Modeling Viscosity of Aqueous and Mixed-Solvent Electrolyte Solutions

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A comprehensive model has been developed for calculating the viscosity of aqueous or mixed-solvent electrolyte systems ranging from dilute solutions to fused salts. The model incorporates a mixing rule for calculating the viscosity of solvent mixtures and a method for predicting the effect of finite electrolyte concentrations. The mixing rule represents the viscosity of multicomponent solvent mixtures using molar volumes and viscosities of pure components together with binary parameters. The effect of electrolyte concentration on viscosity is modeled by combining a long-range electrostatic term obtained from the Onsager-Fuoss theory, a contribution of individual ions, which is quantified by the Jones-Dole B coefficients, and a contribution of specific interactions between ions or neutral species. Formulations have been developed for the contributions of individual ions and species-species interactions to account for the effect of multiple solvents. The model accurately reproduces the viscosity of systems such as salts in water, organic or mixed water-organic solvents and aqueous acids or bases up to the pure solute limit.

1. Introduction

Viscosity of electrolyte solutions is of considerable interest due to its importance in numerous industrial systems, especially those involving electrochemical processes. Variations of viscosity with temperature and solvent composition have also been investigated to understand ion-solvent interactions in electrolyte systems. Extensive experimental viscosity data are available for both aqueous and mixed-solvent electrolyte systems. However, analysis of such data has been commonly performed only on a case-by-case basis and no attempt has been made to develop a comprehensive viscosity model for mixed-solvent electrolyte systems.

Theoretical investigations of viscosity of electrolyte solutions have been focused mainly on systems containing a single solute in dilute solutions with a single solvent, usually water. These theories resulted in the development of a limiting law, which predicts the relative viscosity of the solution as a function of the square root of the concentration in binary systems:

$$\eta/\eta_0 = 1 + A \cdot c^{1/2} \tag{1a}$$

The viscosity A coefficient was shown to be a function of solvent properties and limiting conductivities of ions. The limiting law was extended to somewhat higher concentrations (up to ca. 0.1 – 0.2 M) by Jones and Dole [1], who introduced the viscosity B coefficients, i.e.,

$$\eta/\eta_0 = 1 + A \cdot c^{1/2} + B \cdot c \tag{1b}$$

A further empirical extension of the Jones-Dole equation was proposed by Kaminsky [2], who introduced an additional quadratic term in c. The B coefficients in the Jones-Dole equation are characteristic for individual ions and can be interpreted in terms of ion-solvent interactions. Furthermore, they are additive in terms of contributions from individual cations and anions in a given solvent.

While accurate for relatively dilute solutions, the Jones-Dole equation and its simple extensions cannot reproduce experimental data for concentrated systems. Therefore, more comprehensive models have been recently developed for concentrated solutions [3, 4]. In particular, Lencka et al. [4] developed a speciation-based viscosity model for concentrated multicomponent aqueous electrolyte solutions. The model of Lencka et al. has been shown to reproduce experimental data for concentrations up to 30 molal and temperatures up to 300ºC.

In mixed-solvent electrolyte solutions, viscosity is affected not only by the concentration of electrolytes, but also by the composition of the solvent. Even the viscosity of solvent mixtures may show a complex behavior and change significantly with composition. In addition, in systems with strong ion association effect (e.g., in fully miscible acids or bases), viscosity is affected by concentrations of both ions and associated ion

pairs. Thus, a comprehensive treatment of viscosity of mixed-solvent electrolyte systems requires taking into account not only the ion-solvent and ion-ion interactions that predominate in aqueous solutions, but also the solvent-solvent and ion pair-solvent interactions.

The objective of this work is to develop a comprehensive, engineering-oriented model for predicting viscosities of mixed-solvent electrolyte solutions. The model is designed to be applicable to mixed-solvent electrolyte solutions over wide ranges of solvent composition and electrolyte concentration (i.e. from infinitely dilute to concentrated salt solutions).

2. Viscosities of Solvent Mixtures

It has long been recognized that viscosity *versus* composition curves are not a simple function of composition. They may have a maximum, a minimum or both. Various models for representing the viscosity of a liquid mixture have been described in the literature. Some notable models include those based on the absolute reaction rate theory of Eyring [5] such as the model of McAllister [6] and its various extensions [7-9]; models based on group contribution methods such as of those of Isdale *et al.* [10], Cao *et al.* [11] and Wu [12]; models based on the corresponding-states principle such as those of Teja and Rice [13] and Wu and Asfour [14]; and other empirical approaches such as the models of Giro *et al.* [15] and Grunberg and Nissan [16]. Although these models have been shown to be capable of representing viscosities of a number of binary and some ternary mixtures, insufficiently accurate results can often be obtained for some specific systems, especially those with polar components such as aqueous mixtures [17].

