF SULPHURIC AND ACETIC ACID WITH SODIUM HYDROXIDE

The two acids were both titrated with sodium hydroxide in order to see whether the curves could be interpreted in terms of the values which had been obtained for the B-coefficients of hydrogen sulphate, acetate and acetic acid. The flow times and the plotted curves for these titrations are to be found in tables 4.15 and 4.16, and figures 4.2 and 4.3. In each case flow time, which is directly proportional to the kinematic viscosity, was plotted against volume of NaOH added.

In the case of sulpuric acid 20,00 ml of 0,046 5 M acid was titrated with 0,504 8 M NaOH. The end-points are expected at 1,84 and 3,68 ml. The actual end-points were determined by performing a least squares fit on the straightest portion of each line segment. Points 1-4, 13-6, and 17-18 were used. The equations were then solved simultaneously giving the experimental end-points at 1,76 and 3,67 ml.

The experimental end-points for the acetic acid titration was calculated in the same way, using data points 5-9, and 10-17. The actual end-point occurs at 1,65 ml, as opposed to the expected one at 1,66 ml.

Except for the first sulphuric end-point, and this is to be expected, the stoicheiometric end-point is approached very closely in each case. This could easily be improved upon by using a more sensitive automatic burette, one that can be read accurately to the third decimal place.

4.3.1/...

4.3.1 Interpretation of the titration curves

Up to the first end-point in the sulphuric acid titration curve, hydronium ions are being replaced by sodium ions. Since sodium has a marginally greater effect on the relative viscosity, a slight positive slope is expected. Also, with the removal of hydronium ions the suppression of the dissociation of hydrogen sulphate decreases, resulting in a replacement of hydrogen sulphate by hydronium and sulphate ions, adding to the increase in the slope as well as resulting in a less clearly defined end-point. In the second part of the curve the viscosity changes because of the addition of sodium ions, and the replacement of hydrogen sulphate ions by sulphate. Because of the large difference between the B-coefficients of these two ionic species there is a substantial increase in the slope. Beyond the second end-point, the addition of hydroxyl and sodium ions to the solution result in further viscosity changes. Since the B-coefficient of sodium hydroxide (0,205 1) is greater than the sum of the B-coefficient of sodium and the difference between the B-coefficients of sulphate and hydrogen sulphate (0,208 5 -0,114 + 0,086 3 = 0,180 8), we expect a slight increase in slope. In the case of acetic acid, the replacement of acetic acid molecules by acetate ions, as well as the addition of sodium ions occur up to the end-point.

Because of the large difference in the B-coefficients of acetic acid and acetate, a rapid increase in viscosity is expected.

In/...

In this case the B-coefficient of sodium hydroxide is smaller than the sum B_{Na^+} and the difference between $B_{acetic\ acid}$ and $B_{acetate}$ (0,086 3 + 0,239 -0,109 5 = 0,215 8). This accounts for the decrease in slope beyond the end-point.

The values of the B-coefficients obtained in sections 4.1 and 4.2 thus very satisfactorily explain the curves which result when sulphuric and acetic acid are titrated with sodium hydroxide.

TABLE 4.15

Flow-times for the titration of 20,00 ml 0,046 5 M H_2SO_4 with 0,504 8 M NaOH

Flow-time/s	Volume NaOH/ml	Flow-time/s	Volume NaOH/ml
156,503	0,00	157,030	3,025
156,530	0,285	157,126	3,29
156,560	0,50	157,172	3,50
156,578	0,71	157,228	3,72
156,612	0,97	157,308	3,94
156,650	1,22	157,374	4,11
156,690	1,49	157,483	4,33
156,734	1,74	157,562	4,55
156,794	1,99	157,642	4,76
156,842	2,26	157,731	5,02
156,904	2,51	157,892	5,45
156,974	2,78	158,077	5,96

FIGURE 4.2/...

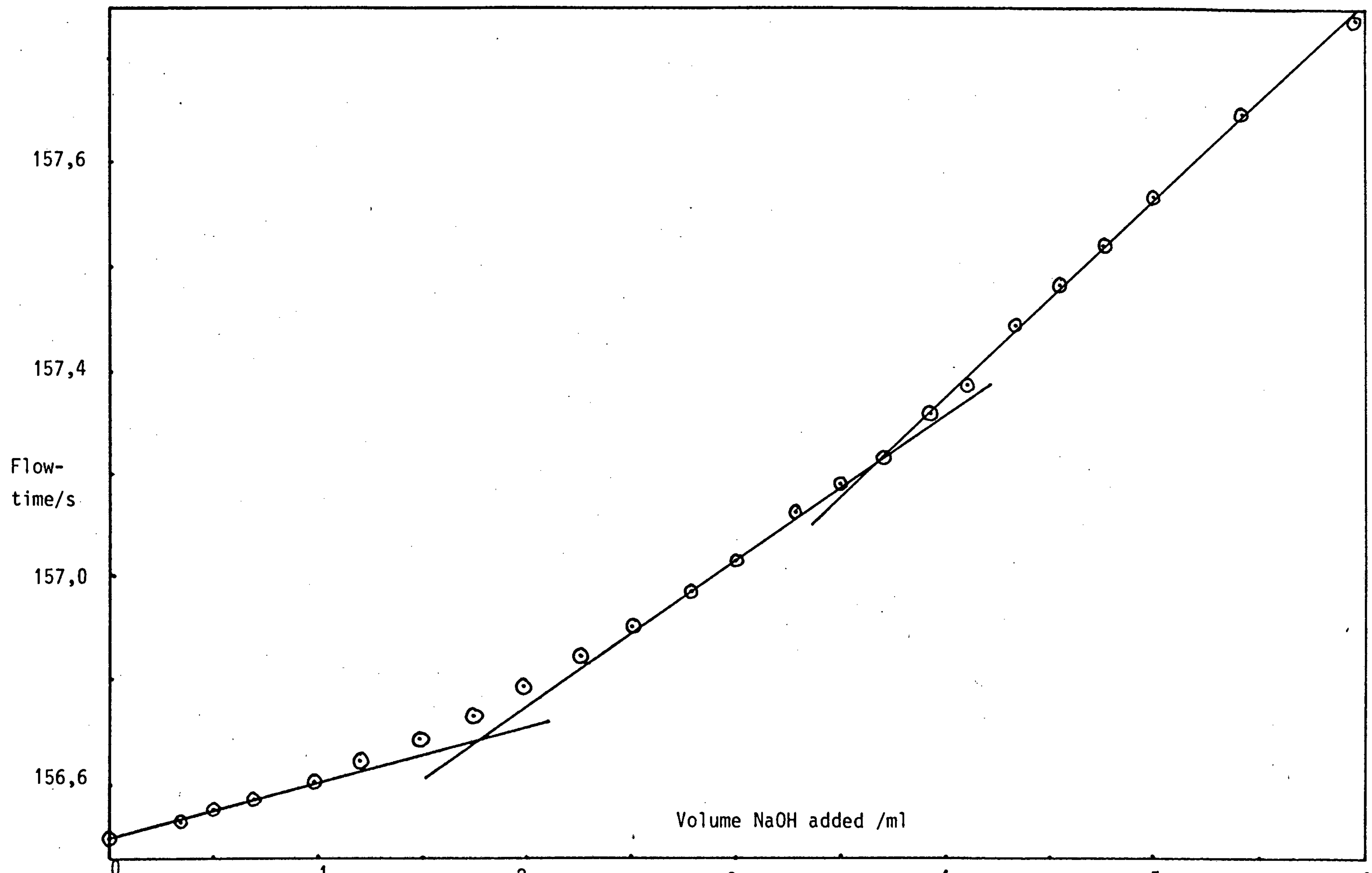


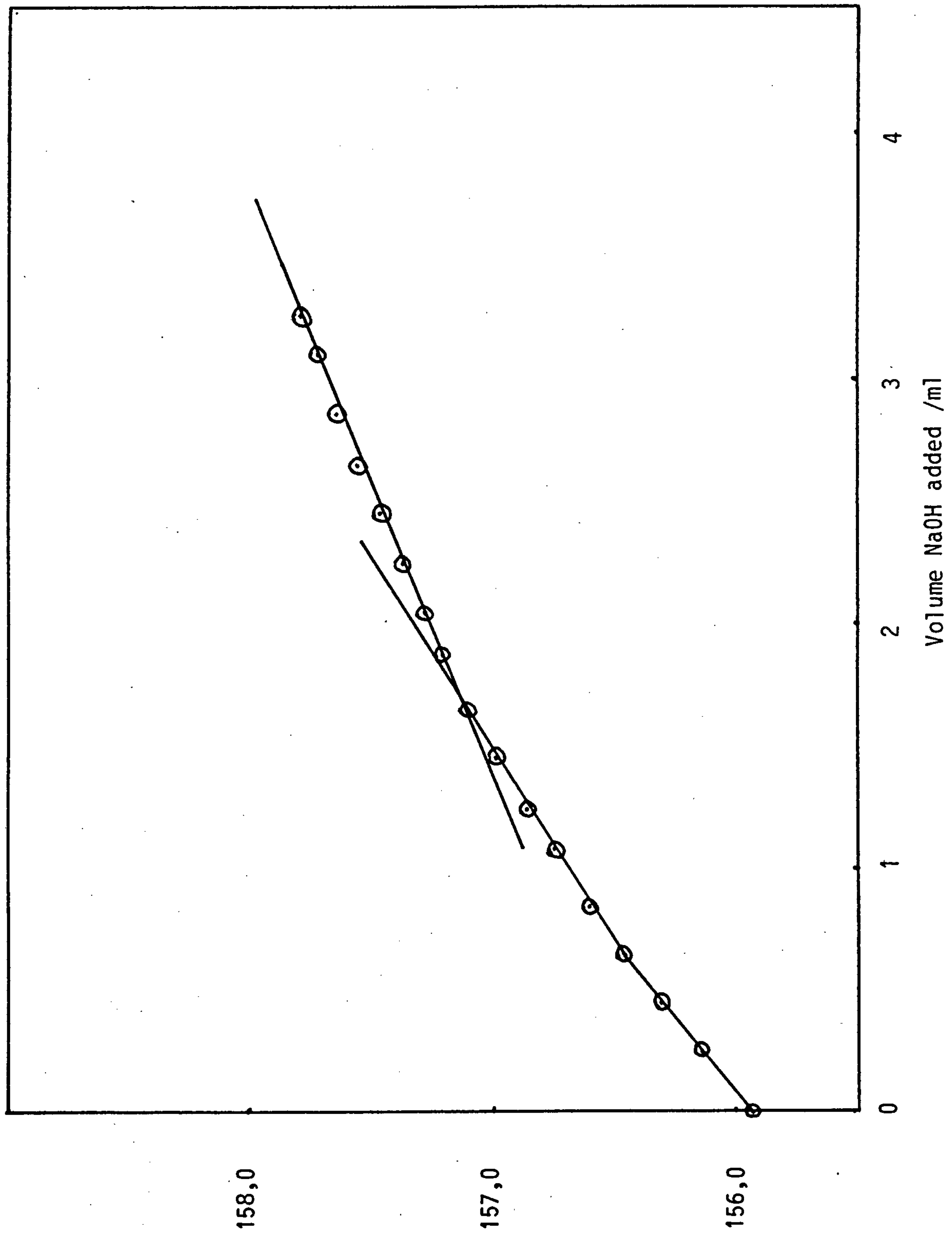
FIGURE 4.2: Titration curve of 20,00 ml 0,046 5 M H_2SO_4 vs 0,504 8 M NaOH

TABLE 4.16

Flow-times for the titration of 20,00 ml 0,042 0 M acetic acid with 0,504 8 M NaOH

Flow-time/s	Volume NaOH/ml	Flow-time/s	Volume NaOH/ml
155,939	0,00	157,202	1,87
156,143	0,24	157,274	2,04
156,299	0,43	157,375	2,25
156,456	0,65	157,473	2,45
156,607	0,85	157,562	2,67
157,750	1,07	157,636	2,87
156,854	1,24	157,718	3,09
156,982	1,45	157,799	3,26
157,120	1,65		

FIGURE 4.3: Titration curve of 20,00 ml 0,042 0 M acetic acid vs 0,504 8 M NaOH.



5. THE VISCOSITY OF CONCENTRATED SOLUTIONS OF AQUEOUS ELECTROLYTES

A common way of obtaining an expression to calculate the viscosity of concentrated solutions of single electrolytes has been to add higher terms in c to the Jones-Dole equation, e.g.

$$\eta_{rel} = 1 + A\sqrt{c} + Bc + Dc^2 \qquad (1.14)$$

Jones and Talley, for example, obtained values for the D-coefficient of KBr and KCl (0,012 21 and 0,008 08 respectively). These extended Jones-Dole equations apply up to 2 M for KBr and up to 3 M for KCl. For more concentrated solutions terms in c^3 and higher have to be added.

This is similar to the case of spherical suspensions. Vand |105|, for example, extended Einstein's limiting theory to higher concentrations and obtained the logarithmic expression

$$\ln \eta_{rel} = \frac{k_1\theta + r_2(k_2 - k_1)\theta^2 + ---}{1 - Q\theta} \qquad (5.1)$$

where θ is the particle volume fraction, k_1 is the Einstein shape factor, k_2 is the shape factor for collision doublets, r_2 is the collision time constant and Q is a hydrodynamic interaction parameter. Substituting the appropriate numerical values for those constants given by Vand into equation (5.1), and expanding the expression as a power series, we obtain

$$\eta_{rel} = 1 + 2{,}5\ \theta + 7{,}349\ \theta^2 + --- \qquad (5.2)$$

Thomas/...

Thomas |100| advanced an equation similar to this (also applicable to spherical suspensions):

$$\eta_{rel} = 1 + 2,5\ \theta + 10,05\ \theta^2 + A'\ \exp B'\ \theta. \tag{5.3}$$

Breslau *et al.* |13, 14| used the Thomas equation to apply to electrolytes. They substituted the transformation,

$$\theta = cV_e\ , \tag{5.4}$$

(where c is the molar concentration and V_e the effective rigid molar volume of the solute) into the Thomas equation and neglected the exponential term to obtain

$$\eta_{rel} = 1 + 2,5\ cV_e + 10,05\ c^2 V_e^2\ . \tag{5.5}$$

By substituting a number of pairs of experimental values for c and η_{rel} into equation (5.5) a mean value for V_e for a particular salt can be obtained. This was done for more than seventy salts. The obvious flaw in their approach is of course that the applicability of the Thomas equation to electrolytic solutions is highly questionable. Equation (5.5) clearly corresponds to the extended Jones-Dole equation (1.14). The electrostatic term is neglected while $B = 2,5V_e$ and $D = 10,05V_e^2$. This implies that $D = 10,05\ B^2/(2,5)^2$. The standard deviations with which the individual values of V_e were obtained ranged from ± 2,08% to ± 108,0 % (the mean standard deviation being ± 16,6%), indicating that this relationship between D and B is at best a rough approximation and that much greater flexibility is attained if no such relationship is assumed. A further weakness is that negative values for V_e is obtained, e.g. in the case of KCl.

As/...

As can be expected from the above considerations, the Breslau equation gives only a rough estimate of the relative viscosity.

Another attempt at finding a relationship between B and D was that of Moulik and Rakshit's. They wrote the expanded Jones-Dole equation in the form

$$\eta_{rel} = 1 + Bc + (B^2)^n \, c^{(1 + \ell)} \qquad (5.6)$$

where n and ℓ are constants, the values of ℓ being restricted within the limits $1 \leqq \ell \leqq 2$. They obtained values for n and ℓ for 13 salts at various temperatures. No constant general relationship between B and D coefficients was found.

Out of interest three independently determined pairs of values for B and D were tested against equation (5.6) in the cases where Moulik and Rakshit report $n = \ell = 1$, i.e. where $D = B^2$. These values are compared in table 5.1 below.

TABLE 5.1

Salt	B	D	B^2	% Difference	Reference
KF (25°C)	0,127	0,008	0,016	100%	23
LiCl (25°C)	0,138	0,013	0,019	46,2%	23
NaCl (35°C)	0,090 1	0,007 1	0,008 1	14,1%	97

We/..

We can conclude that D is of the order B^2, although the equality does not hold. This is true in most cases cited in the literature.

Desnoyer and Perron |23| reported the D-coefficients for a large number of alkali and tetraalkylammonium halides. Some of these are listed in table 5.2 below.

TABLE 5.2

Salt	D	D(NaX) - D(KX)
NaF	0,030	0,022
KF	0,008	
NaCl	0,007	0,005
KCl	0,002	
NaBr	0,011	0,000
KBr	0,011	
NaI	0,070	0,049
KI	0,021	

It is clear that there is no constant difference between the D-values of the halides of sodium and potassium. The same is true for the D-coefficients of the other pairs of alkali halides as reported by the above authors. This immediately rules out the possibility of splitting D into ionic components. They concluded that the main contributions to D are (i) higher terms of the long-range coulombic forces, (ii) higher terms of the hydrodynamic effect, and (iii) interactions arising from changes in solute-solvent interaction with concentration. D is thus more complex than the B-coefficient and to date no way has been found to calculate this parameter from single salt data for mixtures of electrolytes.

Suryanarayana and Venkatesan |99| proposed an equation which takes the form (A' and B' not equal to the Thomas coefficients (5.3))

$$\eta^* = A' \exp B' c^* . \qquad (5.7)$$

A' and B' are empirical constants, η^* is the ratio of the viscosity of the solution to that at saturation at the same temperature and c^* is the ratio of the mole fraction of the solute to that at saturation at the same temperature. Equation (5.7) was applied to the viscosity of NaCl at temperatures between 30°C and 55°C. A constant value for B' was obtained throughout this temperature range. Their expression can of course be expanded as a power series,

$$\text{viz.} \quad \eta^* = A' + A'B' c^* + A'(B')^2(c^*) + \text{-----}. \qquad (5.8)$$

Since $\eta^* = \eta_{soln}/\eta_{satn}$ and $c^* = c_{sol}/c_{satn}$ we can rearrange equation (5.8) to give

$$\eta_{rel} = A'' + A''B''c_{sol} + A''(B'')^2 + c^2{}_{sol} + \text{---} \qquad (5.9)$$

where $A'' = A'\eta_{satn}/\eta_{H_2O}$ and $B'' = B'/c_{satn}$. Again the expression is similar to the extended Jones-Dole equation, the electrostatic term being neglected.

