

CHAPTER-II

General Introduction

One of the interesting facts of solution chemistry is that the exact structure of the solvent molecule in a solution is not known with certainty. The introduction of an ion or solute modifies the solvent structure to an extent whereas the solute molecules are also modified. The interactions between solute and solute, solute and solvent, and solvent and solvent molecules and the resulting ion-solvation become predominant. The assessment of ion pairing in these systems is important because of its effect on the ionic conductivity and hence the mobility of the ions in solution. This explains the spurt in research in solution chemistry to elucidate the exact nature of these interactions through experimental studies involving conductometric, viscometric, densitometry, spectroscopy, ultrasonic interferometer and other suitable methods and to interpret the experimental data collected ⁽¹⁻⁷⁾.

The majority of the reactions occurring in solutions are of either chemical or biological in nature. The solvent only provides an inert medium for chemical reactions previously presumed. The significance of solute-solvent interactions was realized only recently as a result of extensive studies in aqueous, non-aqueous and mixed solvents ⁽⁸⁻¹³⁾.

The behavior of electrolytes in solution depends mainly on ion-ion and ion-solvent interactions. The former interaction, in general, is stronger than the latter. Ion-ion interaction in dilute electrolytic solutions is now theoretically well understood, but the ion-solvent interaction or ion-solvation still remains a complex process.

In the last few decades, considerable emphasis has been placed on research in the behavior of electrolytes in non-aqueous and mixed solvents to investigate the ion-ion (solute-solute) and ion-solvent (solute-solvent) interactions under varied conditions. Different sequences of solubility,

differences in solvating power and possibilities of chemical or electrochemical reactions unfamiliar in aqueous chemistry have opened new vistas for physical chemists and interest in these organic solvents transcends traditional boundaries of inorganic, organic, physical, analytical and electrochemistry⁽¹⁰⁾.

The organic solvents based on dielectric constants, organic group type, acid-base properties or association through hydrogen bonding⁽⁹⁾, donor – acceptor properties⁽¹⁴⁾, hard and soft acid-base principles⁽¹⁵⁾ etc. have been classified. As a result, the different solvent systems show a wide divergence of properties, which would naturally be reflected on the thermodynamic and transport properties of electrolytes and non-electrolytes in these solvents. The determination of thermodynamic and transport properties of different electrolytes in various solvents would thus provide an important step in this direction. Naturally, in the development of theories, dealing with electrolyte solutions, much attention has been devoted to ion-solvent interactions, which are the “controlling forcers” in infinitely dilute solutions where ion-ion interactions are absent. It is possible by separating these functions into ionic contributions to determine the contributions due to cations and anions in the ion – solvent interactions. Thus ion-solvent interactions play a very important role to understand the physico-chemical properties of solutions.

In ion-solvation studies, broadly three types of approaches have been made to estimate the extent of solvation. The first is the solvational approach involving the studies of viscosity, conductance, etc., of electrolytes and the derivation of various factors associated with ionic solvation⁽¹⁶⁾, the second is the thermodynamic approach by measuring the free energies, enthalpies and entropies of solvation of ions from which factors associated with solvation can be elucidated⁽¹⁷⁾, and the third is to use spectroscopic measurements where the spectral solvent shifts or the chemical shifts determine their qualitative and quantitative nature⁽¹⁸⁾.

We shall particularly dwell upon the different aspects of transport and thermodynamic properties as the present dissertation is intimately related to the studies of viscosity, conductance, ultrasonic speed and isentropic compressibility of alkali metal halides, some nitrate and tetraalkylammonium salts in the pure as well as in the mixed organic and also in binary aqueous solvents systems.

2.1. Thermodynamics of Ion-Pair Formation

The standard Gibbs energy changes (ΔG°) for the ion- association process can be calculated from the equation

$$\Delta G^\circ = -RT \ln K_A \quad (1)$$

The values of the standard enthalpy change, ΔH° , and the standard entropy change, ΔS° , can be evaluated from the temperature dependence of ΔG° values as follows,

$$\Delta H^\circ = -T^2 \left(\frac{d(\Delta G^\circ / T)}{dT} \right)_p \quad (2)$$

$$\Delta S^\circ = -T^2 \left(\frac{d\Delta G^\circ}{dT} \right)_p \quad (3)$$

The ΔG° values can be fitted with the help of a polynomial of the type.

$$\Delta G^\circ = c_0 + c_1(298.15 - T) + c_2(298.15 - T)^2 \quad (4)$$

and the coefficients of the fits can be compiled together with the $\sigma\%$ values of the fits.

The standard values at 298.15 K are then:

$$\Delta G_{298.15}^{\circ} = c_0 \quad (5)$$

$$\Delta S_{298.15}^{\circ} = c_1 \quad (6)$$

$$\Delta H_{298.15}^{\circ} = c_0 + 298.15c_1 \quad (7)$$

The main factors which govern the standard entropy of ion-association of electrolytes are: (i) the size and shape of the ions, (ii) charge density on the ions, (iii) electrostriction of the solvent molecules around the ions, and (iv) penetration of the solvent molecules inside the space of the ions, and the influence of these factors are discussed later.

The non-columbic part of the Gibbs energy, ΔG^* , can also be calculated using the following equation ^(19b)

$$\Delta G^* = N_A W_{\pm}^* \quad (8)$$

$$K_A = (4\pi N_A / 1000) \int_a^R r^2 \exp(2q/r - W_{\pm}^*/kT) dr \quad (9)$$

where the symbols have their usual significance. The quantity $2q/r$ is the Columbic part of the interionic mean force potential and W_{\pm}° is its non-columbic part.

The procedure for the evaluation of the non-columbic part of the entropy and enthalpy (and ΔS^* and ΔH^* respectively) is the same as that used for obtaining ΔS^* and ΔH^* .

The ΔG^* values at different temperatures can be fitted to the polynomial:

$$\Delta G^* = c_0^* + c_1^* (298.15 - T) + c_2^* (298.15 - T)^2 \quad (10)$$

and the coefficients of the fits along with the $\sigma\%$ values can be determined.

