PROPERTIES AND STRUCTURES OF ELECTROLYTE SOLUTIONS FOR LITHIUM BATTERIES

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Summary

Rules which have been employed to explain and predict solvent properties of lithium battery electrolytes are described and results reviewed. The equilibrium behavior of moderate to high concentration electrolyte solutions is also reviewed. Recent theoretical approaches to explain the behavior are discussed, and a new theory incorporating contact ion pair concepts into an advanced statistical theory for free ions is proposed.

Introduction

The role of the electrolyte solution in lithium batteries is central. As the medium to carry the internal current, the electrolyte solution must have adequate conductivity. It also must be stable, chemically and electrochemically, to all other materials in the battery. Because of these requirements, the solvents for use with lithium batteries are the dipolar aprotic class of organic and inorganic solvents. This paper will discuss the rules which the author has found to be useful in dealing with mixtures of solvents. The paper will also discuss the application of recent theoretical advances to the structure of electrolyte solutions within this class of solvents.

Solvent properties

It has been found after many years of experimentation that single solvents often do not have the required combination of physical properties to give satisfactory electrolyte solutions for lithium batteries. In consequence, an investigation of mixture rules has been undertaken in an attempt to bring some order into the search for mixed solvent systems and to help to understand why some mixtures are more successful than others.

Table 1 gives the mixture rules which have been found to be most successful in explaining the data for solvents of interest. The first rule for molar volumes simply gives the ideal solution relationship. This rule has been found to be accurate to about 1% in reproducing data in systems of

TABLE 1

Mixing rules for solvents

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1. Molar volume of mixture (V_m, cm^3/mole)

$V_m = x_1 V_1 + x_2 V_2 + \ldots$
      x_i = mole fraction component i
      v_i = molar volume component i

2. Average molecular weight of mixture (M_m, g/mole)

$M_m = x_1 M_1 + x_2 M_2 + \ldots$
      M_i = Molecular weight of component i

3. Density of mixture (ρ_m, g/cm^3)

$\rho_m = M_m / V_m$

4. Dielectric constant of mixture (ϵ_m)

$\epsilon_m = y_1 \epsilon_1 + y_2 \epsilon_2 + \ldots$
$y_i = x_i V_i / V_m$ = Volume fraction component i
ϵ_i = dielectric constant component i

5. Viscosity of mixture (η_m, Poise)

Log $\eta_m = x_1 \log \eta_1 + x_2 \log \eta_2 + \ldots$
η_i = viscosity component i

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interest. It does not necessarily imply that the solutions are, in fact, ideal. It is often the case that mixtures with small or negligible excess volumes and excess entropies still have significant excess enthalpies. The second and third rules from Table 1 are simply useful in obtaining the estimated density of the mixture in combination with rule 1.

Rule 4 of Table 1 for the dielectric constant is derived from the fact that the latter is a volume related property, so that additivity is shown for the volume fraction of each component in an ideal mixture [1]. The accuracy of this relation has been found to be within about 5% for solutions of interest for lithium batteries.

Rule 5 of Table 1 for viscosity is not a theoretically exact relationship for ideal solutions. It does, however, have some justification from the hole theory of liquids [2] and has been found to reproduce experimental viscosity data on solutions of interest within about 8%.

Results presented in ref. 3 show how well these rules apply to several liquid mixtures composed of dipolar aprotic solvent components. The molar volume and dielectric constants are well within the accuracy needed for semiquantitative judgments on the possible usefulness of a mixture. The accuracy of the viscosity rule is not as good, but as a general guide it is still quite useful. It is important to note that the logarithmic rule for viscosity compared with the volume fraction rule for dielectric constant causes the viscosity of a mixture to fall more rapidly than the dielectric constant starting with a viscous, high dielectric constant component and adding a

low dielectric constant, fluid component. It is this fact which allows more flexibility in the solvent choice when mixtures are used rather than single solvents.

One other property of importance is the donicity of the solvent in terms of the Lewis base theory. It appears from the author's work on ion pair association constants that the donicity of the solvent in a solvent mixture is governed by the stronger donor solvent as long as there is enough of this solvent present to fully coordinate with the Lewis acid present in the system, *e.g.*, lithium ions.

Electrolyte solution properties

Much progress has been made in recent years toward understanding the equilibrium properties of concentrated electrolyte solutions. First of all the Monte Carlo method has been applied to the primitive model electrolyte to calculate radial distribution functions and thermodynamic properties. This has allowed various statistical mechanical theories to be compared with "experimental" data on this hypothetical system without having to be concerned with complicated structural effects which may arise from real solvents and salts. In other words the Hamiltonian for the theory matches that for the "real" system. Theories such as the hypernetted chain (HNC), the Percus–Yevick theory or the mean spherical approximation (MSA), then, are approximate solutions to the Hamiltonian embodying varying assumptions. Of the above theories, the HNC theory has been found to give the best agreement with radial distribution functions from Monte Carlo calculations, although all the new theories give reasonable agreements with Monte Carlo results [4] for osmotic and activity coefficients. The MSA theory has the great advantage over other theories that the principle results can be described in closed form, and thus numerical data can be obtained without extensive calculations [4, 5]. Another feature of all of the above theories is that no specific account is taken of ion pairs. However, Friedman and Larsen [6] have shown that a running coordination number can be defined for the HNC theory which corresponds rather well to the concentration of ion pairs (as defined by the Bjerrum theory) at low salt concentration, thus bringing these diverse theoretical approaches into closer conceptual frameworks.