Another/...

Another viscosity expression for concentrated electrolytes is that of Moulik's |71|,

$$(\eta_{rel})^2 + M + Kc^2 \ . \qquad (5.10)$$

M and K are empirical constants. In a rearranged and expanded form it becomes

$$\eta_{rel} = M^{\frac{1}{2}} + (K/2M^{\frac{1}{2}})\ c^2 + --- \ . \qquad (5.11)$$

The linear term thus falls away. It is not obvious why equation (5.10) should represent an advantage over the other expressions mentioned.

The approach taken by Goldsack and Franchetto |40, 41, 78| who extended the absolute rate theory developed by Eyring *et al.* |39| to apply to concentrated aqueous electrolytes, does offer distinct advantages since (i) the two parameters in their proposed equation do have a theoretical basis (as opposed to e.g. equations (5.10) and (5.7) whose coefficients are purely emperical, hence offering now new interpretive information) and (ii) their equation can be extended to apply to mixtures of electrolytes as well.

As starting point they used the basic equation for the viscosity of a fluid derived from the absolute rate theory, which has been shown to be

$$\eta = \frac{hN}{V} \exp \Delta G^*/RT \qquad (5.12)$$

where/...

where h is Planck's constant, N is Avogadro's number, R is the gas constant, V is the molar volume of the hole in the liquid, and ΔG^* the molar free energy of activation for creating this hole in the liquid by the particle moving in the fluid. They made the assumption that the two parameters, V and ΔG^*, were average values that include solvent, anion and cation components. For a 1:1 electrolyte they made the substitution

$$V_T = X_1 V_1 + X_c V_c + X_a V_a \tag{5.13}$$

and

$$\Delta G^* = X_1 \Delta G_1^* + X_c \Delta G_c^* + X_a \Delta G_a^* \tag{5.14}$$

where X_1, X_c, and X_a are the mole fractions of the solvent, cation, and anion respectively, V_1, V_c, and V_a are the molar volumes of the solvent molecule hole, the cation hole, and the anion hole respectively, and ΔG_1^*, ΔG_c^*, and ΔG_a^* the free energy of activation per mole of solvent, cation and anion respectively.

Since the mole fraction must take all distinct particles into account, the mole fraction of cations is given by

$$X_c = \frac{m_c}{55{,}509 + 2m} \tag{5.15}$$

where m is the molality of the 1:1 salt. Equation (5.15) applies to water only. For other solvents the appropriate number of moles

per/...

per kg must be substituted. For a 1:1 salt we have $X_c = X_a$ and also $X_c + X_a + X_1 = 1$. Therefore

$$X_1 = 1 - 2X_c \ . \qquad (5.16)$$

When substituting (5.16) into (5.13) and (5.14) one obtains

$$V_T = V_1 \{ 1 + X_c \left(\frac{V_c + V_a}{V_1} - 2 \right) \} \qquad (5.17)$$

and

$$\Delta G^* = \Delta G_1^* + X_c \left(\Delta G_c^* + \Delta G_a^* - 2\Delta G_1^* \right). \qquad (5.18)$$

Substitution of these last two equations into (5.12) results in

$$\eta = \frac{hN}{V_1 \{ 1 + X_c \left[\frac{V_c + V_a}{V_1} - 2 \right] \}} \cdot \exp\{\Delta G_1^*/RT + X_c((\Delta G_c^* + \Delta G_a^* - 2\Delta G_1^*)/RT)\} \qquad (5.19)$$

For the pure solvent equation (5.12) becomes

$$\eta_1 = \frac{hN}{V_1} \exp \Delta G_1^*/RT$$

and, therefore

$$\eta = \frac{\eta_1 \exp XE}{1 + XV} \qquad (5.20)$$

where/...

where

$$E = (\Delta G_c^* + \Delta G_a^* - 2\Delta G_1^*)/RT \quad ,$$

$$V = \frac{V_c + V_a}{V_1} - 2 \quad ,$$

and

$$X = X_c \; .$$

It is clear that (5.20) is a two-parameter equation. V and E, as defined above, apply only to 1:1 electrolytes. Appropriate definitions for all salt types (e.g. 1:2, 2:1, 1:3, etc.) are easily derived in the same manner as above (with the basic form of equation (5.20) staying the same, of course).

Numerical values for E and V can now be determined by fitting equation (5.20) to experimental data. This is done by rearranging (5.20) to read

$$Y = \ln \left| \frac{\eta}{\eta_1}(1 + XV) \right| = XE. \qquad (5.21)$$

A plot of Y against X should yield a straight line of slope E. The value of V which gives the best straight line, E, can thus be computed. This was done by trial and error, varying V from 0 to 50 in increments of 0,01. The viscosity parameters of several alkali and ammonium halides were determined and equation (5.20) was found to predict observed viscosities within experimental error over the high concentration region. Furthermore, as opposed to other viscosity equations which have an exponential form, equation (5.20) can also account for negative viscosity increments, as in the cases of e.g. KCl, CsCl, KI, etc. where the plots of η vs. m have distinct minima.

If equation (5.20) is expanded, the terms in X^2 and higher are ignored, and the approximation is made that at low concentration $X \cong \frac{m}{55,51}$, we can write

$$\eta_{rel} = 1 + \left(\frac{E - V}{55,51} \right) m. \tag{5.22}$$

Good correspondence between (E - V)/55,51 and the Jones-Dole B-coefficient was observed for several electrolytes. Exact agreement should not be expected since B-coefficients are determined at low-concentration taking into account the electrostatic contribution.

5.1 APPLICATION OF THE GOLDSACK AND FRANCHETTO EQUATION TO MIXTURES OF ELECTROLYTES.

Equation (5.20) has been extended |41| to apply to mixtures of binary, as well as ternary, electrolytes. The expression for a binary mixture of 1:1 salts takes the form

$$\eta_{rel} = \frac{\eta_1 \exp(X_{\mathcal{C}_1}E_1 + X_{\mathcal{C}_2}E_2)}{1 + X_{\mathcal{C}_1}V_1 + X_{\mathcal{C}_2}V_2} \tag{5.23}$$

with/...

with X_{c_1} the mole fraction of the cation of the first electrolyte, E_1 the free energy parameter of the first electrolytes, and so on, E_1, E_2, V_1, and V_2 being defined as in equation (5.20) above. The expression was found to predict viscosities of binary mixtures with reasonable accuracy |41, 78|. Modified to apply to ternary mixtures |41| the expression still proved accurate within experimental error.

As a matter of curiosity equation (5.23) was used to predict the course of a viscometric titration where HCl is titrated with NaOH. For this purpose the viscosity parameters of NaOH, which are not available in the literature, had to be calculated. A FORTRAN program was written to perform the necessary calculations (Appendix C), using viscosity data taken from the International Critical Tables |106|. For NaOH up to 10 $\underline{M}$ at 25°C the following values were obtained: E = 30,14 and V = 26,99.

HCl was titrated with NaOH at both low (figure 5.1) and high (figure 5.3) concentrations. The curves predicted for these two titrations by equation (5.23) can be found in figures 5.2 and 5.4. For the purpose of calculation the values E = 5,67 and V = 12,00 were used for NaCl, and E = 6,66 and V = 5,69 for HCl |41|. In each case the molalities of the salts present in solution had to be calculated from the known molarities of the starting solutions. The density values required were obtained from the literature |96 and 106 for HCl and NaOH respectively|. For comparison the curve predicted by equation (1.11),

i.e. $\eta_{rel} = 1 + a\sqrt{\Gamma} + b\Gamma$, was calculated for the titration at low concentration (figure 5.2).

Both equations predict the sharp experimental end-point (figures 5.1 and 5.2). The discrepancy between the two sets of values for the relative viscosity along the curve can be explained by the fact that the values for V and E were calculated by fitting a curve to viscosity data at high concentration, normally from 0,5 *m* upward. Equation (1.11) can therefore be expected to be much more accurate in the low concentration region than the Goldsack and Franchetto equation. It is therefore also not surprising that the curve predicted by equation (1.11) resembles the experimental curve more closely.

At high concentration the predicted end-point is again experimentally confirmed, although there is a considerable difference in the shapes of the calculated and experimental curves. Since the experimental curve is a plot of flow-time against volume of titrant added, this difference could be attributed to the changes in density which are not taken into account, and which are much more marked at high than at low concentration. Nevertheless, in both the experimental and calculated curves there is considerable deviation from linearity, which will make any discontinuity much more difficult to observe in cases where the difference between the contributions to the relative viscosity made by the salts involved is small (as apposed to the case of HCl and NaOH).

A disadvantage of the Goldsack and Franchetto equation is that the individual ionic viscosity parameter values cannot be calculated.

Table 5.3/...

Table 5.3 below contains values of E and V calculated for potassium and sodium halides |40, 41|.

TABLE 5.3

Salt	V	(NaX - KX)	E	(NaX - KX)	E - V	(NaX - KX)
NaF	20,45		30,97		10,52	
		12,94		16,76		3,82
KF	7,51		14,21		6,70	
NaCl	12,00		15,67		3,67	
		3,67		8,13		4,46
KCl	8,33		7,54		-0,79	
NaBr	16,21		16,98		0,77	
		5,13		8,82		3,69
KBr	11,08		8,16		-2,92	
NaI	11,35		11,82		0,47	
		-2,00		3,74		5,74
KI	13,35		8,08		-5,27	

Now from the definitions of V and E in equation (5.20) it is clear that there should be a constant difference in the values for these parameters for pairs of salts involving the same two cations and a single anion in each case. In other words, since

$$\Delta G_c^* + \Delta G_a^* = ERT + 2\Delta G_1^*$$

and

$$V_c + V_a = (V + 2)V_1$$

(where/...

(where ΔG_1^* and V_1 are constant since they are applicable to the solvent only) it follows that

$$V(NaF) - V(KF) = V(NaCl) - V(KCl) = V(NaBr) - V(KBr) \text{ etc.}$$

and the same for values of E.

The experimental values listed in table 5.3, however, do not display this constant difference. There is more of a constant difference in the values of (E-V). This is to be expected from the expanded form of the Goldsack and Franchetto equation (5.22), since this property has repeatedly been confirmed experimentally for the B-coefficient.

It should be noted that Nowlan *et al.* |78| found the Goldsack and Franchetto equation to fail in such cases as $Ca(NO_3)_2$ and $MgSO_4$ where ion-pairs and neutral molecules ($Ca(NO_3)_1^+$ and $MgSO_4{}^0$) appear. The Goldsack and Franchetto equation assumes complete dissociation, of course.

Since, therefore, the viscosity parameters of individual ionic (or neutral) species in solution cannot be calculated, but only for a salt as a whole, it follows that in the case of weak electrolytes or where complex formation occurs, the equation will lose much of its usefulness.

From the above considerations one is lead to conclude that at high concentration matters are far less clear cut than at low concentration where the equation

η_{rel}/...

$$\eta_{\mathrm{rel}} = 1 + a\sqrt{\Gamma} + b\Gamma \qquad (1.11)$$

(where a is calculable from Asmus' theory and b can be obtained from individual values of b_i) is applicable. Since the D-coefficient in the extended Jones-Dole equation (1.14) cannot be split into its ionic components, as has been mentioned earlier, it is unfortunately doubtful whether it is possible to extend equation (1.11) to

$$\eta_{\mathrm{rel}} = 1 + a\sqrt{\Gamma} + b\Gamma + d\Gamma^2 \qquad (5.24)$$

where d is calculable from single salt data.

For work where one wants to obtain the exact composition of a multiionic solution, such as for the determination of equilibrium constants, equation (1.11) in the low concentration region certainly, therefore, seems to be the most appropriate.

FIGURE 5.1/...

FIGURE 5.1: Titration curve of 20,02 ml 0,046 1 M HCl vs 0,494 6 M NaOH.

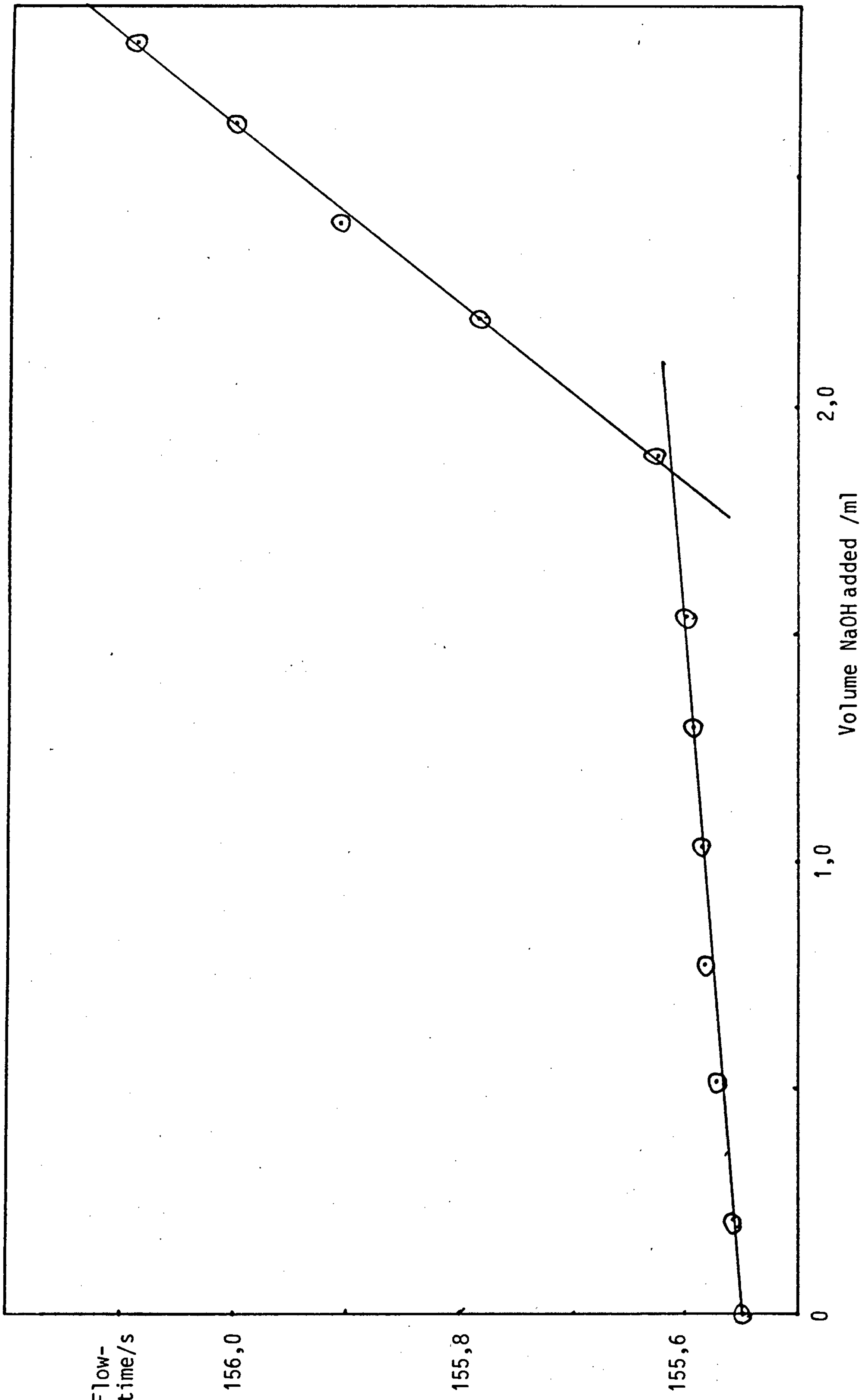


FIGURE 5.2: Calculated curve for titration of 20,02 ml 0,046 1 M HCl vs 0,494 6 M NaOH.