The values of ΔG° , ΔS° and ΔH° at 298.15 K are then easily obtained from the following equations.

$$\Delta G_{298.15}^* = c_0^* \quad (11)$$

$$\Delta S_{298.15}^* = c_1^* \quad (12)$$

$$\Delta H_{298.15}^* = c_0^* + 298.15c_1^* \quad (13)$$

2.2. Viscosity

Viscosity, one of the most important transport properties is used for the determination of ion-solvent interactions and studies extensively⁽¹⁻²⁾. Viscosity is not a thermodynamic property but viscosity of an electrolyte solution along with the thermodynamic property, partial molar volume, gives much information and insight regarding the ion-solvent interactions, structures of electrolytic solutions and solvation.

The concentration dependence of the viscosity of electrolyte solutions is described by the Jones and Dole⁽²⁰⁾ semi-empirical equation.

$$\eta_r = \eta/\eta_0 = 1 + Ac^{1/2} + Bc \quad (14)$$

where η and η_0 respectively, are the dynamic viscosities of solution and solvent, η_r is the relative viscosity of the solution, A is the Falkenhagen coefficient⁽²¹⁾ and is a measure of ion-ion interactions theoretically. On the other hand, B , the Jones-Dole coefficient, is empirical and is a function of the ion-solvent interaction. The equation is equally applicable to aqueous and non-aqueous systems where there is no ion-association. The term $Ac^{1/2}$, arose from the long range coulombic forces between the ions. The significance of the term

has since been realized due to the development of Debye-Huckel theory ^(22a) of interionic attractions, Falkenhagen's theoretical calculations of 'A' using the equilibrium theory ⁽²¹⁾ and the theory of irreversible processes in electrolytes developed by Onsagar and Fuoss ^(22b).

The 'A' coefficient depends on the ion-ion interactions and can be calculated using the Falkenhagen-Vernon equation ⁽²¹⁾

$$A_{\text{theo}} = \frac{0.2577 A^{\circ}}{\eta_0(\varepsilon T)^{1/2} \lambda_+^{\circ} \lambda_-^{\circ}} \left[1 - 0.6863 \left(\frac{\lambda_+^{\circ} - \lambda_-^{\circ}}{A^{\circ}} \right)^2 \right] \quad (15)$$

where A° , λ_+° and λ_-° are the limiting conductances of the electrolyte, cations and anion respectively, at temperature T , ε is the dielectric constant and η_0 is the viscosity of the solvent. For most solutions this equation is valid up to 0.1M ^(19, 23).

At higher concentration, the extended Jones-Dole equation-14 involving an additional constant, D , originally used by Kaminsky ⁽²⁴⁾ has been used by several workers ⁽²⁵⁻²⁶⁾. The constant D cannot be evaluated properly and the significance of the constant is also not always meaningful and therefore, the equation -14 is used by the most of the workers.

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc + Dc^2 \quad (16)$$

The plots of $(\eta/\eta_0-1)/\sqrt{c}$ against \sqrt{c} for the electrolyte should give the value of A . But sometimes, the values come out to be negative or considerably scatter and also deviation from linearity occur ^(8, 27-28). Thus, instead of determining A -values from the plots or by the least square method, the values are generally calculated using Falkenhagen- Vernon equation -15.

2.2.1. Division of B -Coefficients into Ionic Values

The splitting of the B -coefficient into the contributions of individual ions cannot be done in the same way as the division of limiting equivalent conductances, since there is no quantity corresponding to the transport numbers. Accordingly, the separation of the observed B -coefficient has been an arbitrary process⁽²⁹⁻³¹⁾.

In order to identify the separate contributions of cations and anions to the total solute-solvent interactions, the B -coefficients as determined by Jones-Dole's equation has to be resolved into ionic components. For this Cox and Wolfenden⁽³¹⁾, Gurney⁽³⁰⁾, Sacco *et al*⁽³²⁾, Tuan and Fuoss⁽³³⁾, and several authors used different approximations and assumptions for different systems. For example, Sacco *et al*⁽³²⁾ proposed the widely used 'reference electrolyte' method. Thus, for Ph_4PBPh_4 in water, we have,

$$B_{\text{BPh}_4^-} = B_{\text{Pph}_4^+} = B_{\text{Ph}_4\text{PBPh}_4} / 2 \quad (17)$$

$B_{\text{Ph}_4\text{PBPh}_4}$ is obtained from,

$$B_{\text{Ph}_4\text{PBPh}_4} = B_{\text{NaBPh}_4} + B_{\text{Ph}_4\text{PBr}} - B_{\text{NaBr}} \quad (18)$$

(Since Ph_4PBPh_4 is scarcely soluble in water). These values are in good agreement with those obtained by other methods.

The method, however, have been strongly criticized by Krumgalz⁽³⁴⁾. According to him, any method of resolution based on the equality of equivalent conductances for certain ions suffers from the drawback that it is impossible to select any two ions for which $\lambda_+^\circ = \lambda_-^\circ$ in all solvents and at proper temperatures. Also, even if the mobilities of some ions are equal at infinite dilution, they are not necessarily equal at moderate concentrations. Further, equality of ionic dimensions does not necessarily imply equality of B -coefficients of these ions, as they are likely to be solvent and ion-structure dependent.

Krumgalz ⁽³⁵⁾ has recently proposed a method for the resolution of B -coefficient. The method is based on the fact that the large tetraalkylammonium ions are not solvated in organic solvents. So, the ionic B -values for large R_4N^+ ions (where $R \geq Bu$) in organic solvents are proportional to their ionic dimensions.

$$B_{R_4NX} = a + br^3_{R_4N^+} \quad (19)$$

where, $a = B_x^+$ and b is a constant independent of temperature and solvent nature. Extrapolation of the plot of B_{R_4NX} ($R > Pr$ or Bu) against $r^3_{R_4N^+}$ to zero cations dimension gives B_x^+ directly in the proper solvent from which other ionic B -values can be calculated.

Ionic B -values can also be calculated from the following equations:

$$B_{R_4N^+} - B_{R_4^+N^+} = B_{R_4NX} - B_{R_4^+NX} \quad (20)$$

and

$$B_{R_4N^+}/B_{R_4^+N^+} = r^3_{R_4N^+}/r^3_{R_4^+N^+} \quad (21)$$

The radii of the tetraalkylammonium ions have been calculated from the accurate conductance data ⁽³⁶⁾.