In this section, we outline a new mixing rule that relates the viscosities of solvent mixtures to those of pure components. Here, emphasis is put on the accurate representation of the complex composition dependence of viscosity, which is frequently observed in aqueous systems. No attempt is made to predict the viscosities of pure components since this is the domain of group contribution methods. Rather, we utilize empirical correlations for the viscosity of pure components as a function of temperature [18, 19] and develop a mixing rule to capture the composition dependence of the viscosity of mixtures. This mixing rule will provide a basis for the computation of viscosities in mixed-solvent electrolyte solutions.

The new mixing rule relates the viscosity of a solvent mixture η_{mix} to pure component viscosities using modified volume fractions, i.e.,

$$\eta_{mix} = \sum_i \sum_j Y_i Y_j \eta_{ij} \qquad (2)$$

where Y_i is a modified volume fraction of component i:

$$Y_i = \frac{v_i^* x_i}{\sum_k v_k^* x_k} \qquad (3)$$

In eq. (3), the effective volume v_i^* is related to the actual volume v_i^0 by

$$v_i^* = v_i^0 + \sum_{k \neq i} x_k^{1/4} v_k^0 g_{ik} \qquad (4)$$

The parameter η_{ij} in eq. (2) is a modified arithmetic average of pure component viscosities:

$$\eta_{ij} = \frac{1}{2}\left(\eta_i^0 + \eta_j^0\right)\left(1 + k_{ij}\right) \qquad (5)$$

In Eqs. 2-5, x_i is the mole fraction of component i, and v_i^0 and η_i^0 are the liquid molar volume and viscosity of component i, respectively. The binary parameters g_{ij} and k_{ij} can be determined from experimental viscosity data for mixtures. The g_{ij} parameter accounts for the effect of asymmetry of molar volumes on the variation of the viscosity with composition. It has been found that the symmetry of the viscosity versus composition curve (including the location of a possible maximum or minimum) strongly depends on the modified molar volumes v_i^* (cf. Eq. 3). The quantity v_i^* may be interpreted as an effective molar volume of a component, which is affected by the presence of other components in the mixture. This effect can be represented by Eq. 4 where the pure liquid molar volume (v_i^0) is corrected for the presence of other components, k ($k \neq i$).

2. Effect of Electrolyte Concentration

In the model of Lencka *et al.* [4], the dependence of viscosity on electrolyte concentration is represented by three contributions, i.e., (1) the long-range electrostatic term (η^{LR}), which accounts for the interactions between point charges in a dielectric continuum and is calculated based on the Onsager - Fuoss theory [20]; (2) the

contribution of individual ions (η^s), which is characterized by the viscosity B coefficients; and (3) the contribution of interactions between ions or neutral species (η^{s-s}). The general methodology used in the model of Lencka *et al.* is applicable to electrolyte solutions in any single solvent. To extend this methodology to mixed-solvent electrolyte systems, it is necessary to take into account the effects of changing solvent composition on the contributions of individual ions and on the interactions between species. An extension of the approach of Lencka et al. to mixed-solvent electrolytes is outlined in this section. In this study, the term "mixed solvent electrolytes" is used in the broadest possible sense to include (1) electrolytes in pure organic or mixed organic-water solvents, (2) fully miscible acids or bases in water, and (3) aqueous electrolyte solutions from the dilute region to the molten salt limit.

For the analysis of the viscosity of aqueous solutions, expressions for the relative viscosity, η_r, are commonly used to represent the effect of electrolyte concentrations. In mixed-solvent solutions, due to the combined effects of electrolyte concentration and solvent composition, the relative viscosity is no longer an obvious measure of the electrolyte effect. Analysis of experimental viscosity data of such systems has revealed that the difference between the viscosity of the solution (η) and that of the solvent mixture (η_{mix}^0) shows relatively simple regularities as a function of both the electrolyte concentrations and solvent composition. On the other hand, no such regularities can be observed for the relative viscosity. Thus, we express the $\eta - \eta_{mix}^0$ difference as a sum of a long-range electrostatic interaction term, contributions of individual species and those of species-species interactions:

$$\eta - \eta_{mix}^0 = \Delta\eta^{LR} + \Delta\eta^s + \Delta\eta^{s-s} \tag{6}$$