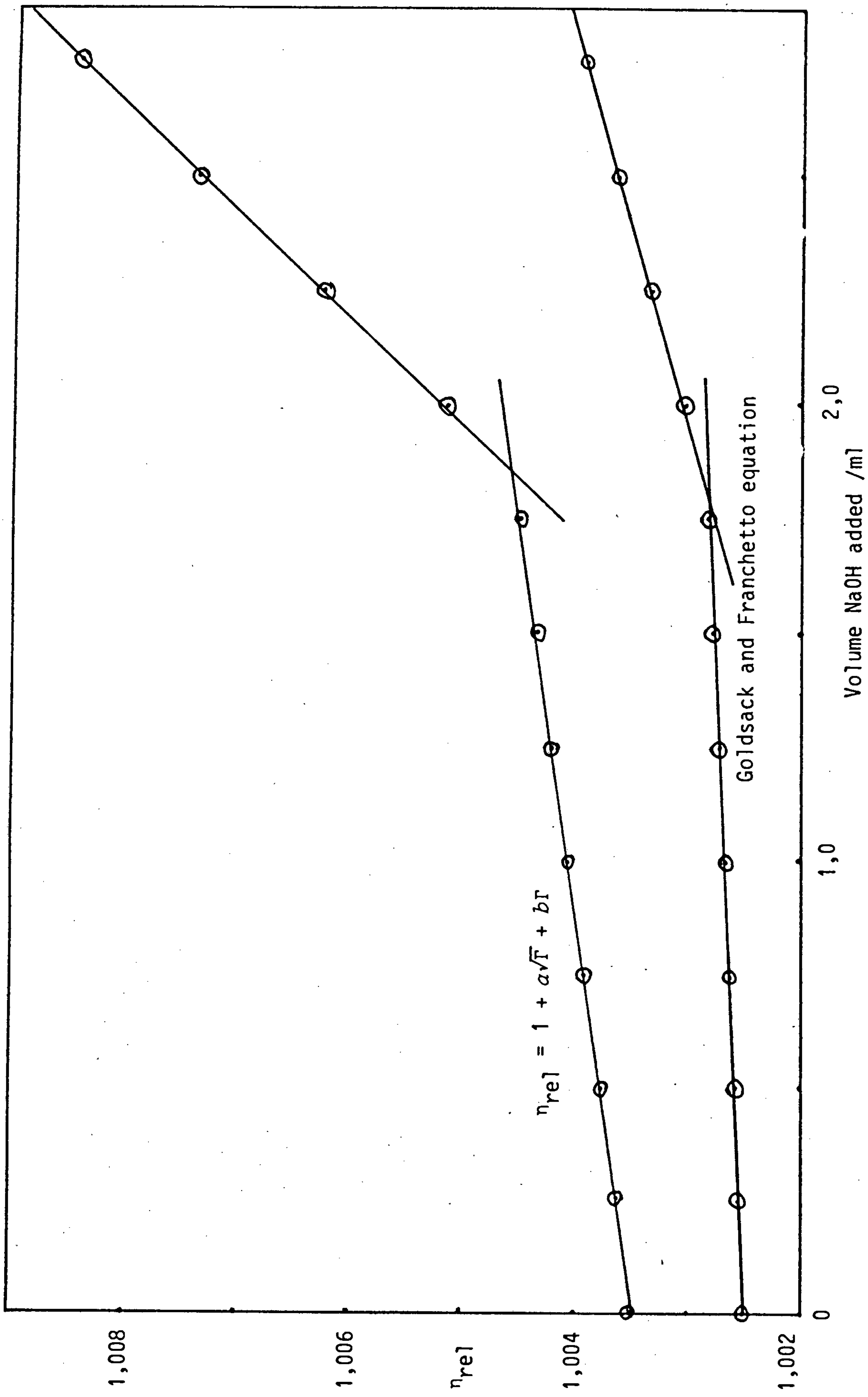


FIGURE 5.3: Titration curve of 20,02 ml 1,002 6 M HCl vs 5,019 0 M NaOH

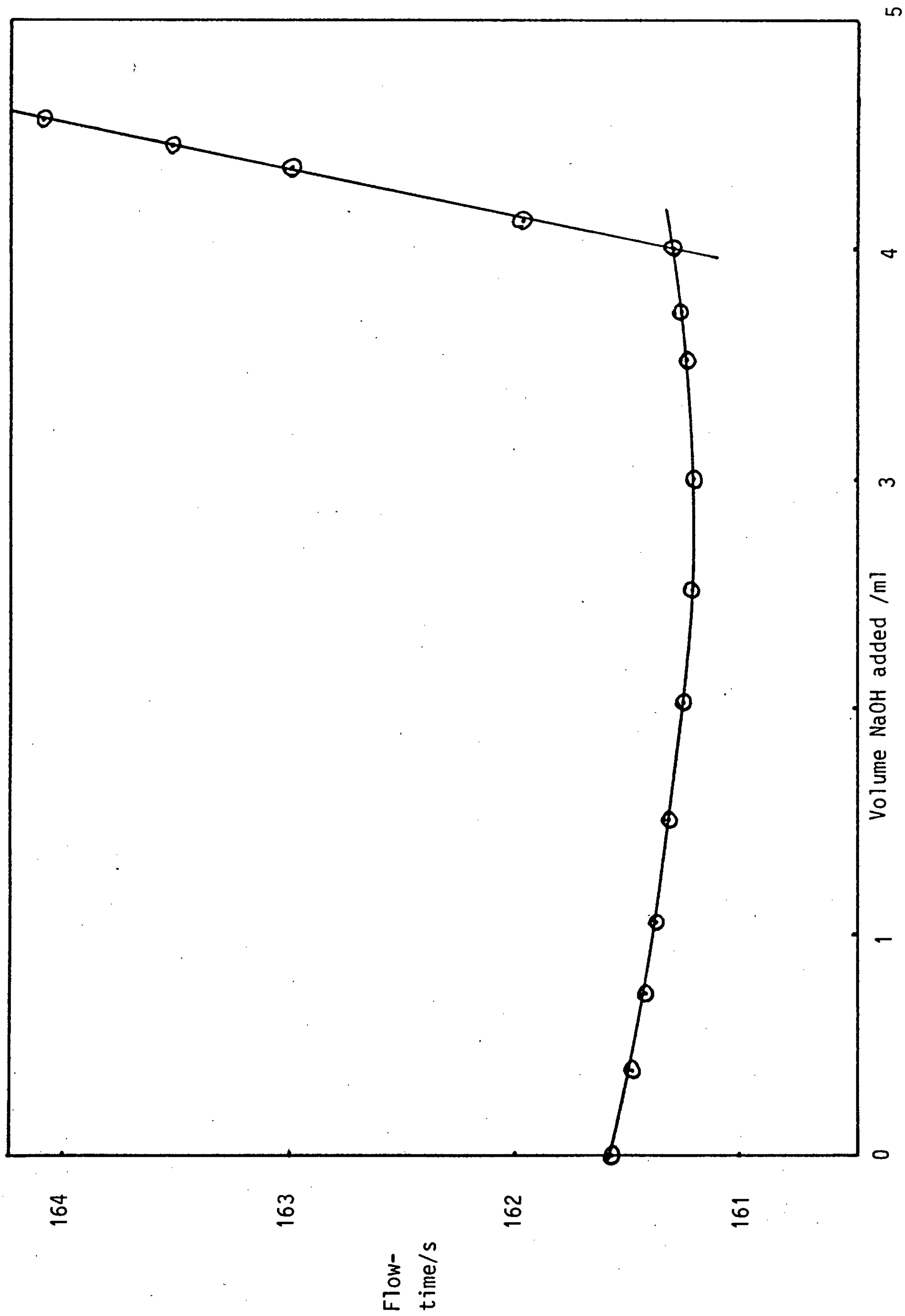
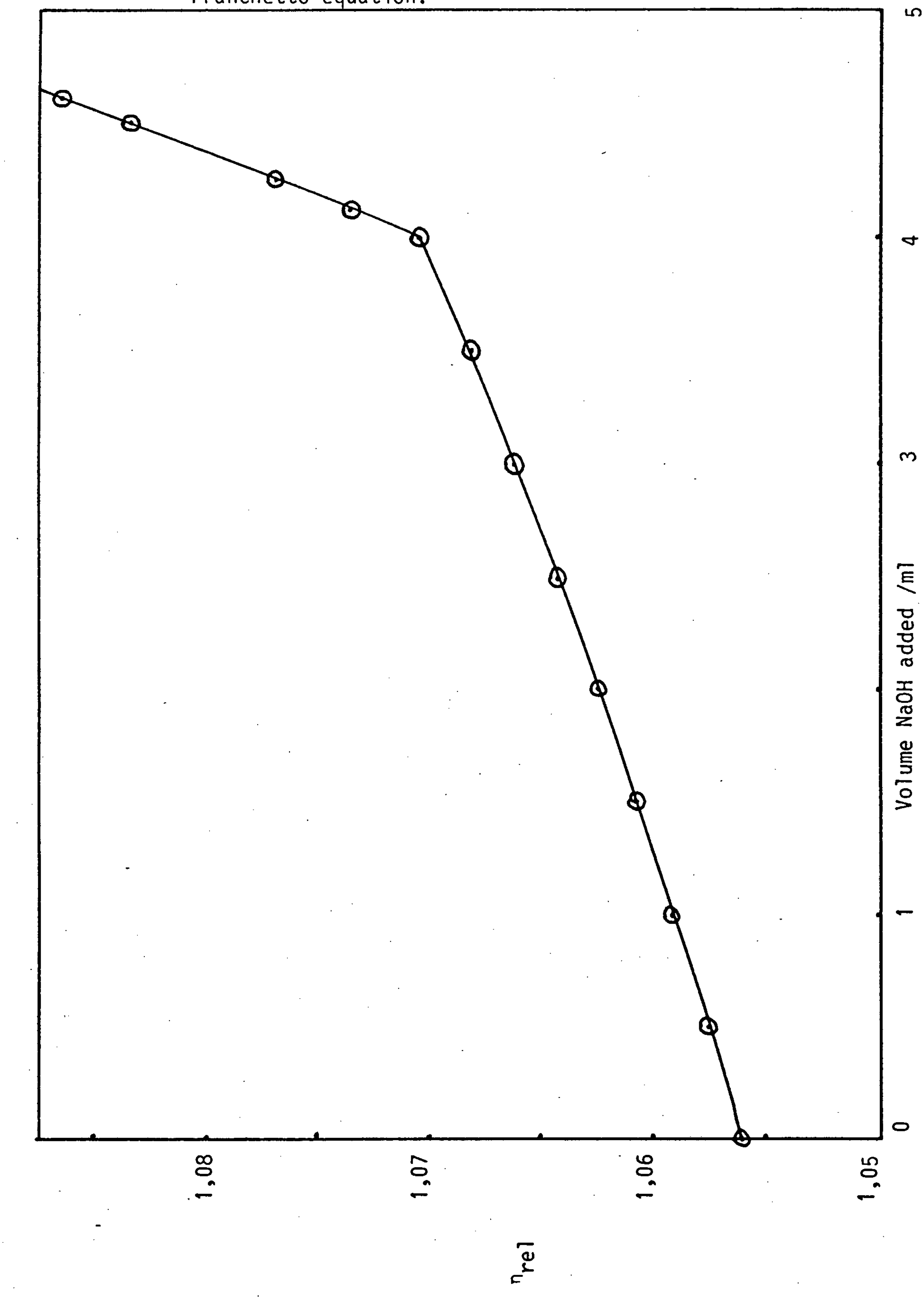


FIGURE 5.4: Calculated curve for titration of 1,002 6 M HCl with 5,019 0 M NaOH using the Goldsack and Franchetto equation.



6. COMPLEXOMETRIC TITRATIONS OF ZINC, CADMIUM, AND MERCURY

The viscosity of a series of solution mixtures in the $CdCl_2$-MCl-H_2O system, where $M = H^+$, Li^+, Na^+, K^+, and NH_4^+, was studied by Galinker *et al.* |35| in order to establish how complex formation is reflected in the relative viscosity, whether it is possible to determine the composition of the complexes formed in solution, and also to test the applicability of a few equations to mixtures of electrolyte solutions. The system was chosen because complex formation is well established here, having been confirmed by various techniques, e.g. polarography, potentiometry and by measurement of refractive index.

For each system a series of isomolar mixtures were prepared from individual 2,5 <u>M</u> starting solutions. From the relative viscosities determined separately for $CdCl_2$, HCl, LiCl, NaCl, KCl, the following formulae were used to calculate the relative viscosity for each mixture for each system in order to establish their applicability.

$$\eta_{rel} = \eta_1 x_1 + \eta_1 x_2 \qquad (6.1)$$

where η_{rel}, η_1 and η_2 are the relative viscosities of the mixture and the starting solutions, and x_1 and x_2 are the mole fractions of each component,

$$\eta_{rel}^{1/3} = \eta_1^{1/3} x_1 + \eta_2^{1/3} x_2 \qquad (6.2)$$

log/...

$$\log \eta_{rel} = x_1 \log \eta_1 + x_2 \log \eta_2 \qquad (6.3)$$

and

$$\frac{d_{rel}}{\eta_{rel}} = \frac{x_1 d_1}{\eta_1} + \frac{x_2 d_2}{\eta_2} \qquad (6.4)$$

where d_{rel}, d_1, and d_2 are the relative densities of the mixture and two components.

Equation (6.4) postulates the additivity of kinematic fluidities, while (6.1), (6.2), and (6.3) express the simple additivity of relative viscosity, and the addivity of the cube roots and the logarithms of relative viscosity respectively.

The values calculated from equation (6.2) - (6.4) were approximately similar, with those from equation (6.4) giving the closest agreement with experimental values. The maximum deviations of the predicted values from experimental values were 10-12%, 8-10%, and 6-9% for equations (6.2), (6.3), and (6.4) respectively. For equation (6.1) the maximum deviation was as high as 17%. The maximum deviations of the experimental quantities from those calculated from the four formulae all occur at the same composition, *viz.* 50% $CdCl_2$. In every case the deviation was negative, i.e. the experimental values of relative viscosity was always lower than calculated, giving a pronounced curve towards to the composition axis when relative viscosity is plotted against percentage $CdCl_2$.

Unfortunately/...

Unfortunately the relevant papers from which equations (6.2), (6.3) and (6.4) were taken were not available and hence their validity will not be commented upon. Nevertheless, Galinker *et al.* concluded that since the values calculated from these three equations are approximately equal, the true additive quantity is close to them. Furthermore they concluded that the bend towards the composition axis can at best serve as an indication of the occurence of appreciable interaction between the components of the solution, while it cannot justifiably be used to determine the composition of the complexes present.

Since the calculation of the relative viscosity of mixtures of electrolytes at high concentration is much less simple and less well established than for dilute solutions, as has been shown in section 5, it was decided to titrate $CdCl_2$ viscometrically with HCl and KCl in the dilution range where the linear term, $b\Gamma$, predominates. Whereas the viscosity curves obtained by Galinker *et al.* showed a continuous downward curve at a constant total concentration of 2,5 $\underline{M}$, it was hoped that a viscometric titration in the dilute region would be more meaningful with perhaps one or more clear discontinuities. Furthermore, the concentration of each species in solution could be calculated at every point along the titration curve from known equilibrium constants. It would thus be possible to establish whether any general trend in the speciation curve is reflected in the titration curve. This would be expected, since one would expect differences between the B-coef-

ficients/...

ficients of Cd^{2+} and the various chloride complexes of cadmium. In addition it was also decided to also titrate zinc and mercury with HCl and KCl to establish what changes, if any, occur down the group.

6.1 EXPERIMENTAL DETAIL

The following viscometric titrations were performed:

(i) 20,02 ml 0,099 7 M $ZnSO_4$ vs 0,506 7 M HCl (figure 6.1),
(ii) 20,02 ml 0,099 7 M $ZnSO_4$ vs 1,015 0 M KCl (figure 6.3),
(iii) 20,02 ml 0,095 2 M $CdCl_2$ vs 0,506 7 M HCl (figure 6.5),
(iv) 20,02 ml 0,095 2 M $CdCl_2$ vs 1,015 0 M KCl (figure 6.7),
(v) 20,02 ml 0,102 7 M $HgCl_2$ vs 1,002 6 M HCl (figure 6.9),
(vi) 20,02 ml 0,102 7 M $HgCl_2$ vs 1,015 0 M KCl (figure 6.11),
(vii) 20,02 ml 0,091 4 M $Hg(CH_3COO)_2$ vs 1,002 6 M HCl (figure 6.13).

In each case flow-time (in seconds), which is of course directly proportional to kinematic viscosity, was plotted against volume of titrant added. Each titration was repeated at least three times.

6.2 CALCULATION OF SPECIATION CURVES

The concentrations of the individual species in solution at each point along the titration curves were calculated according to the scheme that follows below.

The stepwise formation constants, K_i, for the three systems under discussion are defined by

$$K_i = \frac{|MCl_i|}{|MCl_{i-1}|\ |Cl|} \ . \tag{6.5}$$

M is Zn, Cd, or Hg. Charges are neglected for convenience.

The overall formation constants, B_i, are in turn defined as

$$B_i = \frac{|MCl_i|}{|M|\ |Cl|^i} \tag{6.6}$$

and of course

$$B_i = \underset{i=1}{\pi} K_i \ . \tag{6.7}$$

Let the subscript, T, indicate total concentration, then

$$|M|_T = |M| + |MCl| + |MCl_2| + |MCl_3| + |MCl_4| \tag{6.8}$$

and

$$|Cl|_T = |Cl| + |MCl| + 2|MCl_2| + 3|MCl_3| + 4|MCl_4| \ . \tag{6.9}$$

Substituting equation (6.6) into (6.8) and (6.9) one gets

$|M|_T$/...

$$|M|_T = |M| + \beta_1|M||Cl| + \beta_2|M||Cl|^2 + \beta_3|M||Cl|^3 + \beta_4|M||Cl|^4 \quad (6.10)$$

and

$$|Cl|_T = |Cl| + \beta_1|M||Cl| + 2\beta_2|M||Cl|^2 + 3\beta_3|M||Cl|^3 + 4\beta_4|M||Cl|^4. \quad (6.11)$$

Rearranging equations (6.10) and (6.11) one obtains

$$|M| = \frac{|M|_T}{1 + \beta_1|Cl| + \beta_2|Cl|^2 + \beta_3|Cl|^3 + \beta_4|Cl|^4} \quad (6.12)$$

and

$$|M| = \frac{|Cl|_T - |Cl|}{\beta_1|Cl| + 2\beta_2|Cl|^2 + 3\beta_3|Cl|^3 + 4\beta_4|Cl|^4}. \quad (6.13)$$

Equating (6.12) and (6.13) we have

$$\begin{aligned}
&\beta_4|Cl|^5 + (4\beta_4|M|_T - \beta_4|Cl|_T + \beta_3)\ |Cl|^4 \\
&\quad + (3\beta_3|M|_T - \beta_3|Cl|_T + \beta_2)|Cl|^3 \\
&\quad + (2\beta_2|M|_T - \beta_2|Cl|_T + \beta_1)\ |Cl|^2 \\
&\quad + (\beta_1|M|_T - \beta_1|Cl|_T + 1)|Cl| - |Cl|_T = 0 \qquad (6.14)
\end{aligned}$$

$|M|_T$/...