On similar reasoning, Gill and Sharma ⁽³⁷⁾ used Bu_4NBPh_4 as the reference electrolyte and proposed the equations

$$\frac{B_{Ph_4B^-}}{B_{Bu_4N^+}} = \frac{r^3_{Ph_4B^-}}{r^3_{Bu_4N^+}} = \left[\frac{5.35}{5.00} \right]^3 \quad (22)$$

and

$$B_{Bu_4NBPh} = B_{Bu_4N^+} + B_{Ph_4B^-} \quad (23)$$

because the ionic radii of Bu_4N^+ (5.00 Å) and of Ph_4B^- (5.35 Å) have been found to remain constant in different non-aqueous and mixed non-aqueous solvents.

Recently, Lawrence and Sacco⁽³⁸⁻³⁹⁾ used Bu_4NBBu_4 as reference electrolytes because these cations and anions are symmetrically shaped and have almost equal van der Waals volumes. Thus, we have,

$$B(\text{Bu}_4\text{N}^+)/B(\text{Bu}_4\text{B}^-) = V_w(\text{Bu}_4\text{N}^+)/V_w(\text{Bu}_4\text{B}^-) \quad (24)$$

or

$$B(\text{Bu}_4\text{N}^+) = B(\text{Bu}_4\text{NBBu}_4) / 1 + V_w(\text{Bu}_4\text{B}^-) / V_w(\text{Bu}_4\text{N}^+) \quad (25)$$

The results and the conclusions of Thomson *et al*⁽⁴⁰⁾ agreed well with the above reported values.

It is obvious that most of these methods are based on certain approximations and anomalous results may arise unless proper mathematical theories are developed to calculate B -values.

2.2.2. Thermodynamics of Viscous Flow

The viscosity data can also be examined in the light of transition state theory of the relative viscosity of electrolytic solutions proposed by Feakins *et al*⁽⁴¹⁾. According to him, B -coefficient is given as,

$$B = (\bar{V}_1^0 - \bar{V}_2^0) / 1000 + \bar{V}_1^0 (\Delta\mu_2^{\text{oh}} - \Delta\mu_1^{\text{oh}}) / 1000 RT \quad (26)$$

where \bar{V}_1^0 and \bar{V}_2^0 are the partial molar volumes of the solvent and solute respectively, $\Delta\mu_1^{\text{oh}}$ is the free energy of activation for viscous flow per mole of the solvent and $\Delta\mu_2^{\text{oh}}$ is the contribution per mole of solute to the free

energy of activation for the viscous flow of the solution. The values of $\Delta\mu_1^{\text{off}}$ and thereafter those of $\Delta\mu_2^{\text{off}}$ were calculated using the following equations.

$$\Delta\mu_1^{\text{off}} = RT \ln (\eta_0 \bar{V}_1^\circ / hN) \quad (27)$$

$$\Delta\mu_2^{\text{off}} = \Delta\mu_1^{\text{off}} + (RT/\bar{V}_1^\circ) [1000B - (\bar{V}_1^\circ - \bar{V}_1^\circ)] \quad (28)$$

Further, if B is known at various temperatures, we can calculate the entropy and enthalpy of activation of viscous flow respectively from the following equations.

$$d(\Delta\mu_2^{\text{off}})/dt = -\Delta S_2^{\text{off}} \quad (29)$$

$$\Delta H_2^{\text{off}} = \Delta\mu_2^{\text{off}} + T\Delta S_2^{\text{off}} \quad (30)$$

2.2.3. Effects of Shape and Size

According to Stokes and Mills⁽⁴²⁾, ions in solution exist as rigid spheres suspended in a continuum. On this basis they proposed an equation for relative viscosity.

$$\eta/\eta_0 = 1 + 2.5\phi \quad (31)$$

where ϕ is the volume of the fraction occupied by the particles.

Modification of the equation have been proposed by (i) sinha⁽⁴³⁾ on the basis of departures from spherical shape and (ii) Vaud on the basis of dependence of the flow patterns around the neighboring particles at higher concentration.

However, considering the different aspects of the problem, spherical shapes have been assumed for electrolytes having hydrated ions of large effective size (particularly polyvalent monatomic cations). Thus, combining the above equation with Jones-Dole equation-14, we have

$$2.5 \phi = Ac^{1/2} + Bc \quad (32)$$

Here $Ac^{1/2}$ can be neglected in comparison with Bc , and substituting $\phi = c\bar{V}_i$, where \bar{V}_i is the partial molal volume of the ion, we get

$$2.5 \bar{V}_i = B \quad (33)$$

Assuming that the ions behave like rigid spheres with effective radii R_{\pm} , moving in a continuum, B_{\pm} can be equated to

$$B_{\pm} = 2.5 V_{\pm} = 2.5 \times 4/3 (\pi R_{\pm}^3 N/1000) \quad (34)$$

R_{\pm} calculated using equation-34 should be close to crystallographic radii or corrected Stokes' radii if the ions are scarcely solvated and behave as spherical entities. But R_{\pm} values of the ions, which are higher than the crystallographic radii, indicate solvation.

The number (n) of solvent molecules bound to the ion in the primary solvation shell can be calculated by comparing the Jones-Dole equation with that of Feakins *et al* ⁽⁴⁴⁾.

$$B_{\pm} = 2.5 (V_i + n V_s) / 1000 \quad (35)$$

where V_i is the bare ion molar volume and V_s the molar volume of the solvent. The above equation has been used by a number of workers ^(26, 67) to study the nature of solvation.

2.3. Conductance

Conductance measurement providing information on the mobility of ionic species in solution is the most direct and accurate technique available at present time to determine the extent to which ions associate in solution⁽⁴⁵⁻⁴⁶⁾. Together with transference number determination, it provides an excellent method for obtaining single ion values. In conjunction with viscosity measurements, conductance data give much information regarding ion-ion and ion-solvent interaction.

Different researchers employed different equation from time to time to know the behavior of ions in electrolytic solution. The conductometric method is well suited to investigate ion-solvent and ion-ion interactions in solutions^(45, 47-51). Onsagar⁽⁵²⁾ was the first to apply successfully Debye-Huckel theory of interionic associations. Subsequently, Pitts⁽⁵³⁾, and Fuoss and Onsagar⁽⁵⁴⁻⁵⁵⁾, independently worked to account for both long and short-range interactions. As Pitt's values different considerably from Fuoss and Onsagar's values, Fuoss and Hsia⁽⁵⁰⁾ modified the original Fuoss-Onsagar equation. The modified Fuoss-Onsagar equation is of the form⁽⁴⁵⁾.

$$A = A^{\circ} - \frac{\sigma A^{\circ} c^{1/2}}{(1+\kappa a)(1+\kappa a/2^{1/2})} - \frac{\beta c^{1/2}}{(1+\kappa a)} + G(\kappa a) \quad (36)$$

where $G(\kappa a)$ is a complicated function of the variable. The simplified form

$$A = A^{\circ} - S c^{1/2} + Ec \ln c + J_1 c - J_2 c^{1/2} \quad (37)$$

is generally employed in the analysis of experimental results. Fuoss and Accascina⁽⁵⁴⁾ made further correction of equation-37 taking into consideration

the change in the viscosity of the solutions and assumed the validity of Walden’s rule. The new equation is

$$A = A^{\circ} - S c^{1/2} + Ec \ln c + J_1 c - J_2 c^{3/2} - B A^{\circ} c \tag{38}$$

In most cases, however, J_2 is made zero, but this leads to a systematic deviation of the experimental data from the theoretical equations.