The $\Delta\eta^s$ and $\Delta\eta^{s-s}$ terms are reformulated in this study to account for solvent effects. The long-range electrostatic contribution to the relative viscosity of the electrolyte solution, $\Delta\eta^{LR}$, is calculated from the expressions of Onsager and Fuoss [20] using the dielectric constant and limiting conductivity models developed in previous papers [21, 22]. The Onsager-Fuoss [20] model includes a leading term in $I^{1/2}$ (or $c^{1/2}$ for single-solute

systems) and a further correction calculated using a recursive formula.

The contribution of individual ions $\Delta\eta^s$ is represented in terms of the viscosity B coefficients. In a solution with a single solvent, this term is rigorously expressed as a simple sum of ionic contributions, i.e.,

$$\Delta\eta^s = \sum_i \eta^0 c_i B_i \tag{7a}$$

where the subscript i denotes all solute species and η^0 is the viscosity of the pure solvent. For mixed-solvent systems, eq. (7a) is generalized by taking into account that the B coefficients are solvent-dependent and η^0 is no longer a single quantity, but is replaced by those for multiple solvents. Thus, eq. (7a) is rewritten for multiple solvents as:

$$\Delta\eta^s = \sum_j \sum_i x_j \eta_j^0 c_i B_{i,j} \tag{7b}$$

where the subscript j denotes the solvent components, i pertains to the solutes (ions and neutral species); η_j^0 is the viscosity of pure solvent j; c_i is the molarity (mol·L^{-1}) of the i-th species, and $B_{i,j}$ is the B coefficient of the i-th species in a pure solvent j.

In a previous paper, an expression for η^{s-s} was developed for multicomponent solutions in a single solvent. This term is proportional to I^2 (where I is the ionic strength of the solution) and is made up of contributions of all species pairs in the system, i.e.,

$$\Delta\eta^{s-s} = \sum_i \sum_j \eta^0 f_i f_j D_{ij} I^2 \tag{8a}$$

where f_i and f_j are fractions of the i-th and j-th species, respectively, and D_{ij} is the interaction parameter between i and j. Ionic association is not treated explicitly in this model. However, specific interactions such as ion association are implicitly taken into account by the D_{ij} terms.

In this study, we generalize this expression to recognize that the effects of species-species interactions are dependent on the solvent combinations. The multi-solvent extension of eq. (8a) is given by

$$\Delta\eta^{s-s} = \sum_j \sum_l \sum_i \sum_k x_j x_l \eta_{jl}^0 f_i f_k D_{ik,jl} I^2 \tag{8b}$$

where the first and second sums (j and l) are over all solvents and the sums over i and k are over all solutes; η_{jl}^0 is an averaged viscosity of solvents

j and l,

$$\eta_{jl}^0 = \frac{1}{2}\left(\eta_j^0 + \eta_l^0\right) \qquad (9)$$

As in the single-solvent model [4], the fractions f_i and f_k are molar fractions of the i-th and k-th species, respectively, adjusted for the charges of species, i.e.,

$$f_i = \frac{c_i / max(1,|z_i|)}{\sum_l c_l / max(1,|z_l|)} \qquad (10)$$

where the factor $max(1,|z_i|)$ ensures that f_i reduces to the molar fraction for neutral species. $D_{ik,jl}$ is a binary parameter between the species i and k in a solvent pair j and l.

The molar concentrations of all species in the above equations are calculated using speciation and density obtained from a recently developed thermodynamic model [23].

4.   Parameter Evaluation

The B Coefficients. The B coefficients for a large number of aqueous species have been determined by analyzing extensive experimental viscosity data [4]. Marcus [24] has compiled the B coefficients for a number of ions in pure organic solvents at 25°C. For systems for which the B coefficients are not available in literature sources, their values have been determined from experimental viscosity data at low electrolyte concentrations (usually below 0.05 M) in pure solvents using a method described by Lencka et al. [4]. The temperature dependence of the B coefficients is expressed using the equation of Out and Los [25]:

$$B = B_E + B_S \, exp\left(-K \cdot (T - T_0)\right) \qquad (11)$$

where T is the temperature in K, $T_0 = 273.15$ K, and K has been set equal to 0.023 for most aqueous [4] and non-aqueous electrolyte solutions.