$|M|_T$ and $|Cl|_T$ are known at each point in the titration, therefore the free chloride concentration, $|Cl|$, and the free metal concentration, $|M|$, can be obtained from equations (6.14) and (6.12), and hence the concentration of each complex present can be computed using equation (6.6).

Since equation (6.14) can only be solved for by employing time-consuming numerical techniques, a FORTRAN program was written which, given the initial metal, chloride, and titrant concentrations, along with the appropriate β-values, computes the concentration of each species in solution along the titration curve. The program can be found in Appendix B.

Because of the extremely high values of β for mercury, Newton's method was found to be in appropriate in practice, and a bisection technique was preferred for solving the fifth power equation. The computed values for each titration are shown in tables (6.2) - (6.8), while the plotted speciation curves are to be found in figures (6.2), (6.4), ---, (6.12), (6.14).

For zinc and cadmium the values for the thermodynamic equilibrium constants found in Martell and Smith |69|, and Bailor |10| respectively, were used. For mercury the stoicheiometric equilibrium constants for an ionic strength of 0,5, found in Martell and Smith |69|, were used. In each case a set of formation constants available closest to the ionic strength region (∿0,05-0,25) in which the titrations were performed, was chosen. Each titration involves a gradually changing ionic strength. The formation constants used were not corrected for ionic strength, therefore the speciation curves should not be regarded as absolute, but rather as fair approximations. The values of the formation constants used in the computation are found in table 6.1 below.

TABLE 6.1

Metal ion	Equilibrium	log β 25°C)	Ionic Strength
Zn^{2+}	$\lvert MCl\rvert / \lvert M\cdot Cl\rvert$	0,43 (log β_1^T)	0
Zn^{2+}	$\lvert MCl_2\rvert / \lvert M\cdot Cl\rvert^2$	0,61 (log β_2^T)	0
Zn^{2+}	$\lvert MCl_3\rvert / \lvert M\cdot Cl\rvert^3$	0,5 (log β_3^T)	0
Zn^{2+}	$\lvert MCl_4\rvert / \lvert M\cdot Cl\rvert^4$	0,2 (log β_4^T)	0
Cd^{++}	$\lvert MCl\rvert / \lvert M\cdot Cl\rvert$	1,32 (log β_1^T)	0
Cd^{++}	$\lvert MCl_2\rvert / \lvert M\cdot Cl\rvert^2$	2,22 (log β_2^T)	0
Cd^{++}	$\lvert MCl_3\rvert / \lvert M\cdot Cl\rvert^3$	2,31 (log β_3^T)	0
Cd^{++}	$\lvert MCl_4\rvert / \lvert M\cdot Cl\rvert^4$	1,86 (log β_4^T)	0
Hg^{++}	$\lvert MCl\rvert / \lvert M\cdot Cl\rvert$	6,74	0,5
Hg^{++}	$\lvert MCl_2\rvert / \lvert M\cdot Cl\rvert^2$	13,22	0,5
Hg^{++}	$\lvert MCl_3\rvert / \lvert M\cdot Cl\rvert^3$	14,1	0,5
Hg^{++}	$\lvert MCl_4\rvert / \lvert M\cdot Cl\rvert^4$	15,1	0,5

6.3 DISCUSSION

In the case of viscometric titrations involving dilute solutions of electrolytes where no ionic association occurs, e.g. KCl with HCl, or vice versa, the resulting plot of flow-time against volume of titrant added is a straight line with a positive, or negative, slope. Any deviation from linearity can immediately be interpreted as evidence of ionic interaction. Since not one of the zinc, cadmium, or mercury titrations performed in this work produced a linear titration curve it follows that complex formation occurs in every case. What is less obvious, however, is to what extent the composition of the complexes in solution are reflected in these curves.

For the purpose of interpreting the titration curves it is necessary to keep in mind that the B-coefficients of potassium and chloride are small and negative (-0,007), while that of the hydrogen ion is positive on an order of magnitude larger (0,07). The B-coefficients of zinc and cadmium are an order of magnitude larger still, being 0,325 5 and 0,241 5 respectively |97|. That of mercury was not available, but it is reasonable to expect it to be at least as large as the values for Cd^{2+} and Zn^{2+}.

Any change in the sign of the slope of any speciation curve, i.e. any maximum or minimum, will be reflected in the titration curve as a discontinuity, provided it is not swamped by other effects, and provided it is sharp enough.

In both zinc sulphate titration curves (figures 6.1 and 6.3) there is a steady downward trend, with a distinct negative deviation from linearity. In the case of the titration with HCl (figure 6.1) the constant downward slope can readily be explained in terms of the speciation curves (figure 6.2). Had no complex formation taken place the rapidly increasing hydrogen ion concentration would have provided a straight line with a positive slope. However, along the titration curve the free zinc ions are rapidly replaced by $ZnCl^+$, and to a lesser extent by $ZnCl_2$, with the concentrations of the other complexes remaining negligible. Because of the decrease in charge one would expect the B-coefficients of $ZnCl^+$ and $ZnCl_2$ to be much smaller than that of Zn^{2+}. The difference is in fact so large that the rapidly decreasing free zinc concentration outweighs the combined effect of the increasing H^+, $ZnCl^+$ and $ZnCl_2$ concentrations. Had the titration been continued further the decrease in $|Zn^{2+}|$ would have become slower and the titration curve would have taken an upward swing due to the increase in $|H^+|$.

The titration with KCl (figure 6.3) is similar, except for obvious reasons the downward trend is more pronounced. In the speciation curve $|ZnCl^+|$ does reach a maximum. However the change in its slope (figure 6.4) is very slow. In fact beyond 6 ml. $|ZnCl^+|$ remains approximately constant. This is reflected in a flattening out of the titration curve, since the increase in $|ZnCl_2|$ and $|ZnCl_3^-|$ is approximately linear while the decrease in $|Zn^{2+}|$ also becomes steadier in this region.

The two $CdCl_2$ titrations (figures 6.5 and 6.7) are more informative. As with the titration of $ZnSO_4$ with HCl, the titration of $CdCl_2$ (figure 6.6) shows a decrease in viscosity. Unlike the zinc case, however, the slope becomes positive after the addition of approximately 4 ml of HCl. The initial drop in viscosity can again be attributed to the removal of free metal ions from solution. The decrease in $|Cd^{2+}|$ is accompanied by a decrease in $|CdCl^{+}|$ and an increase in $|CdCl_2|$ and $|CdCl_3^-|$, with $|CdCl_4^{2-}|$ also increasing but remaining essentialy insignificant (figure 6.6). The end-point at 4 ml. corresponds directly with the maximum in the speciation curve representing $|CdCl_2|$. Beyond this the increase in viscosity is due to the increasing H^+ and $CdCl_3^-$ concentrations.

In the titration of $CdCl_2$ with KCl (figure 6.7) the first portion (0-1 ml.) and the last portion (8-13 ml.) of the curve are linear. If these two parts are joined an end-point at ∿ 4 ml is obtained. Again this clearly reflects the maximum in the speciation curve for $CdCl_2$ (figure 6.8).

In the titrations of $HgCl_2$ with HCl (figure 6.9) and KCl (figure 6.11) the clear discontinuities represent the maximum in the $|HgCl_3^-|$ curve (figures 6.10 and 6.12). The titration with HCl differs from that of zinc and cadmium in that the initial drop in viscosity does not take place. This is so because the concentration of Hg^{2+} and $HgCl^+$ in solution is negligible. In both cases the increase in slope beyond the end-point is due to the increase in the concentration of $HgCl_4^{2-}$ (and H^+ in the titration with HCl).

The titration of mercury acetate with HCl (figure 6.13) provides two end-points, the one very sharp and the other less so. The rapid decrease in the free mercury concentration gives the initial part of the curve a large negative slope. The only effect that the maximum reached by $|HgCl^+|$ (figure 6.14) has on the titration curve is the one point at 3.45 ml which lies slightly below the line, indicating that here the viscosity is decreasing ever faster, due to the now decreasing $|HgCl^+|$. The sharp end-point at 3,7 ml. can be attributed to three effects: firstly the virtual disappearance of free mercury from solution, secondly the maximum reached by $|HgCl_2|$, and thirdly the complete protonation of acetate ions. It is not surprising therefore that the end-point is very close to the expected stoicheiometric value. The second end-point corresponds to the maximum in the $|HgCl_3^-|$ curve. Beyond that the increase in slope is caused by the increase in $|HgCl_4^{2-}|$ and $|H^+|$.

One can therefore conclude that the series of titration curves obtained clearly reflect complex formation occurring in solution, and do so with decreasing ambiguity down the group. Also, since the titrations were carried out at low concentration, they yield substantially more information than do the high concentration viscometric data obtained by Galinker *et al.*

If we are satisfied that the equation

$$\eta_{rel} = 1 + a\sqrt{\Gamma} + b\Gamma \qquad (1.11)$$

(with a calculable by Asmus' method and $b = \sum_i b_i\Gamma_i/\Gamma$) can describe with reasonable accuracy the viscosity of a mixture of electrolytes wherein there is no complex formation we should be able to extend it

to/...

to any mixture of species provided we knew (i) the concentration of each individual species present and (ii) the b_i-coefficient for each one. If there are any uncharged complex molecules in solution the equation will have to take the form

$$\eta_{\text{rel}} = 1 + a\sqrt{\Gamma} + B^* c_{\text{Total}} \tag{4.13}$$

as in section 4.2.1. Alternatively we can use an expression of the form

$$\eta_{\text{rel}} = 1 + a\sqrt{\Gamma} + b^*\Gamma^* \tag{6.15}$$

where for the last term on the right hand side only we adopt the convention that Z = 1 for uncharged species. The problem now is to calculate the b_i- coefficients for the individual complex ions and molecules present.

In systems where the stability of complex ions is known the speciation curve can be calculated as above assuming that changes in the ionic strength are of negligible influence. (At the expense of more computing effort it would be possible to calculate Γ and Γ* with a preliminary set of K values (listed for I = 0) and to recalculate fresh values of K (I ≠ 0) and by successive approximation arrive at a consistent set of data.)

Knowing the concentration of each species at each titration point we can calculate a whence

$$b^*\,\Gamma^* = (\eta_{\text{rel}} - 1 - a\sqrt{\Gamma}\,) = X\ . \tag{6.16}$$

In/...

In this way we would obtain a series of simultaneous area equations of the form

$$X_A = (b_1\Gamma_1 + b_2\Gamma_2 + - - - -)_{(\Gamma^* = A)} \qquad (6.17)$$

$$X_B = (b_1\Gamma_1 + b_2\Gamma_2 + - - - -)_{(\Gamma^* = B)}$$

and so on. Each b_i value can now be computed provided the equations are not ill conditioned.

Of course values of e.g. b_{CdCl^+} , b_{CdCl_2}, $b_{CdCl_3^-}$, and $b_{CdCl_4^{2-}}$ obtained from the titration $CdCl_2$ -HCl must be identical with those obtained from the titration $CdCl_2$ - KCl and thus would be a potent test of the theory. Unfortunately the calculation of *a*-coefficients requires a knowledge of equivalent conductivities Λ_{CdCl^+} , $\Lambda_{CdCl_3^-}$ and $\Lambda_{CdCl_4^{2-}}$ which are not available. However estimates could be made and if complex formation does not proceed to a great extent values of *a* may not differ much from what these values would have been had no complex formation taken place. But this is rather begging the question and in the titration systems involving Hg^{2+} and Cl^- the effect of complex formation will certainly play a significant rôle in the value of both *a*- and *b**-coefficients.

Unfortunately lack of time has prevented these considerations being put to the test. While discontinuities in a viscometric titration curve have now been correlated with complex formation in several systems where this is known to occur and, indeed, with maxima in the concentration

of/...

of significant species present, it has not proved possible in the present work to establish the converse proposition, *viz.* that a discontinuity in a viscometric titration curve unambiguously identifies the occurrence of complex formation in a mixture of electrolytes and enables the composition and stability of such complex ions or molecules to be determined. This will be the next step forward.

FIGURE 6.1/...

FIGURE 6.1: 20,02 ml 0,099 7 <u>M</u> $ZnSO_4$ vs 0,506 7 <u>M</u> HCl -titration curve