2.3.1. Ion-Association

The conductance equation-38 is capable of representing accurately the behavior of completely dissociated electrolytes. The plot A versus $c^{1/2}$ (limiting Onsagar equation) is used to determine the dissociation or association of electrolytes. If $A^{\circ}_{(expt)} > A^{\circ}_{(theo)}$, the electrolyte may be regarded as completely dissociated but if $A^{\circ}_{(expt)} < A^{\circ}_{(theo)}$, the electrolytes may be regarded as associated. The difference between $A^{\circ}_{(expt)}$ and $A^{\circ}_{(theo)}$, would be considerable with increasing association ⁽⁵⁶⁾.

For strongly associated electrolytes, association constants K_A and A° were determined using the Fuoss-Kraus equation ⁽⁵⁷⁾ or Shedlovsky’s equation ⁽⁵⁸⁾,

$$\frac{T(z)}{A} = \frac{1}{A^{\circ}} + \frac{K_A}{(A^{\circ})^2} \times \frac{c \gamma_{\pm}^2 A}{T(z)} \tag{39}$$

where $T(z) = F(z)$ for the Fuoss and Kraus’ method and $1/T(z) = S(z)$ for the Shedlovsky method.

$$F(z) = 1 - z (1-z(1-z(1- \dots)^{-1/2})^{-1/2} \tag{40}$$

$$\text{and } S(z) = 1 + z + z^2/2 + z^3 / 8 + \dots \tag{41}$$

A plot of $T(z) / \Lambda$ against $c\gamma_{\pm}^2 \Lambda / T(z)$ should be a straight line having $1/\Lambda^0$ for its intercept and $K_A / (\Lambda^0)^2$ for its slope. . When K_A is large, there will be considerable uncertainty in the values of Λ^0 and K_A determined from the equation -39.

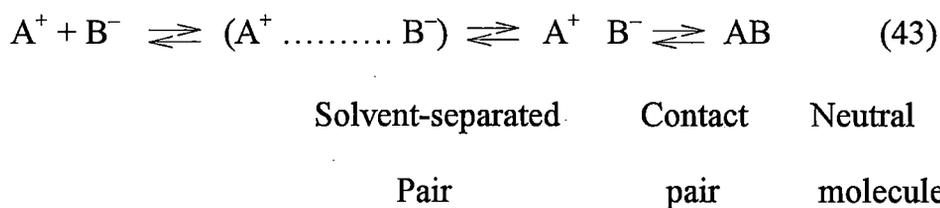
The Fuoss-Hsia conductance equation for associated electrolytes is given as

$$\Lambda = \Lambda^0 - S(\alpha c)^{1/2} + E(\alpha c) \ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{1/2} - K_A \Lambda \gamma_{\pm}^2(\alpha c) \quad (42)$$

This equation was modified by Justice ⁽⁵⁹⁾.

2.3.2. Ion-Size Parameter and Ionic Association

Fuoss in 1978 put forward a new conductance-concentration equation ⁽⁶⁰⁾. He developed the equation on the following basis: (i) those which find an ion of opposite charge in the first shell of the nearest neighbors (contact pairs) with $r_{ij} = a$; (ii) those with overlapping Gurney co-spheres (solvent separated pairs); and (iii) those which find no other unpaired ion in a surrounding sphere of radius R , where R is the diameter of the co-sphere (unpaired ions). Thermal motion and forces establish a steady state, represented by the equilibria



From this equation Fuoss derived an expression for the association constant or conductometric-pairing constant.

$$K_A = K_R (1 + K_s) \quad (44)$$

where, K_R describes the formation and separation of solvent-separated pairs by diffusion, in and out of the spheres of diameter R around the cations (calculated using the continuum theory), K_s is a constant describing the specific short range ion-solvent and ion-ion interactions by which contact pairs form and dissociate.

The details of the calculations are presented in the Fuoss 1978 paper. The shortcomings of the previous papers have been rectified in the present set of equations that are more general than the previous ones and can be used in higher concentration regions (0.1 N in aqueous solutions).

For a given set of conductivity values, three adjustable parameters, the limiting molar conductivity (Λ^0), association constant (K_A), and the co-sphere diameter (R), are derived from the following set of equations:

$$\Lambda = p[\Lambda^0(1 + R_x) + E_L] \quad (45)$$

$$p = 1 - \alpha(1 - \gamma) \quad (46)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (47)$$

$$-\ln f = \beta k / 2(1 + kR) \quad (48)$$

$$\beta = e^2 / \epsilon k_B T \quad (49)$$

$$K_A = K_R / (1 - \alpha) = K_R(1 + K_s) \quad (50)$$

where R_x is the relaxation field effect, E_L is the electrophoretic countercurrent, ϵ is the dielectric constant of the solvent, e is the electronic charge, k^{-1} is the radius of the ion atmosphere, K_B is the Boltzmann constant, γ is the fraction of solute present as unpaired ion, c is the molarity of the solution, f is the activity coefficient, T is the temperature in absolute scale, and β is twice the Bjerrum distance. The computations can be performed on a computer using the program suggested by Fuoss. The initial (Λ^0) values for the iteration procedure can be obtained from a Shedlovsky extrapolation⁽⁵⁸⁾ of the data. Input for the

program is the set $(c_j, A_j, j = 1, \dots, n)$, n , ε , η , T , initial values of Λ° , and an instruction to cover a preselected range of R values.