The $D_{ik,jl}$ Parameters. The ionic strength dependence of the $D_{ik,jl}$ parameters is given by [4]

$$D_{ik,jl} = d_{ik,jl}^{(1)} + d_{ik,jl}^{(2)}I + d_{ik,jl}^{(3)} \exp\left(aI^{3/2}\right) \qquad (12)$$

where a is set equal to 0.08 for most aqueous and non-aqueous electrolyte solutions. The temperature dependence of each of the $d_{ik,jl}^{(m)}$ ($m = 1, 2, 3$) parameters is given by

$$d_{ik,jl}^{(m)} = d_{ik,jl}^{(m0)} \exp\left(d_{ik,jl}^{(m1)} \cdot (T - T_0)\right) \text{ (m=1,2,3) (13)}$$

5. Results and Discussion

As discussed above, the viscosity model of Lencka *et al.* [4] has been shown to be accurate for aqueous electrolyte solutions with concentrations up to 30 molal. The new viscosity model reduces to the model of Lencka *et al.* [4] when water is the only solvent in the system. Thus, validation of the new viscosity model has been focused on (1) electrolytes in pure organic and mixed solvents and (2) aqueous electrolyte solutions ranging from the dilute region to fused salts or pure acids or bases.

The performance of the model for electrolytes in mixed solvents is shown in Figs 1-2. In these figures, experimental viscosity data for the systems $LiNO_3$ + ethanol + water and Na acetate + acetone + water are compared with calculated results at various solvent compositions, electrolyte concentrations, and temperatures.

As shown in Figure 1, viscosity increases more rapidly with $LiNO_3$ concentration as the ethanol weight fraction increases in the $LiNO_3$ + ethanol + H_2O system. Upon addition of a salt, the qualitative trends in the composition dependence of viscosity in salt + solvent mixtures remain similar to those in salt-free solvent mixtures. In the case of the Na acetate + acetone + H_2O system, the viscosities show a maximum with changing solvent composition at all salt concentrations. These trends are accurately reproduced by the model.

Metal nitrates in water can be continuously miscible from infinite dilution to the fused salt limit. Since extensive experimental viscosity data are available for such systems, they provide a stringent test of the performance of the model over the full concentration range of electrolyte components. Figure 3 shows the results for the ternary system $AgNO_3$ - $TlNO_3$ -water at water contents ranging from $x_w=0$ to $x_w=0.98$ and at a constant Ag/Tl molar ratio of 1.06, which corresponds to a eutectic mixture of $AgNO_3$ and $TlNO_3$.

Fully miscible aqueous acids and bases are another important class of mixtures. Because of their usually strong association effects, such systems provide not only good test cases, but also offer an excellent opportunity to examine the effect of speciation on viscosity. In these systems, speciation can change dramatically as acid concentration increases. Figures 4 and 5 show the results for the HNO_3 + H_2O and H_2SO_4 + H_2O systems, respectively.
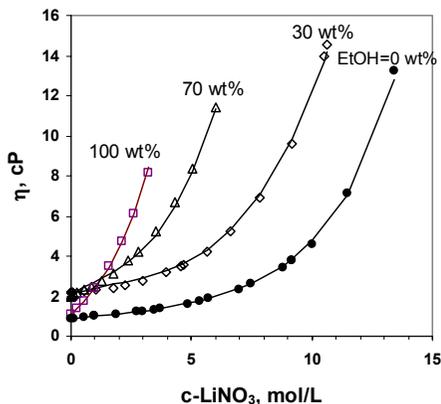
Figure 1. Viscosities of ternary $LiNO_3$-ethanol-H_2O solutions for various solvent compositions at 25 °C.
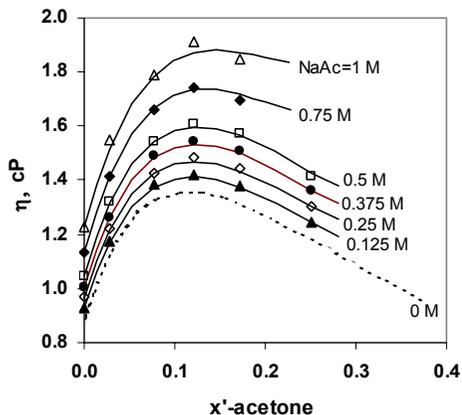