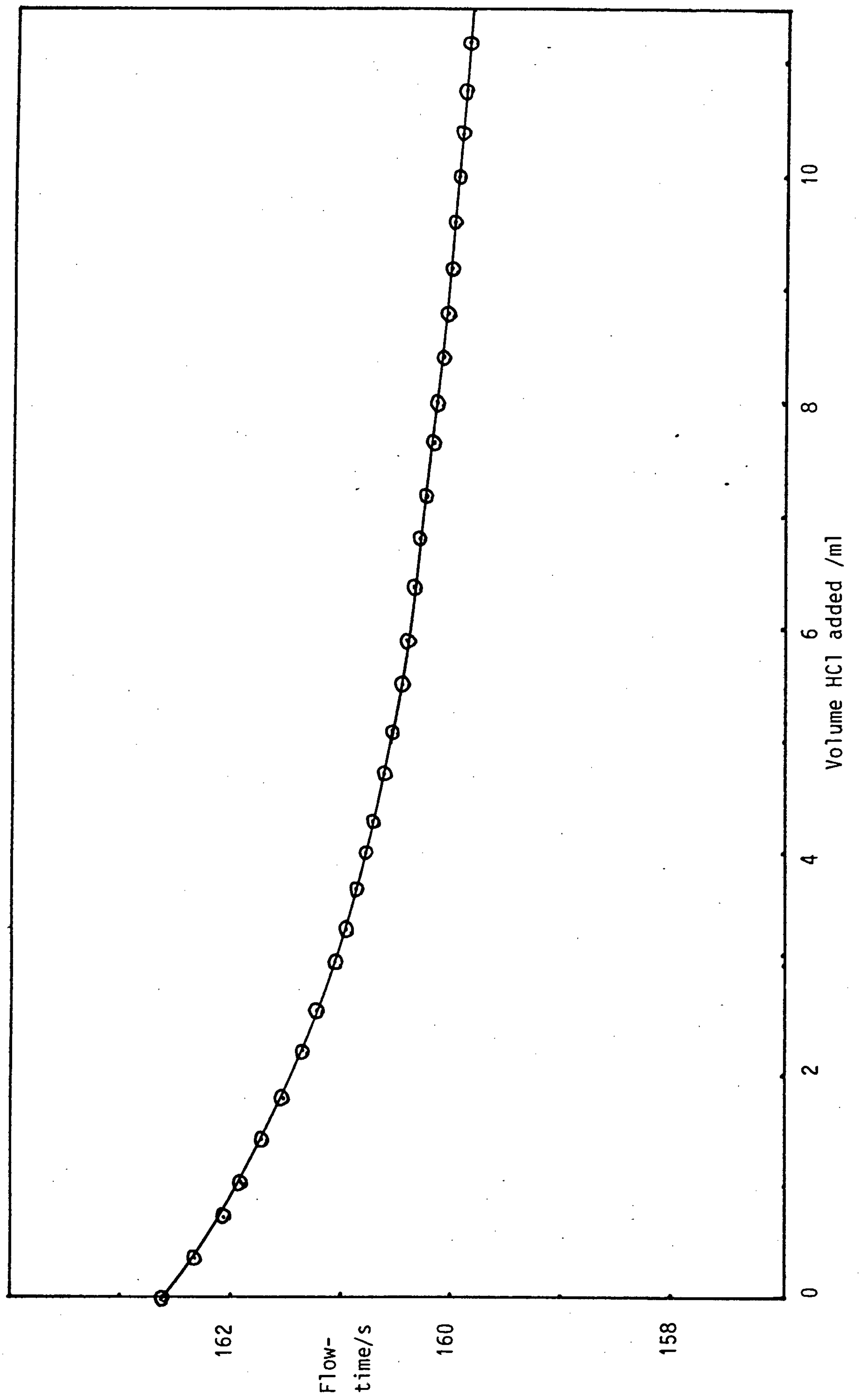


FIGURE 6.2: 20,02 ml 0,099 7 M $ZnSO_4$ vs 0,506 7 M HCl -speciation curve

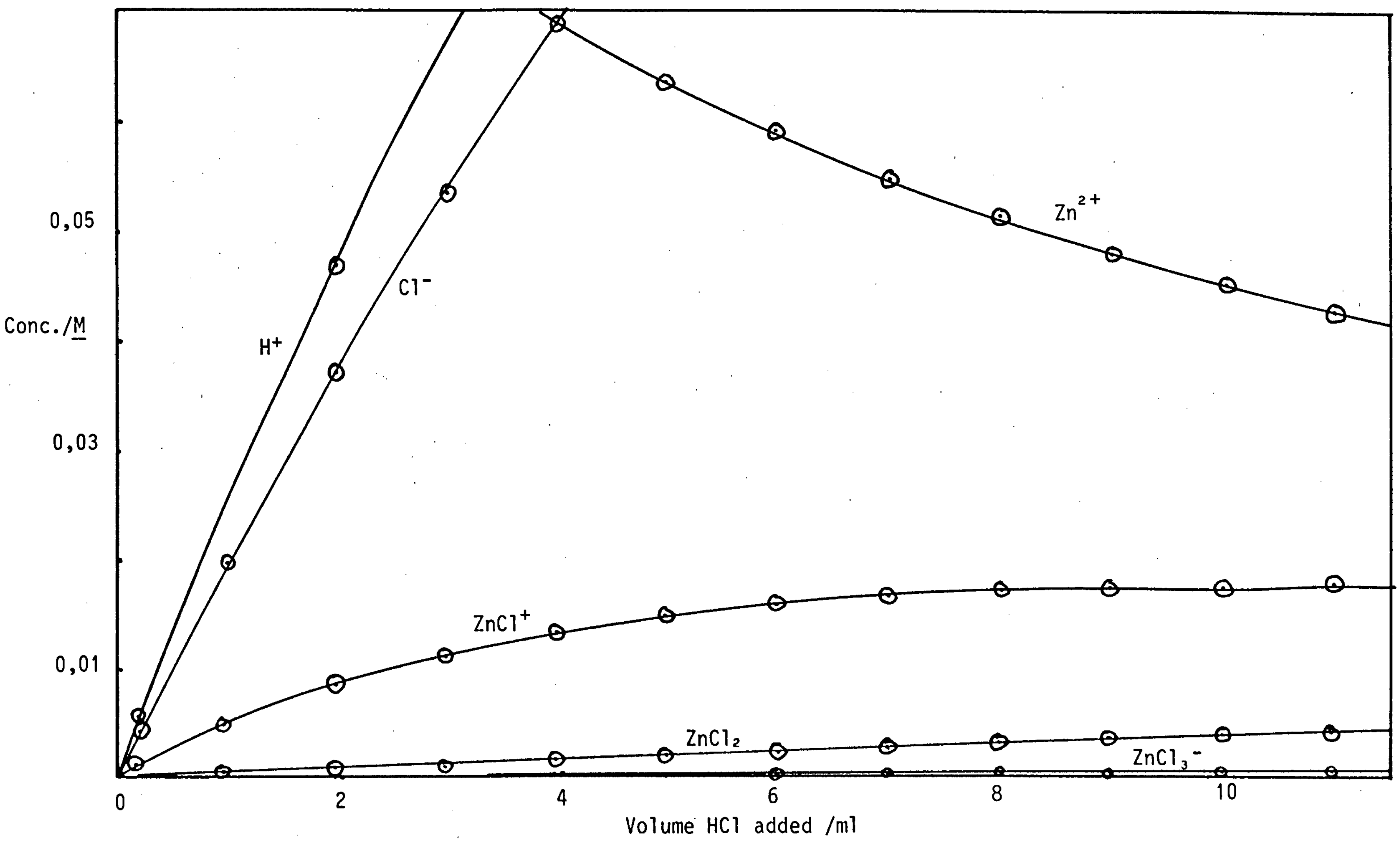
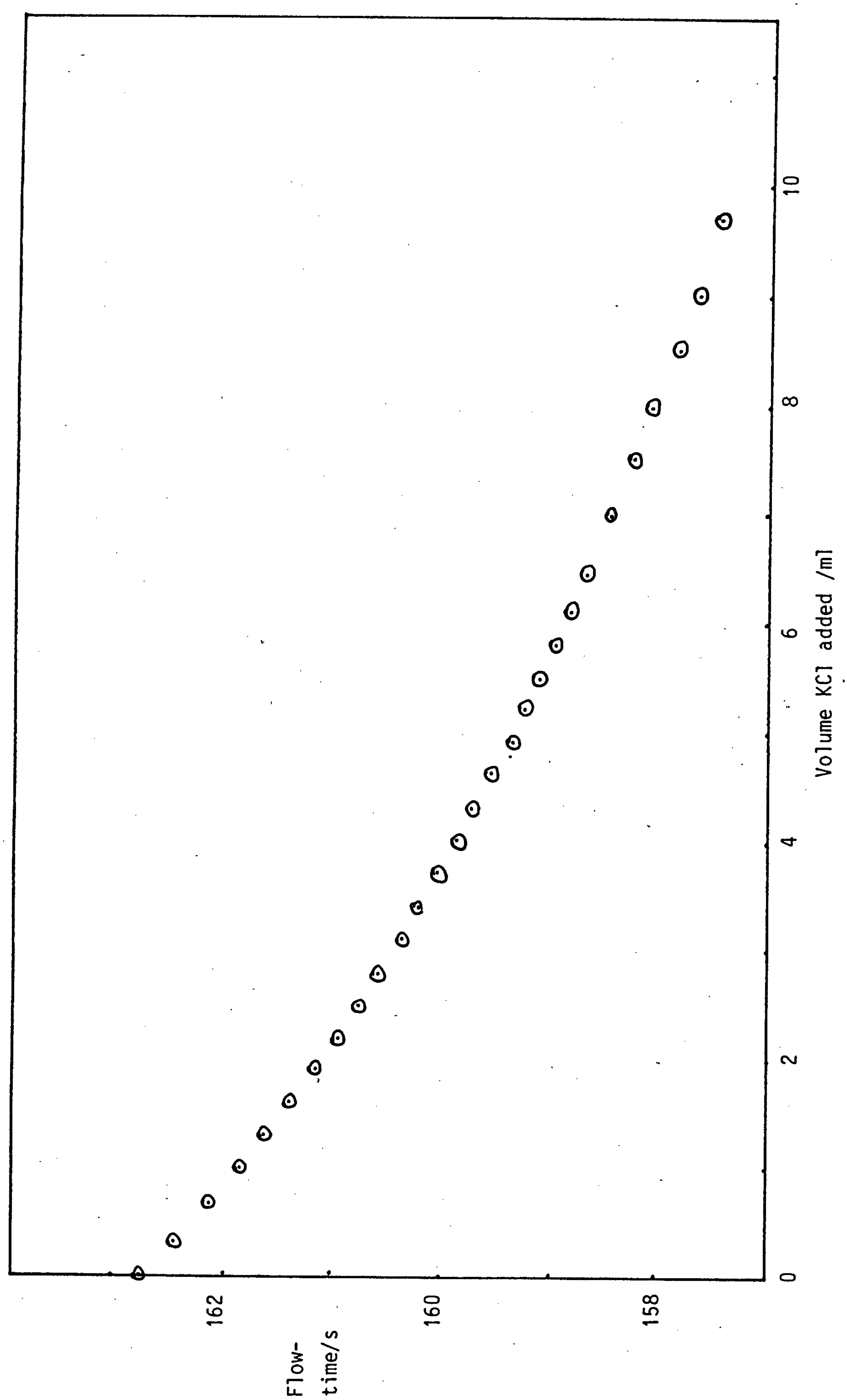


TABLE 6.2

Computed concentration values for the titration of 20,02 ml 0,099 7 M $ZnSO_4$ with 0,506 7 M HCl used for speciation curve plot.

Titre/ml	$\lvert Zn^{++}\rvert$	$\lvert Cl^-\rvert$	$\lvert ZnCl^+\rvert$	$\lvert ZnCl_2\rvert$	$\lvert ZnCl_3^-\rvert$	$\lvert ZnCl_4^{2-}\rvert$
0,0	0,099 7	0	0	0	0	0
0,2	0,097 7	0,003 96	0,001 04	0,000 01	-	-
1,0	0,090 2	0,019 18	0,004 65	0,000 14	-	-
2,0	0,082 0	0,036 92	0,008 15	0,000 46	0,000 01	-
3,0	0,075 0	0,053 40	0,010 78	0,000 87	0,000 04	-
4,0	0,062 9	0,068 75	0,012 76	0,001 33	0,000 07	-
5,0	0,063 6	0,083 08	0,014 23	0,001 79	0,000 12	0,000 01
6,0	0,059 0	0,096 51	0,015 32	0,002 24	0,000 17	0,000 01
7,0	0,054 9	0,109 11	0,016 11	0,002 66	0,000 23	0,000 01
8,0	0,051 2	0,120 96	0,016 67	0,003 05	0,000 29	0,000 02
9,0	0,047 9	0,132 13	0,017 05	0,003 41	0,000 35	0,000 02
10,0	0,045 0	0,142 67	0,017 29	0,003 73	0,000 41	0,000 03
11,0	0,042 4	0,152 64	0,017 42	0,004 02	0,000 48	0,000 04
12,0	0,040 0	0,162 08	0,017 46	0,004 28	0,000 54	0,000 04
13,0	0,037 9	0,171 04	0,017 43	0,004 51	0,000 60	0,000 05
14,0	0,035 9	0,179 54	0,017 35	0,004 71	0,000 66	0,000 06

FIGURE 6.3: 20,02 ml 0,099 7 M $ZnSO_4$ vs 1,015 0 M KCl -titration curve



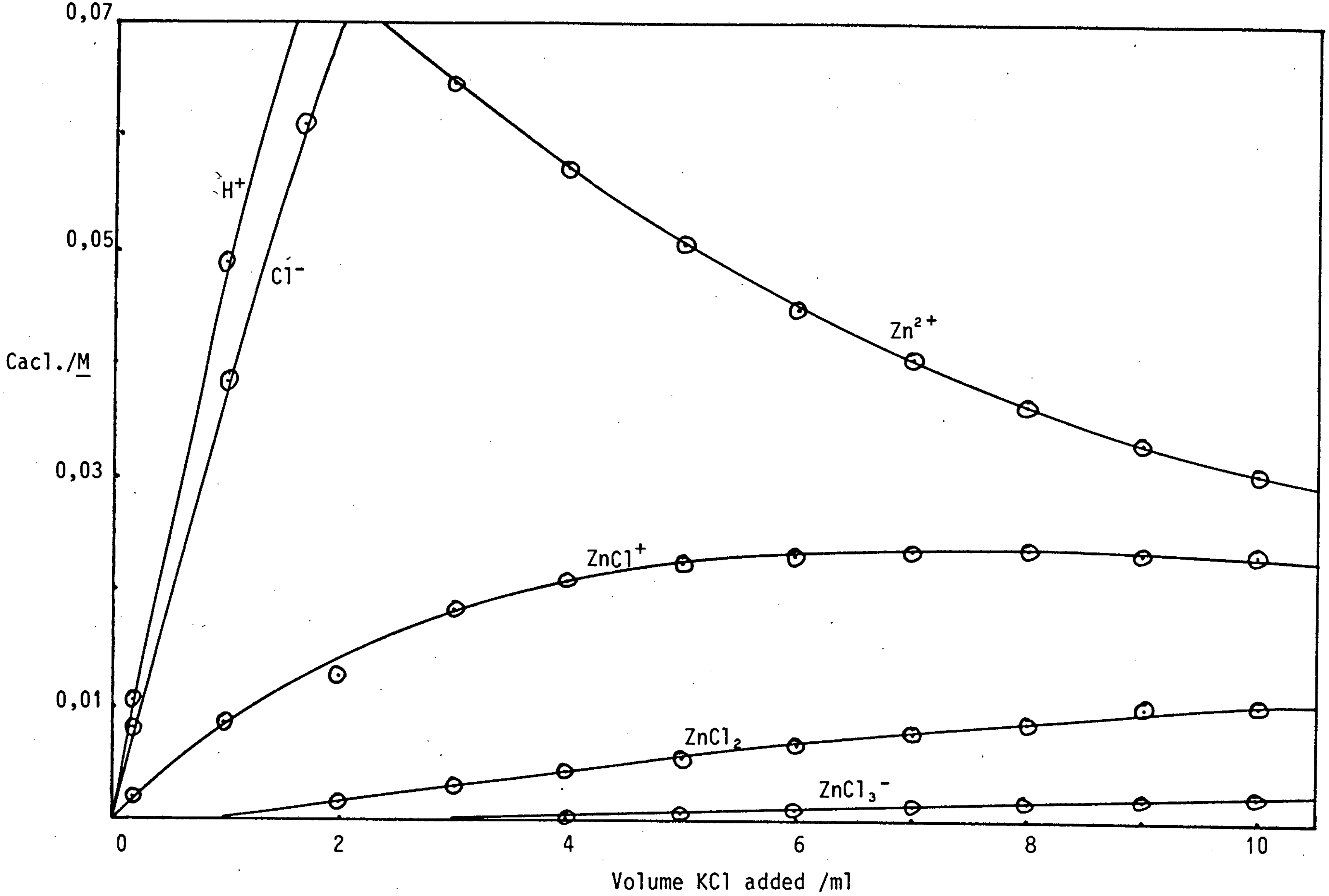


FIGURE 6.4: 20,02 ml 0,099 7 M $ZnSO_4$ vs 1,015 0 M KCl -speciation curve.

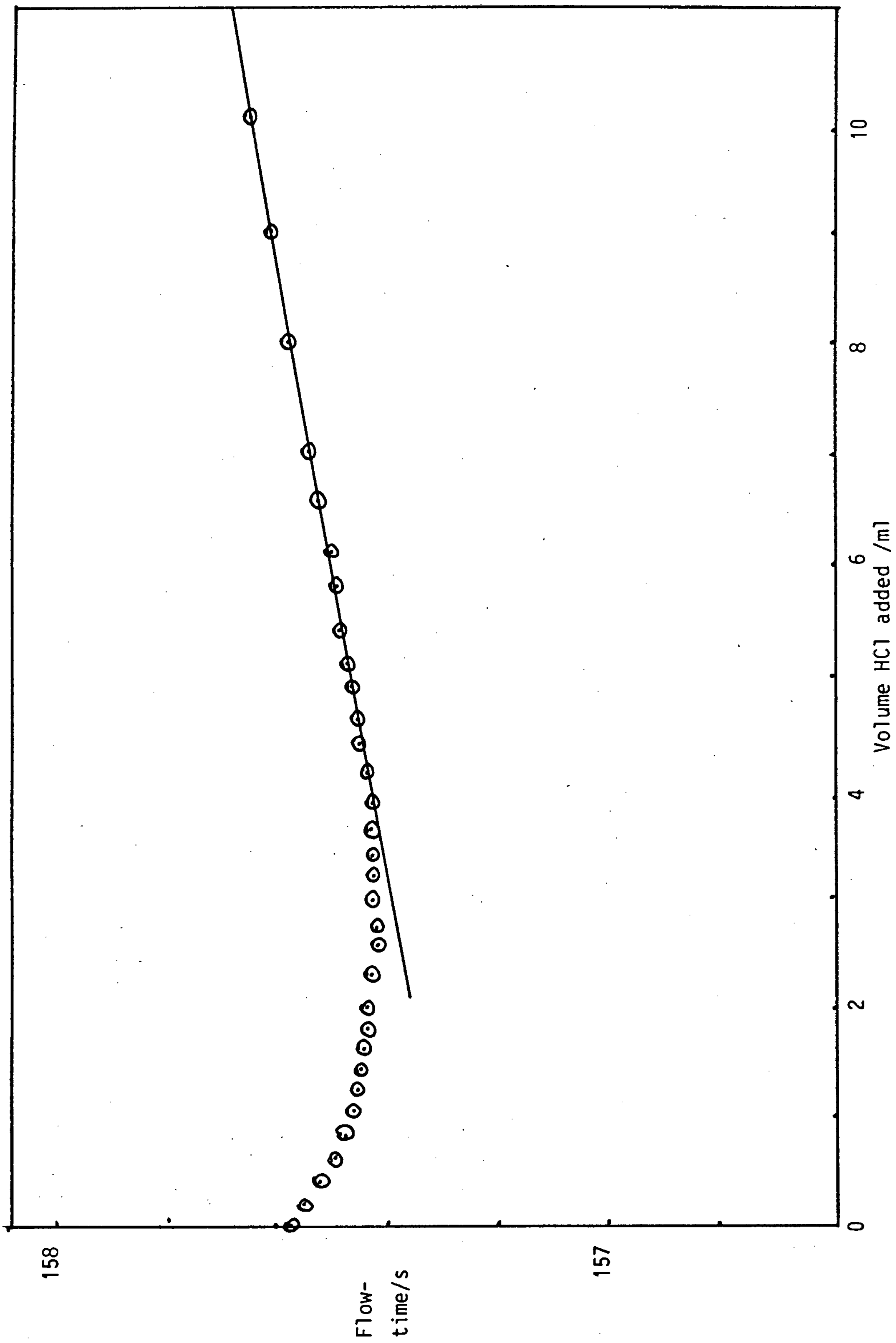
TABLE 6.3

Computed concentration values for the titration of 20,02 ml 0,099 7 M $ZnSO_4$ with 1,015 0 M KCl used for speciation curve plot.

titre/ml	$\|Zn^{++}\|$	$\|Cl^-\|$	$\|ZnCl_2\|$	$\|ZnCl_3^-\|$	$\|ZnCl_3^-\|$	$\|ZnCl_4^{2-}\|$
0,0	0,099 7	0	0	0	0	0
0,2	0,096 6	0,007 93	0,002 06	0,000 03	-	-
1,0	0,085 6	0,038 37	0,008 84	0,000 51	0,000 02	-
2,0	0,074 2	0,073 86	0,012 67	0,001 65	0,000 09	-
3,0	0,064 8	0,106 82	0,018 63	0,003 01	0,000 25	0,000 01
4,0	0,057 1	0,137 56	0,021 13	0,004 40	0,000 47	0,000 03
5,0	0,050 6	0,1663 2	0,022 66	0,005 70	0,000 74	0,000 06
6,0	0,045 2	0,193 29	0,023 51	0,006 88	0,001 03	0,000 10
7,0	0,040 6	0,218 64	0,023 89	0,007 91	0,001 34	0,000 15
8,0	0,036 7	0,242 53	0,023 93	0,008 76	0,001 65	0,000 20
9,0	0,033 3	0,265 06	0,023 75	0,009 53	0,001 96	0,000 26
10,0	0,030 4	0,286 36	0,023 40	0,010 14	0,002 26	0,000 32
11,0	0,027 8	0,306 52	0,022 95	0,010 65	0,002 53	0,000 39
12,0	0,025 6	0,325 63	0,022 43	0,011 06	0,002 80	0,000 46
13,0	0,023 6	0,343 77	0,021 87	0,011 38	0,003 04	0,000 52
14,0	0,021 9	0,361 01	0,021 29	0,011 63	0,003 26	0,000 59

TABLE 6.4/...

FIGURE 6.5: 20,02 ml 0,095 2 M $CdCl_2$ vs 0,506 7 M HCl -titration curve.