Ebeling and Grigo [7] have taken the fusion of these concepts a step further. They have used a modified Bjerrum theory to define the ion pair concentration in the solution and the MSA theory to define the activity coefficients of the free ions. This approach leads to some very interesting results. For moderate to low dielectric constant liquids the degree of dissociation of ion pairs was found to go through a minimum as a function of concentration. This result was described as a redissociation of ion pairs and is caused by the lowering of the activity coefficient of the free ions. The Bjerrum theory missed this effect because the Debye–Huckel theory was

used to calculate the activity coefficients. There are two problems with this theory. The first is a fundamental one because the portion of phase space allocated to free ions extends into that portion of phase space allocated to ion pairs and this must result in an overemphasis on the effects of the free ions. This could be avoided in an exact Bjerrum theory by taking the distance of close approach of the free ions to be the Bjerrum length. Another problem with the theory is that no specific solvent effects are taken into account and thus no distinction between contact and solvent separated ion pairs can be made.

An approach to remedy both of these shortcomings follows. The contact ion pairs can be defined as resulting from the displacement reaction of a solvent molecule in the solvation sheath of the cation by the approaching anion [8]. As shown previously, this approach can give contact ion pair concentrations in good agreement with spectroscopically measured values. Then the free ion distribution can be calculated by MSA theory using the solvent separated distance as a distance of closest approach for the MSA theory. The mass action law for the association constant for contact ion pairs, K_A, is

$$K_A = (1 - \alpha)/\alpha^2 c f^2 \tag{1}$$

where α is the degree of dissociation of the contact ion pairs, f is the mean activity coefficient for the free ions and c is the concentration of added salt. Equation (2) gives the expression for determining K_A from the solvent/salt properties

$$K_A = (4\pi N \beta^3/6000) \{[\exp(b')/b'] (1 + 1/b' + 2/b'^2) -$$
$$- [\exp(b)/b] (1 + 1/b + 2/b^2) - Ei(-b') -$$
$$- Ei(-b)\} \exp(k_G W/RT) \tag{2}$$

where:

$$b = z^2 e^2/a_0 \epsilon_0 \epsilon kT, \ b' = z^2 e^2/a_0' \epsilon_0 \epsilon kT, \ W = (DN_a - DN_s),$$

$$- Ei(-x) = \int_{-\infty}^{x} [\exp(u)/u] du, \text{ and } \beta = z^2 e^2/\epsilon_0 \epsilon \kappa T$$

and where ϵ_0 is the vacuum dielectric constant, ϵ is the dielectric constant, a_0 is the sum of anion and cation radii, d_s is the solvent diameter, DN_s and DN_a are the donor numbers of solvent and anion, and k_G and a_0' are empirically determined parameters for alkali salts [9]. Equation (3) gives the MSA result for the activity coefficient,

$$\ln f = -(z^2 e^2/4\pi\epsilon_0 \epsilon kTR^2 \kappa(\alpha)^{1/2}) [1 + \kappa R\alpha^{1/2} - (1 + 2\kappa R\alpha^{1/2})^{1/2}] \tag{3}$$