2.3.3. Limiting Ionic Equivalent Conductances

By separating a number of molal functions of electrolyte solutions into ionic contributions, it is possible to isolate the contributions due to cations and anions in the solute-solvent interaction. At present, a limiting equivalent conductance is the only function, which can be divided into ionic components by a commonly accepted direct method. The rigorous method for the separation of the limiting equivalent conductances (Λ°) of electrolytes into ionic conductances (λ_\pm) is based on the use of transference numbers (t_\pm) for infinite dilutions.

$$\lambda_+^\circ = t_+ \Lambda^\circ \text{ and } \lambda_-^\circ = t_- \Lambda^\circ \quad (51)$$

Unfortunately, accurate transference number determinations are limited to only a few solvents.

In the absence of experimentally measured transference numbers it would be useful to develop indirect methods to obtain the ionic limiting equivalent conductances in solvents for which experimental transference numbers are not yet available.

Various attempts were made to develop indirect methods to obtain the limiting ionic equivalent conductance, in ionic solvents for which experimental transference numbers are not yet available. These methods have been well described by Walden⁽⁶¹⁾, Fuoss⁽⁶²⁾, and Gill⁽⁶³⁾.

Krumgalz⁽⁶⁴⁾, suggested a new method based on the fact, confirmed by NMR studies that the large tetralkyl (aryl) ammonium ions are not solvated in organic solvents, in the kinetic sense, due to the extremely weak electrostatic

interactions between the solvent molecules and the large ions with low surface charge density.

The radius of the dynamic particle can be calculated by employing Stokes equation.

$$r_s = |Z| F^2 / (A\pi N\eta_o\lambda_{\pm}^{\circ}) \quad (52)$$

where A is a coefficient varying from 6 (in the case of perfect sticking) to 4 (in the case of perfect slipping). Since the r_s values, the real dimensions of the non-solvated tetraalkyl (aryl) ammonium ions, must be constant, we have

$$\lambda_{\pm}^{\circ} \eta_o = \text{constant} \quad (53)$$

This relation has been tested using the λ_{\pm}° values determined with precise transference numbers. The product becomes constant and independent of the chemical nature of the organic solvents for the $i\text{-Am}_4\text{B}^-$, Ph_4As^+ and Ph_4B^- ions and for tetraalkylammonium cations starting from Et_4N^+ . The relation can also be well utilized to determine λ_{\pm}° values of ions in other organic solvents from the determined Λ° values.

In the absence of accurate transference number data for studied systems, we have used the 'reference electrolyte' method for the division of Λ° into their ionic components. Bu_4NBPh_4 has been used as the "reference electrolyte"⁽⁶⁴⁾. Fuoss and Hirsch⁽⁶⁵⁾ to evaluate the limiting ionic conductances in several solvents. We have divided the Λ° values using a method similar to that proposed by Krumgalz⁽³⁴⁾ for division of B -values.

$$\frac{\lambda^{\circ}(\text{Bu}_4\text{N}^+)}{\lambda^{\circ}(\text{Ph}_4\text{B})} = \frac{r(\text{Ph}_4\text{B})}{r(\text{Bu}_4\text{N}^+)} = \frac{5.35}{5.00} = 1.07 \quad (54)$$

The r -values have been taken from the works of Gill *et al*⁽⁶³⁾.

The values calculated by this method seem to be correct in different organic and mixed organic solvents. However, in aqueous binary mixtures, the solvation pattern may be different and the validity of this equation may be questioned.

Recently, Gill *et al*⁽⁶⁶⁾ proposed the following equation

$$\frac{\lambda^{\circ}(\text{Bu}_4\text{N}^+)}{\lambda^{\circ}(\text{Ph}_4\text{B}^-)} = \frac{5.35 - (0.0103\epsilon_0 + r_y)}{5.00 - (0.0103\epsilon_0 + r_y)} \quad (55)$$

and the ratio is close to 1.07 as used by us.

2.3.4. Solvation Number

Various types of interactions exist between the ions in solutions. These interactions result in the orientation of the solvent molecules towards the ion. The number of solvent molecules that are involved in the solvation of the ion is called solvation number. If the solvent is water, this is called hydration number⁽²⁶⁾.

Solvation region can be classified as primary and secondary solvation regions. Here we are concerned with the primary solvation region. The primary solvation number is defined as the number of solvent molecules which surrender their own translational freedom and remain with the ion, tightly bound, as it moves around, or the number of solvent molecules which are aligned in the force field of the ion.

If the limiting conductance of the ion i of charge Z_i is known, the effective radius of the solvated ion can be determined from Stokes' law. The volume of the solvation shell is given by the equation.

$$V_s = (4\pi/3) (r_s^3 - r_c^3) \quad (56)$$

where r_c is the crystallographic radius of the ion. The solvation number n_s would then be obtained from

$$n_s = V_s / \bar{V}_0 \quad (57)$$

Assuming Stokes' relation to hold well, the ionic solvated volume can be obtained, because of the packing effects⁽⁶⁸⁾, from

$$V_s^0 = 4.35 r_s^3 \quad (58)$$

where V_s^0 is expressed in mol/lit. and r_s in angstroms. However, this method is not applicable to ions of medium size though a number of empirical⁽⁶⁹⁾ and theoretical corrections⁽⁷⁰⁻⁷¹⁾ have been suggested in order to apply it to most of the ions.

2.3.5. Stokes' Law and Walden's Rule

The starting point for most evaluations of ionic conductances is Stokes' law that states that the limiting Walden product (the limiting ionic conductance-solvent viscosity product) for any singly charged, spherical ion is as function only of the ionic radius and thus, under normal conditions, is constant. The limiting conductances λ_i^0 of a spherical ion of radius R_i moving in a solvent of dielectric continuum can be written, according to Stokes' hydrodynamics, as

$$\lambda_i^0 = 0.819 |Z_i| / \eta^0 R_i \quad (59)$$

If the radius R_i is assumed to be the same in every organic solvent, as would be the case of bulky organic ions, we get

$$\lambda_i^0 \eta^0 = 0.819 |Z_i| / R_i = \text{constant} \quad (60)$$

This is known as the Walden rule ⁽⁷²⁾. The effective radii obtained using this equation can be used to estimate the solvation numbers. However, Stokes' radii failed to give the effective size of the solvated ions for small ions.

2.4. Apparent and Partial Molar Volumes

Thermodynamic properties of solutions are not useful for estimating the feasibility of reactions in solution, but also offer one of the better methods of investigating the theoretical aspects of solution structure. This is particularly true for the standard partial molal entropy, heat capacity, and volume of the solutes, values of which are sensitive to the rearrangement of solvent molecules around a solute particle. These properties are also very useful for interpreting solute-solvent interactions.