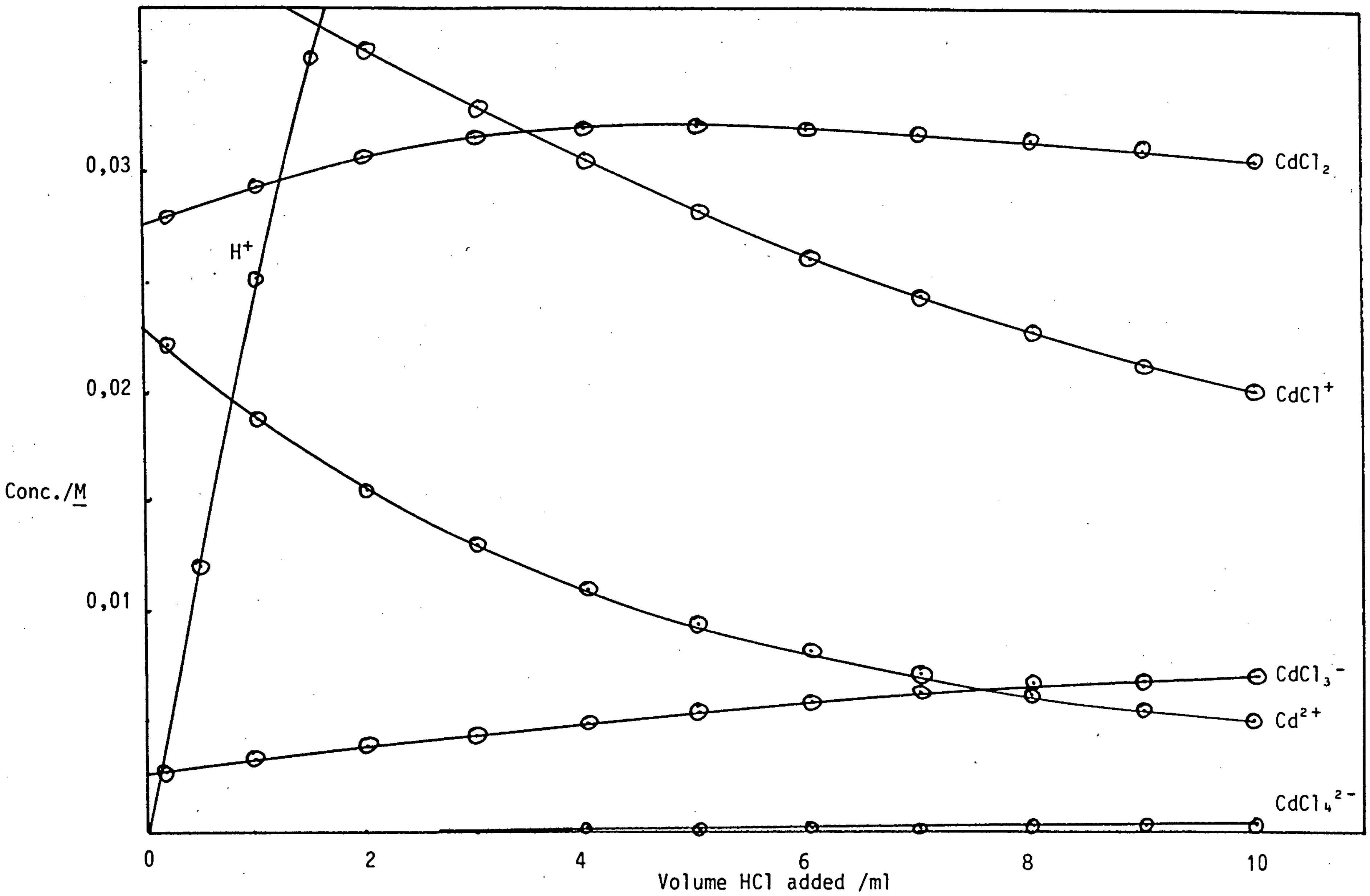


FIGURE 6.6: 20,02 ml 0,095 2 M $CdCl_2$ vs 0,506 7 M HCl -speciation curve.

TABLE 6.4

Computed concentration values for the titration of 20,02 ml 0,095 2 M $CdCl_2$ with 0,506 7 M HCl used for speciation curve plot.

titre/ml	$\lvert Cd^{2+} \rvert$	$\lvert Cl^- \rvert$	$\lvert CdCl^+ \rvert$	$\lvert CdCl_2 \rvert$	$\lvert CdCl_3^- \rvert$	$\lvert CdCl_4^{2-} \rvert$
0,0	0,023 3	0,084 71	0,041 21	0,027 73	0,002 89	0,000 09
0,2	0,022 3	0,087 14	0,040 67	0,028 15	0,003 02	0,000 09
1,0	0,019 0	0,096 81	0,038 45	0,029 57	0,003 52	0,000 12
2,0	0,015 7	0,108 73	0,035 71	0,030 84	0,004 13	0,000 16
3,0	0,013 2	0,120 37	0,033 10	0,031 65	0,004 69	0,000 20
4,0	0,011 2	0,131 67	0,030 67	0,032 08	0,005 20	0,000 24
5,0	0,009 55	0,142 59	0,028 46	0,032 23	0,005 65	0,000 29
6,0	0,008 27	0,153 10	0,026 44	0,032 16	0,006 06	0,000 33
7,0	0,007 22	0,163 19	0,024 62	0,031 92	0,006 41	0,000 37
8,0	0,006 36	0,172 85	0,022 98	0,031 55	0,006 71	0,000 41
9,0	0,005 65	0,182 09	0,021 50	0,031 10	0,006 97	0,000 45
10,0	0,005 06	0,190 91	0,020 17	0,030 59	0,007 19	0,000 49

TABLE 6.5/...

FIGURE 6.7: 20,02 ml 0,095 2 M $CdCl_2$ vs 1,015 0 M KCl
-titration curve

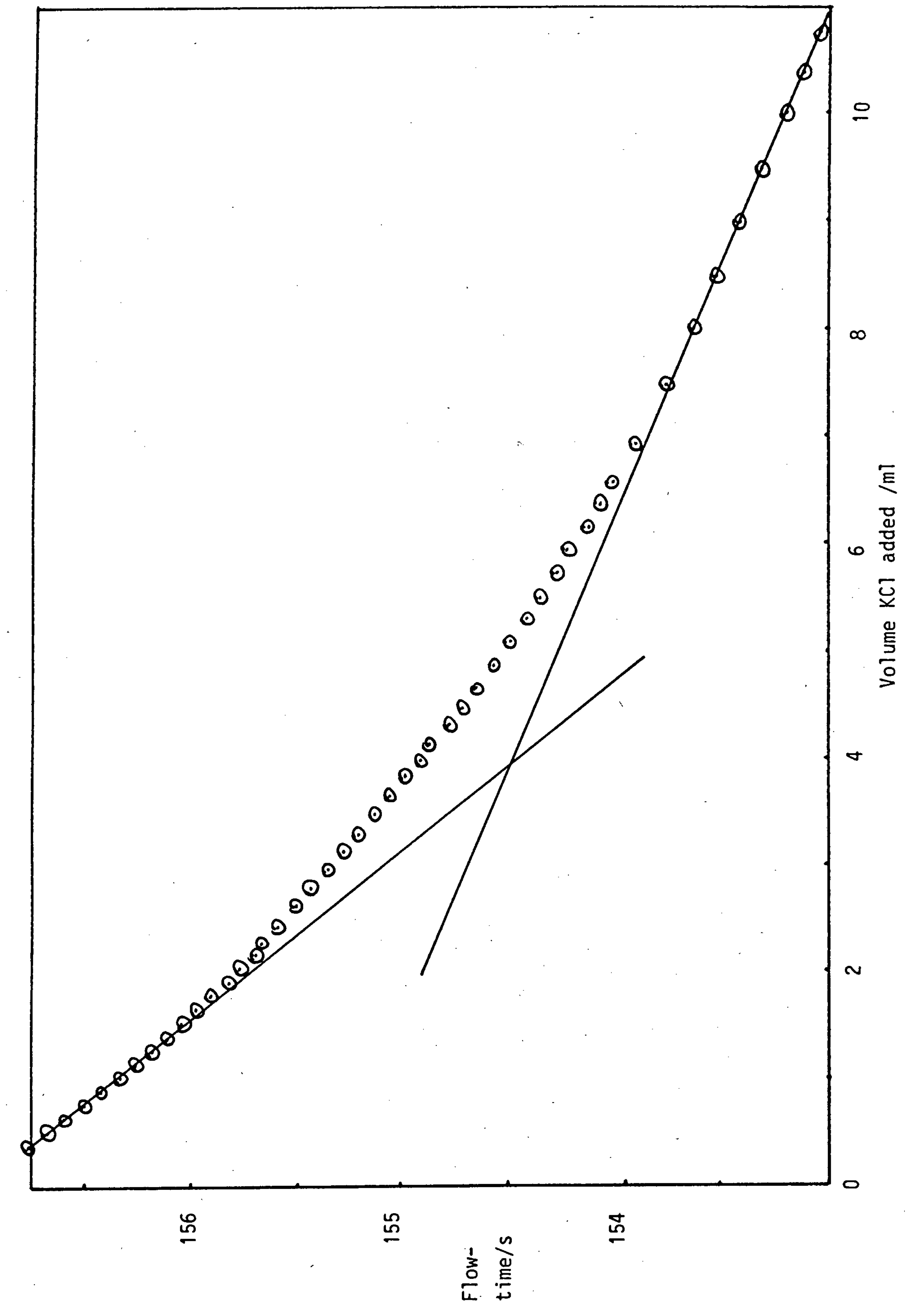


FIGURE 6.8: 20,02 ml 0,095 2 M $CdCl_2$ vs 1,015 0 M KCl -speciation curve.

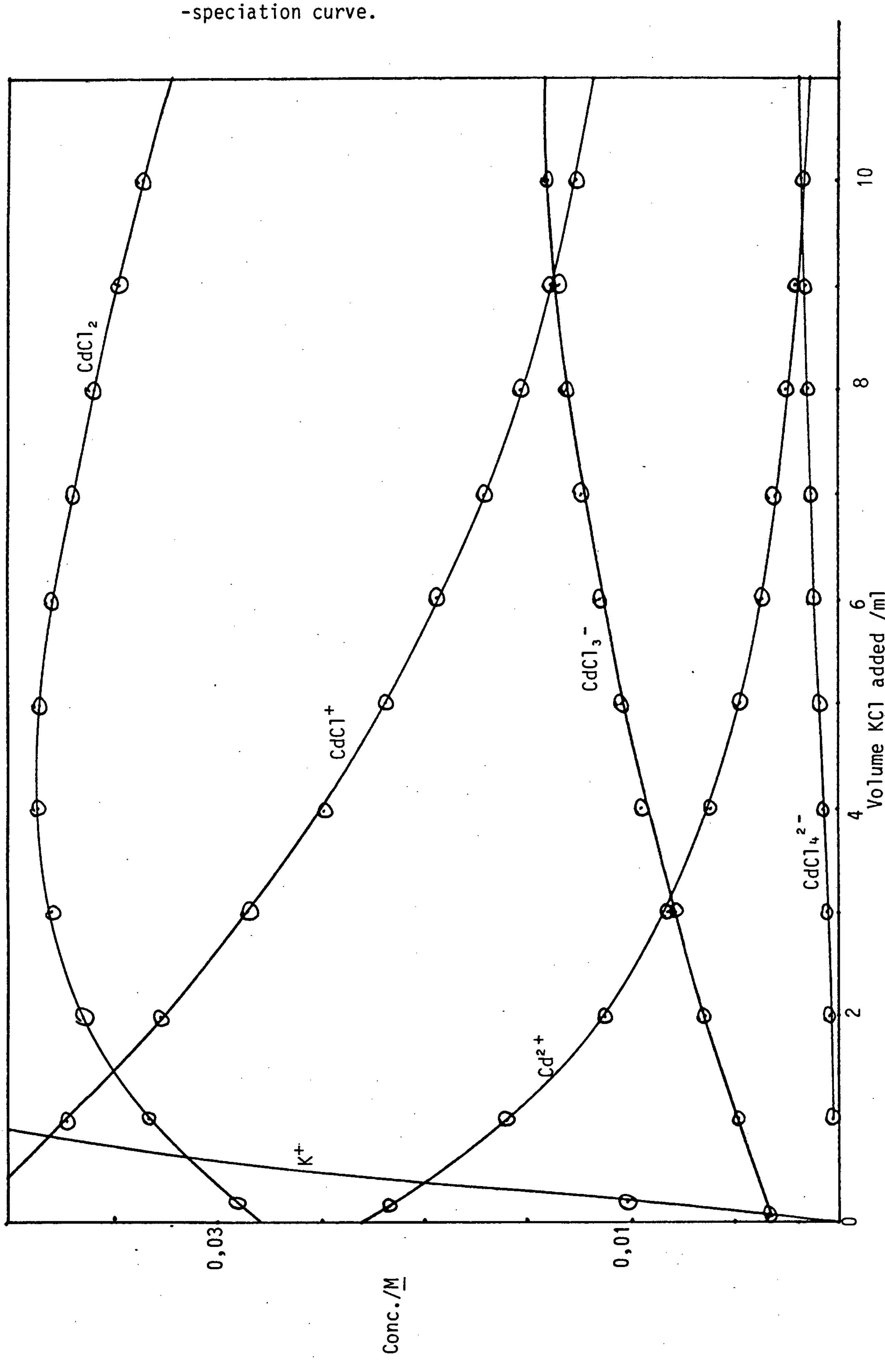


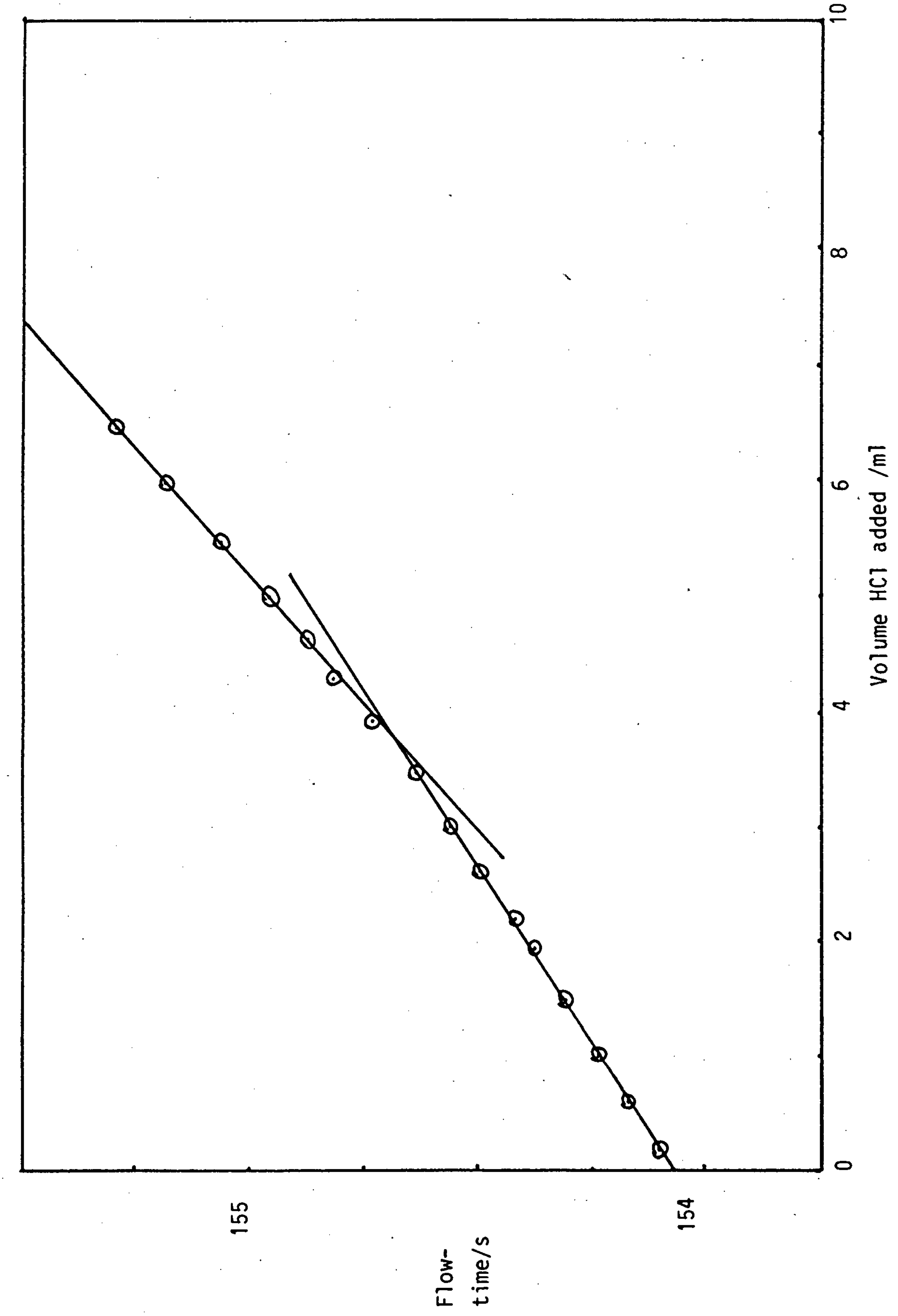
TABLE 6.5

Computed concentration values for the titration of 20,02 ml 0,095 2 M $CdCl_2$ with 1,015 0 M KCl used for speciation curve plot.