where κ is the reciprocal of the Debye length ($\kappa^2 = 2z^2 e^2 n/\epsilon_0 \epsilon kT$), n is the number density of anions or cations and $R = a_0 + d_s$ the distance of close approach of solvent separated anion and cation.
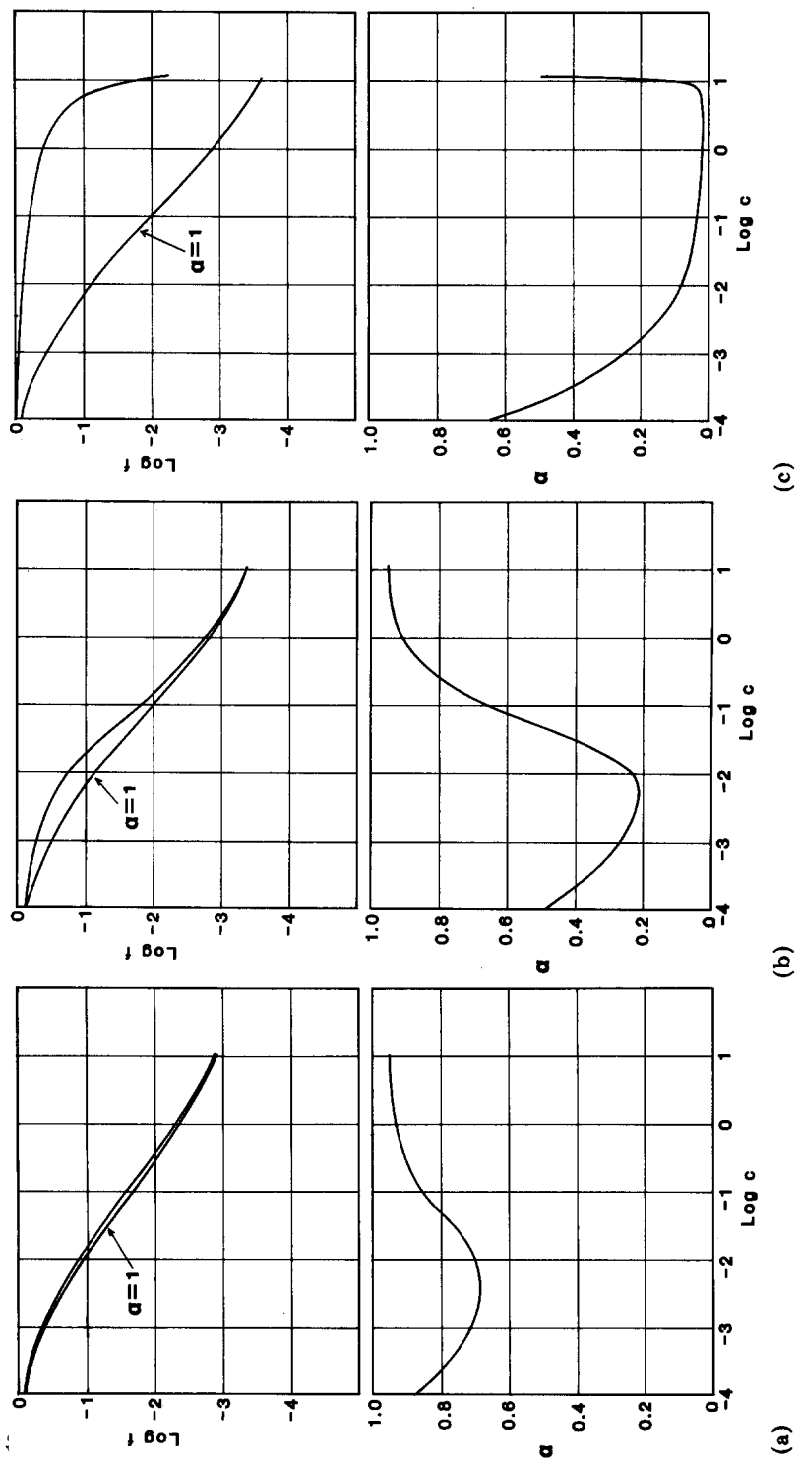
(a)

(b)

(c)

Fig. 1. Theoretical values for degree of dissociation of ion pairs (α) and logarithm of the activity coefficient of free ions $vs.$ the logarithm of concentration. (a) Lithium tetraphenylboron in tetrahydrofuran at 25 °C, calculated $K_A = 3.37 \times 10^3$ dm^3/mole, $R = 8.87 \times 10^{-10}$ m; (b) lithium tetraphenylboron in 2-methyltetrahydrofuran, calculated $K_A = 4.57 \times 10^4$ dm^3/mole, $R = 8.87 \times 10^{-10}$ m; (c) lithium perchlorate in tetrahydrofuran, calculated $K_A = 1.0 \times 10^7$ dm^3/mole, $R = 6.88 \times 10^{-10}$ m.

Figure 1 shows the theoretical behavior of the degree of dissociation and the activity coefficients for three specific cases chosen for a wide range of K_a. All three solutions show the minimum in the degree of dissociation discussed by Ebeling and Grigo [7]. Also, the rise of α following the minimum is very steep, as is implied by conductivity measurements on similar systems [10]. This qualitative behavior cannot be accounted for by conventional assumptions about triple ions. The steep drop in the activity coefficient relative to that for $\alpha = 1$ shows how the activity coefficient governs the dissociation behavior.

The author believes that the above work points to a picture of ion association and solution structure for dipolar aprotic solvents and alkali metal salts which is at least qualitatively consistent with spectroscopic and conductivity measurements. The picture is also rather simple and straightforward, invoking only physically measurable contact ion pairs and a good theory for the thermodynamic properties of free ions. Future work will concentrate on the application of these concepts to conductivity theories appropriate to the free ion concentrations calculated by the equilibrium theory. The ultimate goal is to develop a basis for setting directions in electrolyte research for lithium batteries and other electrochemical problems.

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