Various concepts regarding molecular processes in solutions such as, electrostriction ⁽⁸⁾, hydrophobic hydration ⁽⁷³⁾, micellization ⁽⁷⁴⁾ and co-sphere overlap during solute-solute interactions ^(30, 75) have to a large extent been derived and interpreted from the partial molar volume data of many compounds.

The apparent molar volumes, (ϕ_v), can be calculated from the densities of the solutions using the following equation.

$$\phi_v = M/\rho_0 - 1000(\rho - \rho_0)/(c\rho_0) \quad (61)$$

where c is the molarity of the solution, M is the molar mass of the solute, ρ and ρ_0 are the densities of the solution and solvent, respectively. The partial molar volume, \bar{V}_2 can be obtained from the equation

$$\bar{V}_2 = \phi_v + \frac{1000 - c \phi_v}{2000 + c^{3/2} (d\phi_v / d c^{1/2})} c^{1/2} \frac{d\phi_v}{d c^{1/2}} \quad (62)$$

Masson ⁽⁷⁶⁾ found that ϕ_v varies with the square root of the molar concentration by the linear equation

$$\phi_v = \phi_v^\circ + S_v^\circ \sqrt{c} \quad (63)$$

where ϕ_v° is the apparent molar volume at infinite dilution (equal to the partial molar volume at infinite dilution) and S_v° is the experimental slope, which varies with electrolyte, and is only approximately equal to the theoretical limiting slope. Redlich and Meyer ⁽⁷⁷⁾ have shown that an equation -63 cannot be any more than a limiting law where for a given solvent and temperature, the slope S_v° should depend only upon the valence type. They suggested the equation

$$\phi_v = \phi_v^\circ + S_v \sqrt{c} + b_v c \quad (64)$$

where $S_v = Kw^{3/2}$, is the theoretical slope, based on molar concentration, including the valence factor where

$$w = 0.5 \sum_i \gamma_i Z_i^2 \quad (65)$$

and,

$$K = N^2 e^3 (8\pi / 1000 \epsilon^3 RT)^{1/2} (\delta \ln \epsilon / \delta P)_T - \beta/3 \quad (66)$$

In equation-66, β is the compressibility of the solvent and the other terms have their usual significance.

The Redlich-Meyer's extrapolation equation ⁽⁷⁷⁾ adequately represents the concentration dependence of many 1:1 and 2:1 electrolytes in dilute solutions; however, studies ⁽⁷⁸⁾ on some 2:1, 3:1 and 4:1 electrolytes show deviations from this equation. Thus, for polyvalent electrolytes, the more complete Owen-Brinkley equation ⁽⁷⁹⁾ can be used to aid in the extrapolation to

infinite dilution and to adequately represent the concentration dependency of ϕ_v . The Owen-Brinkley equation ⁽⁷⁹⁾ which includes the ion-size parameter, a (cm), is given by

$$\phi_v = \phi_v^0 + S_v \tau (\kappa a) \sqrt{c} + 0.5 W_v \theta (\kappa a) c + 0.5 K_v c \quad (67)$$

where the symbols have their usual significance. However, this equation is not widely used for non-aqueous solutions.

Recently, the Pitzer formalism has been used by Pogue and Atkinson ⁽⁸⁰⁾ to fit the apparent molal volume data. The Pitzer equation for the apparent molar volume of a single salt $M\gamma_M X\gamma_X$ is

$$\phi_v = \phi_v^0 + v \left[Z_M Z_X \left| A_v / 2b \ln(1 + b\sqrt{I}) + 2\gamma_M \gamma_X RT [mB_{MX}^2 + m^2 (\gamma_M \gamma_X)^{1/2} C_{MX}^2] \right. \right] \quad (68)$$

where the symbols have their usual significance.

2.5. Ionic Limiting Partial Molar Volumes

Most of the existing ionic limiting partial molar volumes in organic solvents were obtained by the application of methods developed for aqueous solutions. For sometime, the method of Conway *et al* ^(81a) was widely used. They plotted the limiting partial molar volume, $\bar{V}_{R_4NX}^0$ for a series of homologous tetraalkylammonium chlorides, bromides and iodides with a halide ion in common, as a function of the formula weight of the cation, $M_{R_4N^+}$, and obtained straight-line graphs for each series. Their results were claimed to fit the equation.

$$\bar{V}_{R_4NX}^0 = \bar{V}_{X^-}^0 + b M_{R_4N^+} \quad (69)$$

and the extrapolation to zero cationic formula weight gave the limiting partial molar volumes of the halide ions, $V_{X^-}^0$. Uosaki *et al* ^(81b) and later Krumgalz ^(81c)

applied the same method to non-aqueous electrolyte solutions in a wide temperature range.

2.6. Ultrasonic Sound Speed

In recent years, there has been considerably progress in the determination of thermodynamic, acoustic and transport properties of working liquids from ultrasonic speeds, density and viscosity measurement. The study of ultrasonic speeds and isentropic compressibilities of liquids, solutions and liquid mixtures ⁽⁸²⁾ provide useful information about molecular interactions, association and dissociation. Various parameters like molar isentropic and isothermal compressibilities, apparent molal compressibility, isentropic compressibility, deviation in isentropic compressibility from ideality, etc. can very well be evaluated and studied from the measurement of ultrasonic speeds and densities in solutions. Isentropic compressibilities play a vital role in characterization of binary and ternary liquid mixtures.

2.7. Apparent Molal Isentropic Compressibility

The apparent molal isentropic compressibility (or apparent molal adiabatic compressibility) provide very useful information about molecular interaction taking place in solutions and can provide useful information about these, particularly in cases where partial molal volume data alone fail to provide an unequivocal interpretation of the interactions ⁽⁸³⁻⁸⁶⁾. The isentropic compressibility (K_S) or adiabatic compressibility (β) values are calculated using the Laplace equation

$$K_S \text{ (or } \beta) = 1 / (u^2 \rho) \quad (70)$$

where:

ρ = the solution density

u = the sound speed in solution.

The apparent molal isentropic compressibility (K_ϕ) of the liquid solution is calculated using the relation.

$$K_\phi = [(1000/m\rho\rho_0)(K_S\rho_0 - K_S^\circ\rho)] + K_S M/\rho_0 \quad (71)$$

where m is the molality of the solution; K_S° and K_S are the isentropic compressibility of the solvent and solution respectively.