Figure 2. Viscosities of the ternary system sodium acetate + acetone + H_2O at 25ºC as a function of the mole fraction of the organic solvent (on a salt-free basis).
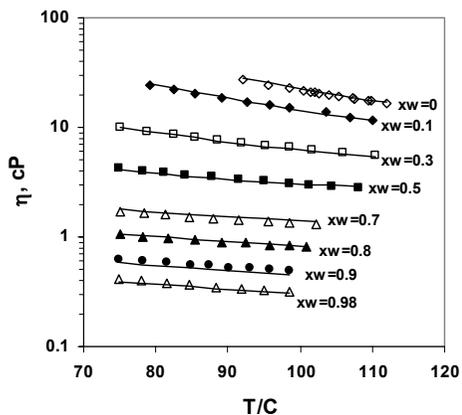

Figure 3. Viscosities of the system $AgNO_3$ - $TlNO_3$ - water at various mole fractions of water (x_w) and at the Ag/Tl molar ratio of 1.06.
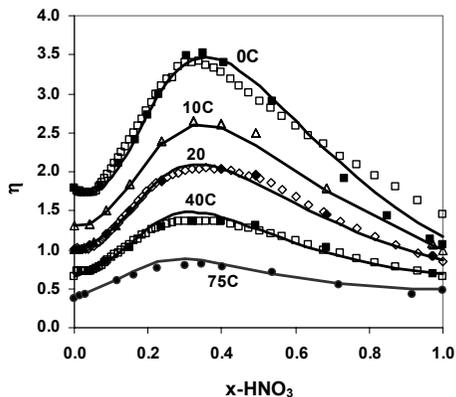

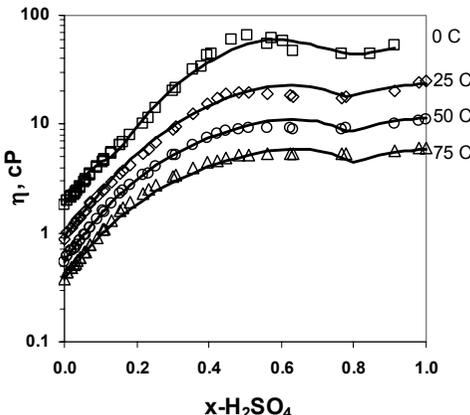Figure 4. Viscosities of HNO_3 - water solutions as a function of the mole fraction of HNO_3.

Figure 5. Viscosities of H_2SO_4 - water solutions as a function of the mole fraction of H_2SO_4.
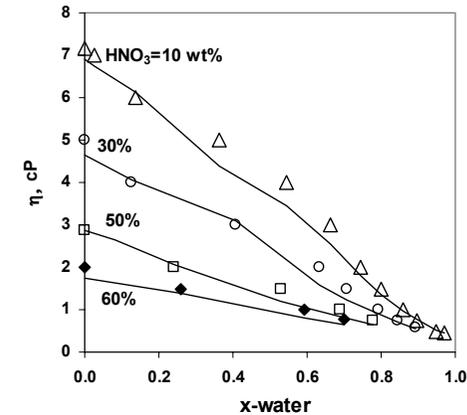

Figure 6. Viscosities of the ternary system HNO_3 - H_2SO_4 - H_2O at 75ºC as a function of water mole fraction at various fixed concentrations of HNO_3.

Results for the ternary mixture of H_2SO_4 + HNO_3 + H_2O at 75 °C are shown in Figure 6. Excellent agreement between experimental and calculated results has been obtained for all acids over wide ranges of temperature.

6. Conclusions

A comprehensive model has been developed for calculating the viscosity of aqueous and mixed-solvent electrolyte solutions. The model consists of two main parts, i.e., a mixing rule for computing the viscosity of solvent mixtures as a function of temperature and solvent composition, and an expression for the effect of finite electrolyte concentrations. To represent the dependence of viscosity on electrolyte concentration, the model includes a long-range electrostatic term obtained from the Onsager-Fuoss theory, a contribution of individual ions as quantified by the Jones-Dole *B* coefficients, and a contribution of specific interactions between ions or neutral species. New formulations have been developed for the latter two terms to account for the effects of multiple solvents. The viscosity model has been coupled with a thermodynamic equilibrium model to provide speciation, which is necessary for viscosity calculations in electrolyte systems. This makes it possible to reproduce the effects of complexation or other reactions in the solution. In all cases in which experimental data are available, the new model has been shown to be accurate for reproducing viscosities over wide ranges of composition with respect to both solvents and electrolytes.

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