Titre/ml	$\lvert Cd^{2+}\rvert$	$\lvert Cl^-\rvert$	$\lvert CdCl^+\rvert$	$\lvert CdCl_2\rvert$	$\lvert CdCl_3^-\rvert$	$\lvert CdCl_4^{2-}\rvert$
0,0	0,023 3	0,084 71	0,041 21	0,027 73	0,002 89	0,000 09
0,2	0,021 5	0,090 10	0,040 48	0,028 97	0,003 21	0,000 10
1,0	0,015 8	0,112 11	0,037 08	0,033 02	0,004 56	0,000 18
2,0	0,011 1	0,140 15	0,032 59	0,036 28	0,006 26	0,000 31
3,0	0,008 09	0,168 10	0,028 43	0,037 96	0,007 85	0,000 47
4,0	0,006 08	0,195 45	0,024 82	0,038 54	0,009 27	0,000 64
5,0	0,004 70	0,221 89	0,021 78	0,038 39	0,010 48	0,000 83
6,0	0,003 72	0,247 23	0,019 24	0,037 78	0,011 49	0,001 01
7,0	0,003 02	0,271 41	0,017 12	0,036 90	0,012 32	0,001 19
8,0	0,002 49	0,294 41	0,015 33	0,035 85	0,012 99	0,001 36
9,0	0,002 09	0,316 25	0,013 83	0,034 73	0,013 51	0,001 52
10,0	0,001 78	0,336 97	0,012 55	0,033 58	0,013 92	0,001 66
11,0	0,001 54	0,356 62	0,011 45	0,032 43	0,014 23	0,001 80
12,0	0,001 34	0,375 27	0,010 50	0,031 30	0,014 45	0,001 92
13,0	0,001 18	0,392 96	0,009 68	0,030 22	0,014 61	0,002 04

TABLE 6.6/...

FIGURE 6.9: 20,02 ml 0,102 7 M $HgCl_2$ vs 1,002 6 M HCl -titration curve.



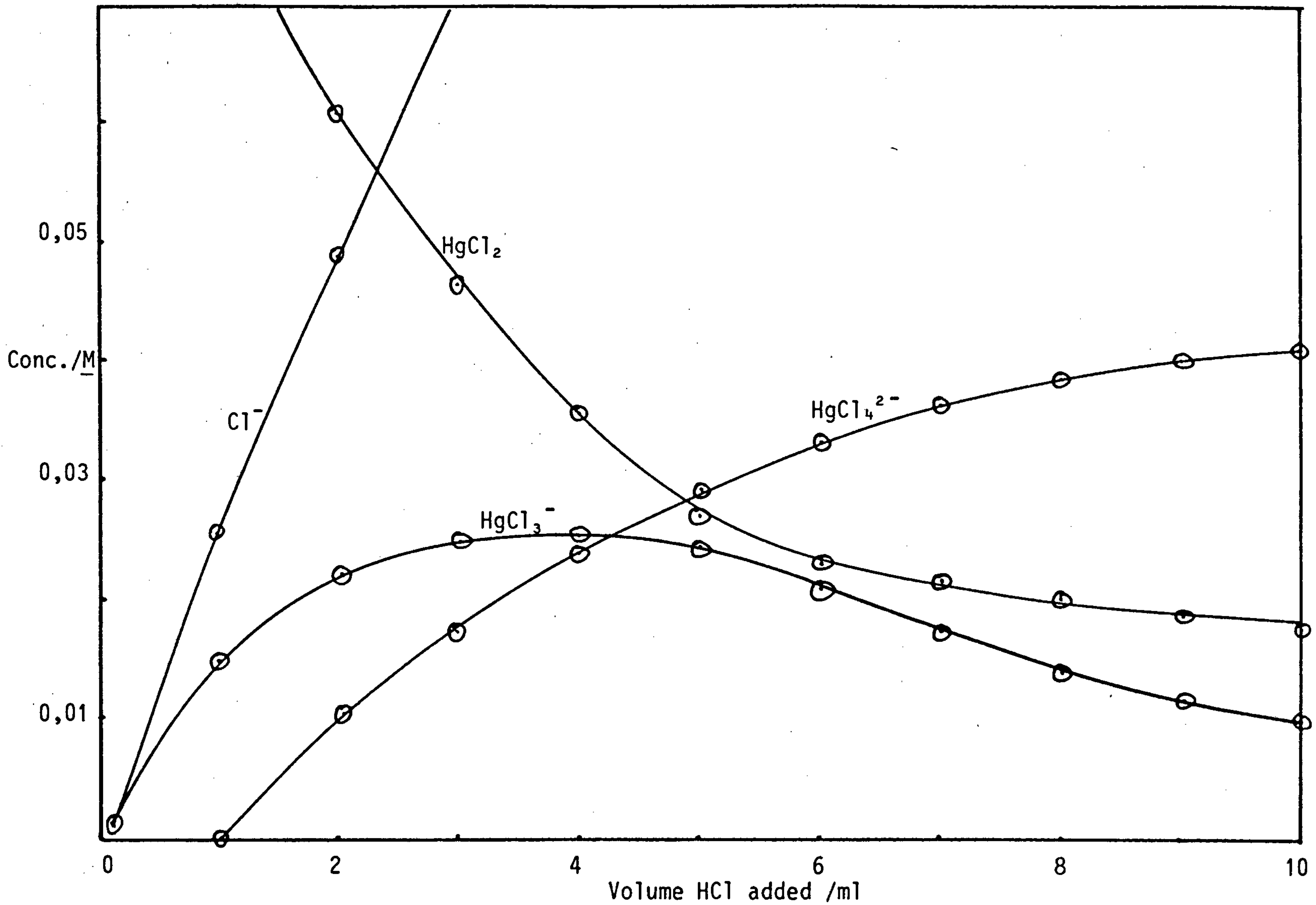


FIGURE 6.10: 20,02 ml 0,102 7 M $HgCl_2$ vs 1,002 6 M HCl -titration curve.

TABLE 6.6

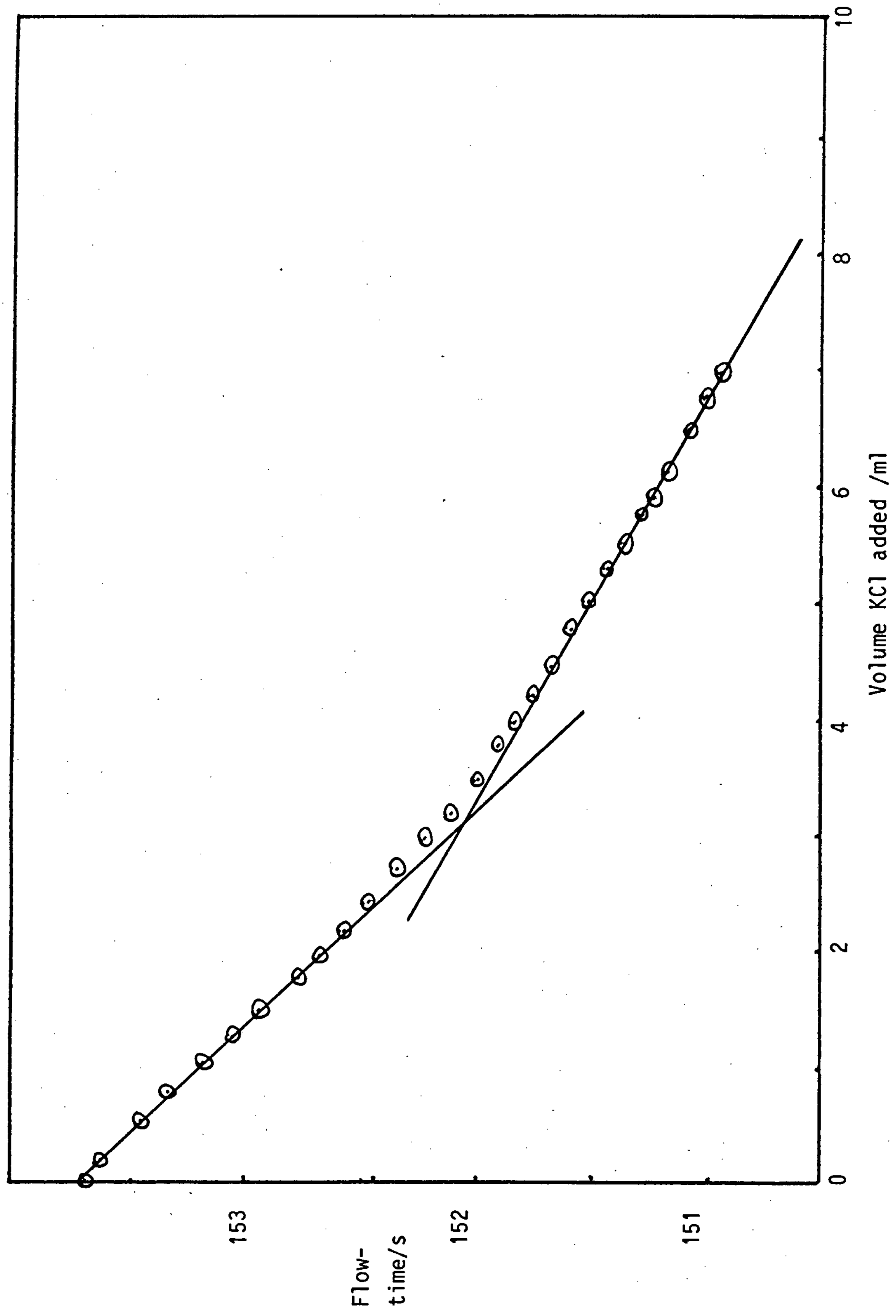
Computed concentration values for the titration of 20,02 ml 0,102 7 M H_gCl_2 with 1,002 6 M HCl used for speciation curve plot.

Titre/ml	$\lvert Cl^-\rvert$	$\lvert H_gCl^+\rvert$	$\lvert H_gCl_2\rvert$	$\lvert H_gCl_3^-\rvert$	$\lvert H_gCl_4^{2-}\rvert$
0,0	0,000 14	0,000 25	0,102 35	0,000 11	-
0,2	0,005 45	0,000 01	0,097 43	0,004 03	0,000 22
1,0	0,025 10	-	0,078 99	0,015 04	0,003 78
2,0	0,047 88	-	0,060 75	0,022 06	0,010 56
3,0	0,070 47	-	0,046 73	0,024 98	0,017 60
4,0	0,093 51	-	0,036 08	0,025 59	0,023 93
5,0	0,117 07	-	0,028 07	0,024 93	0,029 18
6,0	0,140 96	-	0,022 09	0,023 62	0,033 30
7,0	0,164 90	-	0,017 64	0,022 07	0,036 39
8,0	0,188 58	-	0,014 31	0,020 47	0,038 60
9,0	0,211 76	-	0,011 79	0,018 94	0,040 11
10,0	0,234 27	-	0,009 87	0,017 54	0,041 08

$\lvert H_g^{++}\rvert$ is less than 10^{-5} in all cases.

TABLE 6.7/...

FIGURE 6.11: 20,02 ml 0,100 7 M $HgCl_2$ vs 1,050 M KCl -titration curve.



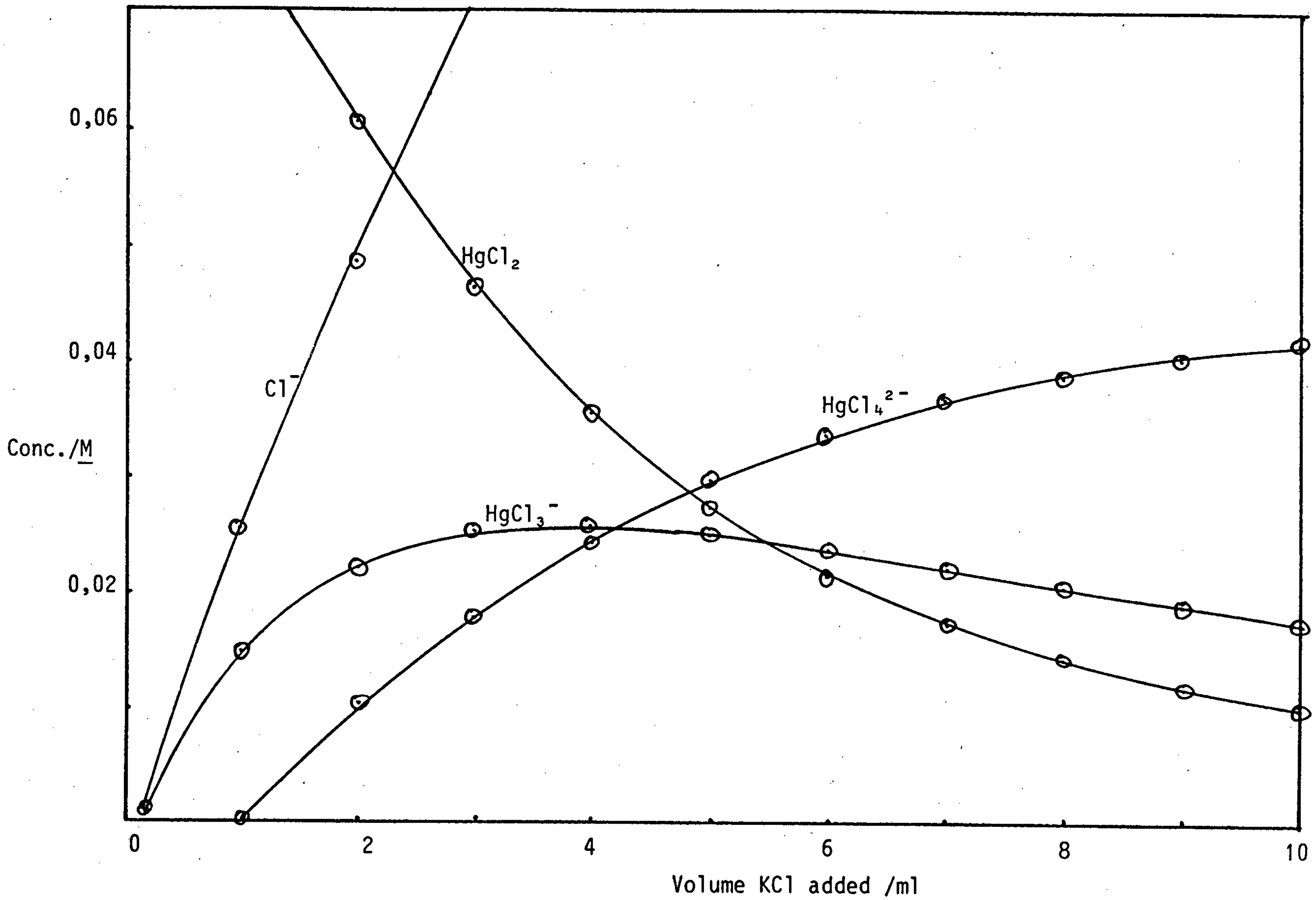


FIGURE 6.12: 20,02 ml 0,100 7 M $HgCl_2$ vs 1,050 M KCl -speciation curve

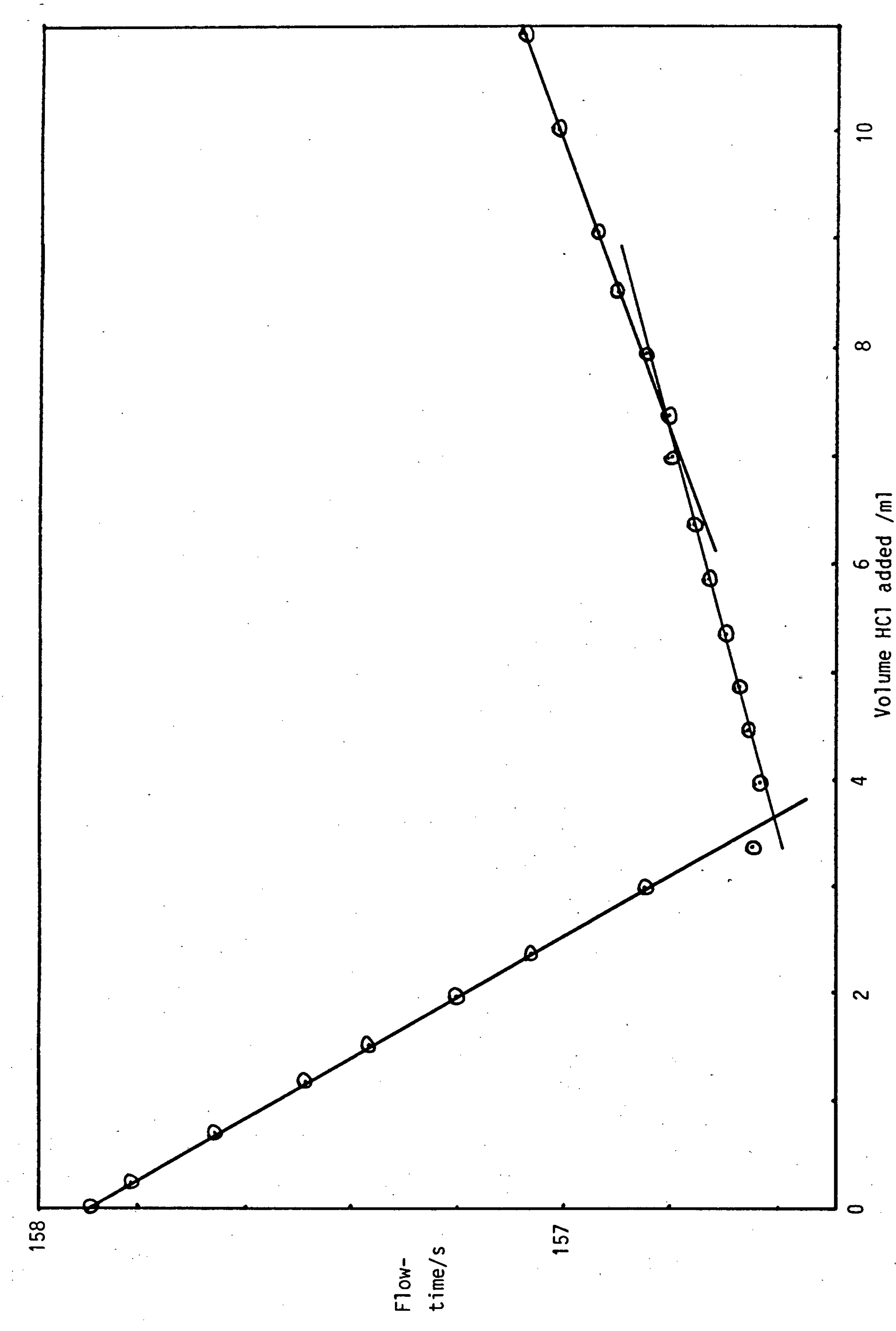
TABLE 6.7

Computed concentration values for the titration of 20,02 ml 0,102 7 M H_gCl_2 with 1,015 0 M KCl used in speciation curve plot.