The limiting apparent isentropic compressibility K_ϕ° may be obtained by extrapolating the plots of K_ϕ versus the square root of the molal concentration of the solutes by the computerized least-square method according to the equation ^(83,86).

$$K_\phi = K_\phi^\circ + S_k^* \sqrt{m} \quad (72)$$

where S_k^* is the experimental slope.

The limiting apparent isentropic compressibility (K_ϕ°) and the experimental slope (S_k) can be interpreted in terms of solute-solvent and solute-solute interactions, respectively. It is well established that the solutes causing electrostriction lead to a decrease in the compressibility of the solution ⁽⁸⁷⁻⁸⁸⁾. This is reflected by the negative values K_ϕ° of electrolyte solutions. Hydrophobic solutes often show negative compressibilities due to the ordering induced by them in the water structure ^(74, 87). The compressibility of hydrogen-bonded structure, however, varies depending on the nature of H-bonds involved ⁽⁸⁷⁾, the poor fit of the solute molecules ⁽⁸⁹⁾ as well as the possibility of flexible H-bond formation causing a more compressible environment (and hence a positive K_ϕ° value) in the aqueous medium. Positive K_ϕ° values have been

reported in aqueous non-electrolytes ⁽⁹⁰⁾ and non-electrolyte-non-electrolyte solution.

2.8. Some Recent Trends in Solvation Models

The last decade (1990-2000) witnessed some interesting trends in development of some solvation models and computer software. Based on a vast collection of experimental free energy of solvation data, C.J.Cramer, D.G.Truhlar and co-workers from the University of Minnesota, USA, constructed a series of solvation models (SMI-SM5 series) to predict and calculate the free energy of solvation of a chemical compound ⁽⁹¹⁻⁹⁵⁾. These models are applicable to virtually any substance composed of H, C, N, O, F, P, S, Cl, Br and/or I. The only input data required are molecular formula, geometry, refractive index, surface tension, Abraham's *a* (acidity parameter) and *b* (basicity parameter) values, and, in the latest models, the dielectric constants. Many of these parameters for a number of compounds are available in the Internet at <http://comp.chem.umn.edu/solvation> ⁽⁹⁶⁾.

The advantage of models like SM5 series is that they can be used to predict the free energy of self-solvation to better than 1 Kcal/mol. They can also be used to predict the vapour pressure at 298.15 K with useful accuracy. They are especially useful when other methods are not available. One can also analyze factors like, electrostatics, dispersion, hydrogen bonding, etc., using these tools. They are also relatively inexpensive and available in easy to use computer codes.

A Galindo *et al* ⁽⁹⁷⁻⁹⁸⁾ have developed Statistical Associating Fluid Theory for Variable Range (SAFT-VR) to model the thermodynamics and phase equilibria of electrolyte aqueous solutions. The water molecules are modeled as hard spheres with four short-range attractive sites to account for the hydrogen-bond interactions. The electrolyte is modeled as two hard spheres of

different diameter to describe the anions and cations. The Debye-Huckel and mean spherical approximations are used to describe the interactions.

Good agreement with experimental data is found for a number of aqueous electrolyte solutions. The relative permittivity takes values very close to unity, especially in the case in which the mean spherical approximation is used, indicating a good description of the solvent. E. Bosch *et al* ⁽⁹⁸⁾, of the University of Barcelona, Spain, have compared several Preferential Solvation Models especially for describing the polarity of dipolar hydrogen bond acceptor-co solvent mixtures.

2.9. Acoustic Parameters

Physico-chemical behavior and molecular interactions occurring in a variety of liquid mixtures and solutions ⁽⁹⁹⁾ can be well studied with the aid of ultrasonic sound speed, density and viscosity data.

The speed of sound u , isentropic compressibility K_s , and excess isentropic compressibility K_s^E are the properties sensitive to different kinds of interactions in the pure components and in the mixtures, and often are related to local order. These properties can be used to investigate the molecular packing, molecular motion, and various types of intermolecular interactions and their strength, influence by the size, shape, and chemical nature of components molecules.

In order to explore the strength and nature of the interactions occurring in the liquid mixtures and solutions various acoustic and thermodynamic parameters from the ultrasonic sound speed and density may be used. Various acoustic parameters such as specific impedance ⁽¹⁰⁰⁾ (Z), intermolecular free length ⁽¹⁰¹⁾ (L_f), Vander Waal's constant (b), molecular radius ⁽¹⁰¹⁾ (r), geometrical volume (B), molar surface area (Y), available volume ⁽¹⁰²⁾ (V_a), molar speed of sound ⁽¹⁰³⁾ (R), collision factor ⁽¹⁰⁴⁾ (S) and molecular

association ⁽¹⁰⁵⁾ (M_A), solvation number (S_n) ⁽¹⁰⁶⁾, free volume (V_f) ⁽¹⁰⁷⁾, and wada's constant (\bar{W}) ⁽¹⁰⁸⁾ have been calculated using the following relations:

$$Z = u \rho \quad (73)$$

$$b = (M/\rho) - (RT/\rho u^2) \{ [1 + (Mu^2/3 RT)]^{1/2} - 1 \} \quad (74)$$

$$r = (3b/16 \pi N)^{1/3} \quad (75)$$

$$L_f = K / (u \rho^{1/2}) \quad (76)$$

$$B = (4/3) \pi r^3 N \quad (77)$$

$$Y = (36 \pi N B^2)^{1/3} \quad (78)$$

$$V_a = V - V_0 \quad (79)$$

$$R = Mu^{1/3} / \rho \quad (80)$$

$$S = u V / u_\infty B \quad (81)$$

$$M_A = [(u_{mix} / \sum x_i u_i)^2 - 1] \quad (82)$$

$$S_n = (n_1/n_2) [1 - (K_s/K_{s,1})] \quad (83)$$

$$V_f = V (u_g/u)^3 \quad (84)$$

$$\bar{W} = M K_s^{-1/7} / \rho \quad (85)$$

where K is a temperature dependent constant ($= (93.875 + 0.375 T) \times 10^{-8}$) ⁽³²⁾, V_0 is volume at absolute zero, u_∞ is taken as 1600 ms^{-1} , u_g is the ultrasonic sound speed in the vapour phase, n_1 and n_2 are the numbers of moles of the respective components and M is the molar mass of the components.

For comparison, the theoretical values of ultrasonic sound speeds, u , can be computed using the following theories and empirical equations

Flory's theory ⁽¹⁰⁹⁾:

$$u_F = (\delta / 6.3 \times 10^{-4} \rho)^{2/3} \quad (86)$$

Free length theory (101):

$$u_{\text{FLT}} = K / (L_f \rho^{1/2}) \quad (87)$$

Collision factor theory (102):

$$u_{\text{CFT}} = u_{\infty} \{x_1 S_1 + x_2 S_2\} [\{x_1 B_1 + x_2 B_2\} / V] \quad (88)$$

Junjie equation ⁽¹¹⁰⁾:

$$u_J = \{(x_1 M_1 / \rho_1) + (x_2 M_2 / \rho_1)\} / [\{x_1 M_1 + x_2 M_2\}^{1/2} \{(x_1 M_1 / \rho_1 u_1^2) + (x_2 M_2 / \rho_1 u_2^2)\}^{1/2}] \quad (89)$$

Nomoto equation ⁽¹¹¹⁾:

$$u_N = [\{x_1 R_1 + x_2 R_2\} / \{x_1 V_1 + x_2 V_2\}]^3 \quad (90)$$

2.10. Excess Functions

Studies of transport properties of electrolytes along with thermodynamic and acoustic studies, give very valuable information about molecular interactions in solutions. The influence of these solute-solvent interactions is sufficiently large to cause dramatic changes in chemical reactions involving ions.

The excess molar volumes, viscosity deviations, excess free energy of activation of viscous flow, and excess isentropic compressibility are the properties sensitive to different kind of interactions in the pure and in the mixtures. They have been used to investigate the molecular packing, molecular motion, and various types of intermolecular interactions, their strength, influenced by the size, shape, and chemical nature of the components molecules.

2.10.1. Excess Molar Volumes

The excess molar volumes, V^E are calculated from the molar masses M_i and the densities of pure liquids and the mixtures according to the following equation ⁽¹¹²⁾:

$$V^E = \sum_{i=1}^n x_i M_i (1/\rho - 1/\rho_i) \quad (91)$$

where ρ_i and ρ are the density of the i^{th} component and density of the solution mixture respectively.

The relative change of volume in mixing ΔV can be computed for the mixtures using the equation ⁽¹¹³⁾:

$$\Delta V = V^E / \sum_{i=1}^n x_i V_i \quad (92)$$

2.10.2. Viscosity Deviations

Quantitatively, as per the absolute reaction rates theory ⁽¹¹⁴⁾, the viscosity deviations from linear dependence on composition can be calculated

$$\Delta\eta = \eta - \sum_{i=1}^n x_i \eta_i \quad (93)$$

where η is the viscosity of the mixture and x_i , η_i are the mole fraction and viscosity of pure component, i respectively.

2.10.3. Gibbs Excess Energy of Activation for Viscous Flow

On the basis of the theory of absolute reaction rates ⁽¹¹⁴⁾, the Gibbs excess energy of activation for viscous flow, G^{*E} can be calculated from

$$G^{*E} = RT [\ln \eta V - \left(\sum_{i=1}^n x_i \ln \eta_i V_i \right)] \quad (94)$$

where, η and V are the viscosity and molar volume of the mixture, η_i and V_i are the viscosities and molar volumes of pure component, i respectively.

2.10.4. Excess Isentropic Compressibility

The excess isentropic compressibility, K_S^E can be calculated using the following equation ⁽¹¹⁵⁻¹¹⁷⁾.

$$K_S^E = K_S - \sum_{i=1}^n x_i K_{S,i} \quad (95)$$

where, x_i , $K_{S,i}$ are the mole fraction and isentropic compressibility of component i , respectively

2.10.5. Deviation of Sound Speeds

The deviations of sound speed (Δu) can be calculated according to the following equation ⁽¹¹⁸⁻¹²⁰⁾.

$$\Delta u = u - \sum_{i=1}^n x_i u_i^0 \quad (96)$$

2.10.6. Excess intermolecular free Length and Excess Acoustic Impedance

The excess functions of acoustic impedance Z and intermolecular free length L_f^E can be calculated using the following equations:

$$L_f^E = L_f - \sum_{i=1}^n x_i L_{fi} \quad (97)$$

$$Z^E = Z - \sum_{i=1}^n x_i Z_i \quad (98)$$

2.11. Correlating Equations

The several models (equations) have been put forward to correlate the viscosity of binary liquid mixtures in terms of pure-components data. Some of them are discussed as under:

(i) Grunberg and Nissan ⁽¹²¹⁾ suggested a logarithmic relation between the viscosity of liquid mixture and that of its pure components,

$$\eta = \exp (x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12}) \quad (99)$$

where G_{12} is a constant, regarded as a measure of the strength of molecular interactions between the mixing components

(ii) Tamura and Kurata ⁽¹²²⁾ developed the following equation for the viscosity of binary liquid mixtures:

$$\eta = x_1 \Phi_1 \eta_1 + x_2 \Phi_2 \eta_2 + 2 (x_1 x_2 \Phi_1 \Phi_2)^{1/2} T_{12} \quad (100)$$

where Φ_1 and Φ_2 are the volume fractions of components 1 and 2, and T_{12} and adjustable parameter.

(iii) Hind *et al.*⁽¹²³⁾ suggested the following equation for the viscosity of the binary liquid mixtures:

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2 x_1 x_2 \eta_1 \eta_2 H_{12} \quad (101)$$

Again, the V^E , $\Delta\eta$, G^{*E} , K_S^E , L_f^E , Z^E , and Δu values can be fitted to Redlich-Kister⁽¹²⁴⁾ equation using the method of least squares involving the Marquardt algorithm⁽¹²⁵⁾ to derive the binary coefficient, A_J :

$$Y^E = x_1 x_2 \sum_{J=1}^k A_{J-1} (x_1 - x_2)^{J-1} \quad (102)$$

Here, Y^E denotes V^E , $\Delta\eta$, G^{*E} , K_S^E , L_f^E , Z^E , and Δu . In each case, the optimum number of coefficients, A_J is ascertained from an examination of the variation of the standard deviation, σ , with:

$$\sigma = [(Y_{exp}^E - Y_{cal}^E)^2 / (n - m)]^{1/2} \quad (103)$$

where n represents the number of measurements and m the number of coefficients.

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