Titre/ml	$\|Cl^-\|$	$\|H_gCl^+\|$	$\|H_gCl_2\|$	$\|H_gCl_3^-\|$	$\|HgCl_4^{2-}\|$
0,0	0,000 14	0,000 25	0,102 35	0,000 11	-
0,2	0,005 52	0,000 01	0,097 38	0,004 08	0,000 23
1,0	0,025 40	-	0,078 78	0,015 18	0,003 86
2,0	0,048 46	-	0,060 41	0,022 21	0,010 76
3,0	0,071 38	-	0,046 33	0,025 08	0,017 91
4,0	0,094 79	-	0,035 66	0,025 64	0,024 30
5,0	0,118 74	-	0,027 67	0,024 92	0,029 59
6,0	0,143 04	-	0,021 73	0,023 57	0,033 72
7,0	0,167 38	-	0,017 31	0,021 98	0,036 80
8,0	0,191 45	-	0,014 02	0,020 37	0,039 00
9,0	0,215 00	-	0,011 54	0,018 83	0,040 48
10,0	0,237 85	-	0,009 65	0,017 42	0,041 42

TABLE 6.8/...

FIGURE 6.13: 20,02 ml 0,091 4 M $Hg(CH_3CO_2)_2$ vs 1,002 6 M HCl -titration curve



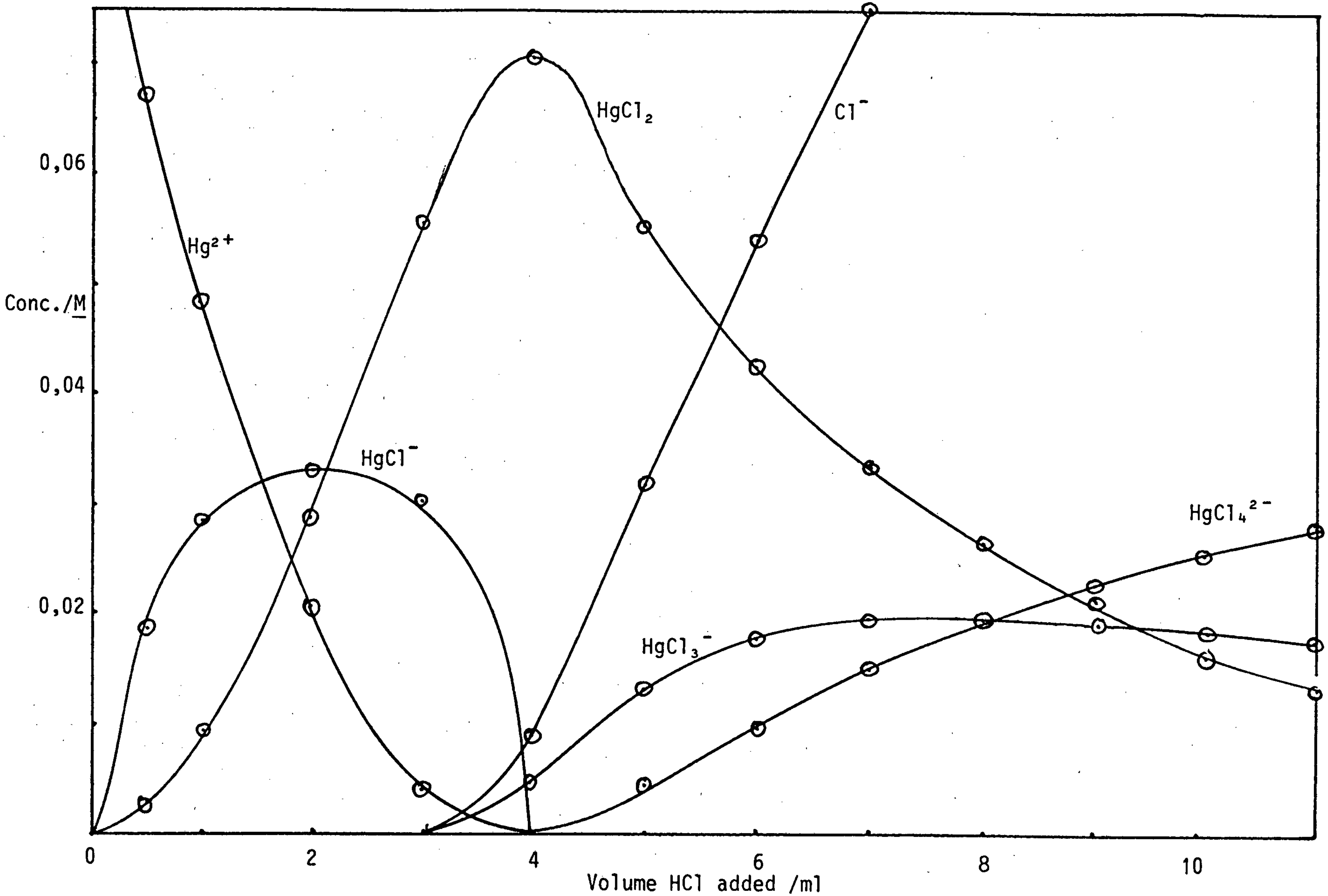


FIGURE 6.14: 20,02 ml 0,091 4 M $Hg(CH_3CO_2)_2$ vs 1,002 6 M HCl -speciation curve.

TABLE 6.8

Computed concentration values for the titration of 20,02 ml 0,091 4 M $Hg(CH_3CO_2)_2$ with 1,002 6 M HCl used for speciation curve plot.

Titre/ml	$\|Hg^{2+}\|$	$\|Cl^-\|$	$\|HgCl^+\|$	$\|HgCl_2\|$	$\|HgCl_3^-\|$	$\|HgCl_4^{2-}\|$
0	0,091 4	0	0	0	0	0
0,5	0,067 77	-	0,018 62	0,002 81	-	-
1	0,048 84	-	0,028 93	0,009 43	-	-
2	0,020 91	-	0,033 21	0,028 98	-	-
3	0,004 05	-	0,020 18	0,055 27	-	-
4	-	0,008 94	-	0,070 96	0,004 81	0,000 43
5	-	0,032 09	-	0,055 31	0,013 46	0,004 32
6	-	0,054 23	-	0,042 89	0,017 64	0,009 57
7	-	0,075 67	-	0,033 71	0,019 35	0,014 64
8	-	0,097 70	-	0,026 49	0,019 63	0,019 18
9	-	0,119 75	-	0,021 06	0,019 13	0,022 91
10	-	0,142 03	-	0,016 91	0,018 22	0,025 87
11	-	0,164 14	-	0,013 76	0,017 13	0,028 11
12	-	0,185 99	-	0,011 72	0,016 53	0,030 75
13	-	0,207 08	-	0,009 51	0,014 94	0,030 94
14	-	0,227 53	-	0,008 09	0,013 96	0,031 76

APPENDIX A/...

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APPENDIX A

The FORTRAN program used to calculate values for the α-coefficient for mixtures of electrolytes is listed below.

```
      DIMENSION LA(4),MU(4),GA(4),C(4),Z(4),S(4),S1(4),R(4),ALPHA(10),
     1RS(6),H(4,4),HE(4,4)
      REAL LA,MU
C     LA=COND.,MU=FRAC. ION.STR.,GA=C(I)*(Z(I)**2,Z=CHARGE,C=CONC.
C     SECTION ONE : DATA INPUT
      READ *,N
C     READ CHARGE,CONC.,COND.FOR EACH ION
      DO 10 I=1,N
10    READ *,Z(I),C(I),LA(I)
C     READ ALPHAS
      ALPHA(1)=-0.1715729
      ALPHA(2)=0.2426407
      ALPHA(3)=-0.1109127
      ALPHA(4)=0.0658640
      ALPHA(5)=-0.0446214
      ALPHA(6)=0.327184
      ALPHA(7)=-0.0252866
      ALPHA(8)=0.0202866
      ALPHA(9)=-0.016741468
      ALPHA(10)=0.014116788
C     OUTPUT OF DATA
      PRINT 85
```

23./...

```
85    FORMAT(//,3X,8H ION NO.,2X,'CHARGE',5X,'CONC.',5X,'COND.')
      DO 26 I=1,N
26    PRINT 95,I,Z(I),C(I),LA(I)
95    FORMAT(3X,I4,7X,F3.0,4X,E9.4,2X,E9.4)
C     SECTION TWO : FIXED CALCULATIONS
C     CALCULATE MU'S AND GAMMA'S
      GAMMA=0
      DO 20 I=1,N
      GA(I)=C(I)*(Z(I)**2.)
20    GAMMA=GAMMA+GA(I)
      DO 30 I=1,N
30    MU(I)=GA(I)/GAMMA
C     CALC X
      X=0
      DO 35 I=1,N
35    X=X+MU(I)*Z(I)/LA(I)
C     CALC A AND B
      A=0
      B=0
      DO 40 I=1,N
      A=A+GA(I)*Z(I)/LA(I)
40    B=B+GA(I)*(Z(I)/LA(I))**2.
      A=A/GAMMA
      B=B/GAMMA
C     CALC R(I) VALUES
      DO 50 I=1,N
50    R(I)=1.-(Z(I)/LA(I))/A
```

50./...

```
C     CALC INITIAL S(I) VALUES
      DO 60 IO=1,N
60    S(IO)=MU(IO)*(Z(IO)/LA(IO)-B/A)
C     CALC H(I,J) VALUES
      DO 80 I=1,N
      D=LA(I)/Z(I)
      DO 80 J=1,N
      IF(I.EQ.J)GO TO 80
      H(J,I)=MU(J)*(LA(J)/Z(J))/(D+(LA(J)/Z(J)))
80    CONTINUE
      DO 90 I=1,N
      H(I,I)=0
      SUM=0
      DO 100 J=1,N
100   SUM=SUM+H(J,I)
90    H(I,I)=SUM+MU(I)
C     CALC |2H-E|
      DO 110 I=1,N
      DO 110 J=1,N
      HE(I,J)=2.*H(I,J)
      IF(I.NE.J)GO TO 110
      HE(I,J)=HE(I,J)-1.
110   CONTINUE
C     SECTION THREE : ITERATIVE CALCULATIONS
      NO=0
65    NO=NO+1
      IF(NO.GT.10)GO TO 160
```

77./...

```
C     CALC 4*ALPHA*R.S
      SUM=0.
      DO 70 I=1,N
70    SUM=SUM+R(I)*S(I)
      RS(NO)=4.*ALPHA(NO)*SUM
C     CHECK IF RS(NO)< E-05
      IF(RS(NO).LT.1.0E-05)GO TO 140
C     CALC |2H-E||S|
      DO 120 I=1,N
      S1(I)=0.
      DO 120 J=1,N
120   S1(I)=S1(I)+HE(I,J)*S(J)
      DO 130 I=1,N
130   S(I)=S1(I)
      GO TO 65
C     SECTION FOUR : OUTPUT OF RESULTS
140   W=0.
      DO 150 I=1,NO
150   W=W+RS(I)
      Y=X-W
155   PRINT 45
 45   FORMAT(/,'CONVERGENCE OF 4*ALPHA*R.S:')
      PRINT 55,(RS(I),I=1,NO)
 55   FORMAT(/6E10.3)
      IF(NO.GT.10)GO TO 500
      PRINT 75,Y
 75   FORMAT(/'Y=',E11.6//)
      GO TO 500
```

105./...

```
160  PRINT 165
165  FORMAT('GREATER THAN 10 ITERATIONS REQUIRED')
     GO TO 155
500  STOP
     END
```

The data to be read in are listed below in the required order:

(i) N = the number of electrolytic species in solution

(ii) the charge (Z), concentration (C), and equivalent conductivity (LA) of the first ionic species

(iii) the same data as in (ii) for the second to the Nth ionic species.

Note that the answer (Y=   ) which is printed out needs to be multiplied by

$$0,362/\sqrt{DT}$$

where D is the dielectric constant of the pure solvent and T is the absolute temperature, to arrive at the value of the a-coefficient.

APPENDIX B

The FORTRAN program used in section 6 to calculate the concentrations of the individual species in solution along the various titration curves is listed below. A bisection technique is used.

```
REAL MTO,LTO,MT,LT,MFT,LFT,ML1,ML2,ML3,ML4
REAL LFTR,LFTL,LFTM
F(X)=A5*X**5+A4*X**4+A3*X**3+A2*X*X+A1*X+A0
READ *,BT1,BT2,BT3,BT4
READ *,MTO,LTO,TIT,NA
READ *,RR,RL,ERR
DO 3 NB=1,NA
LFTR=RR
LFTL=RL
NC=NB-1
PT=NC*TIT
VT=20.02+0.2*NC
MT=20.02*MTO/VT
LT=(20.02*LTO+0.2*PT)/VT
A5=BT4
A4=(BT4*(4*MT-LT)+BT3)
A3=(BT3*(3*MT-LT)+BT2)
A2=(BT2*(2*MT-LT)+BT1)
A1=(BT1*(MT-LT)+1)
A0=-1*LT
DO 9 N=1,50
LFTM=0.5*(LFTR+LFTL)
IF(0.5*ABS(LFTR-LFTL).LT.ERR)THEN
```

24./...

```
      GO TO 8
      ELSE
      IF((F(LFTM)*F(LFTL)).GT.0.0)LFTL=LFTM
      IF((F(LFTM)*F(LFTL)).LT.0.0.)LFTR=LFTM
      END IF
    9 CONTINUE
    8 LFT=LFTM
      MFT=MT/(1+BT1*LFT+BT2*LFT**2+BT3*LFT**3+BT4*LFT**4)
      ML1=BT1*MFT*LFT
      ML2=BT2*MFT*LFT**2
      ML3=BT3*MFT*LFT**3
      ML4=BT4*MFT*LFT**4
      PRINT 5,NC,N,MT,LT,MFT,LFT,ML1,ML2,ML3,ML4
    5 FORMAT(1H ,2I4,2F9.6,E9.3,5E9.6)
    3 CONTINUE
      STOP
      END.
```

The data required to be read in are listed below in the required order:

(i) - (iv) BT1-BT4=the values of the four gross or overall formation constants

(v) MTO = the initial total metal concentration in the sample solution

(vi) LTO = the initial total chloride concentration in the sample solution

(vii) TIT = titrant concentration

(viii)NA = the number of data points required (0,2 ml apart)

(ix) RR = an initial estimate for the free chloride concentration,

greater/...

greater than the highest possible in the titration.

(x) RL = another initial estimate for the free chloride concentration, less than the lowest value possible in the titration.

(xi) ERR = the maximum tolerable difference between the two estimated values for the actual root, the one greater, the other smaller.

It should be noted that the program assumes an initial sample volume of 20,02 ml and speciation is calculated at points 0,2 ml apart. If different values are required lines 12, 13 and 14 can easily be altered accordingly.

The output consists of ten columns, the first two giving the data point number, and the number of bisections required. The last eight columns give the total metal, total chloride, free metal, and free chloride concentrations, followed by the concentrations of the four species: MCl, MCl_2, MCl_3, and MCl_4.

APPENDIX C

The FORTRAN program to compute values of E and V for the Goldsack and Franchetto equation is listed below.

```
      DIMENSION X(1000),Y(1000),ETACAL(1000),ETAEX(1000),ERROR(1000)
      READ *,N
      READ *,(X(I),ETAEX(I),I=1,N)
      ETA0=0.8904
      ERROR(1)=1000000
      SUMX*X=0
      DO 9 I=1,N
      SUMX*X=SUMX*X+(X(I)*X(I))
    9 CONTINUE
      DO 10 M=2,50
      V=M
      SUMX*Y=0
      DO 11 I=1,N
      Y(I)=ALOG(ETAEX(I)*(1+X(I)*V)/ETA0)
      SUMX*Y=SUMX*Y+Y(I)*X(I)
   11 CONTINUE
      E=SUMX*Y/SUMX*X
      ERROR(M)=0
      DO 12 I=1,N
      ETACAL(I)=ETA0*EXP(X(I)*E)/(1+X(I)*V)
      ERROR(M)=ERROR(M)+ABS(ETAEX(I)-ETACAL(I))
   12 CONTINUE
```

23./...

```
      IF(ERROR(M).GT.ERROR(M-1))GO TO 13
   10 CONTINUE
   13 A=M-2
      DO 20 K=2,200
      V=A+0,01*K
      SUMX*Y=0
      DO 21 I=1,N
      Y(I)=ALOG(ETAEX(I)*(1+X(I)*V)/ETA0)
      SUMX*Y=SUMX*Y+Y(I)*X(I)
   21 CONTINUE
      E=SUMX*Y/SUMX*X
      ERROR(K)=0
      DO 22 I=1,N
      ETACAL(I)=ETA0*EXP(X(I)*E)/(1+X(I)*V)
      ERROR(K)=ERROR(K)+ABS(ETAEX(I)-ETACAL(I))
   22 CONTINUE
      PRINT *,V,E,ERROR(K)
      IF(ERROR(K).GT.ERROR(K-1))GO TO 25
   20 CONTINUE
   25 STOP
      END.
```

The data that have to be supplied are N, the number of viscosity data points, followed by N pairs of values for X, the appropriate mole fraction, and absolute viscosity in cP. The output consists of three columns, (i) V, (ii) E, and (iii) a cumulative error that has to be minimised. The second last line contains the required values.