

# Computation of dielectric constants of solvent mixtures and electrolyte solutions

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## Abstract

A general model has been developed for calculating the static dielectric constant of mixed-solvent electrolyte solutions. For mixtures of solvents without electrolyte components, the model is based on an empirical modification of the Kirkwood theory for multicomponent systems. For systems containing electrolytes, the model takes into account the effects of ions and ion pairs and, therefore, it is capable of reproducing the dependence of the dielectric constant on electrolyte concentration. For most solvent mixtures, dielectric constants can be reasonably predicted using only pure solvent properties. In the case of strongly nonideal solvent mixtures, the results can be significantly improved by adjusting a single binary parameter. The model has also been verified for a number of electrolyte solutions in various solvents over wide composition and temperature ranges. In particular, the increase in the dielectric constant due to ion pairing and its decrease due to the presence of ions and their solvation can be accurately represented. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Dielectric constant; Mixed solvents; Electrolyte solutions; Ion pairing; Ion solvation

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## 1. Introduction

The static dielectric constant is of central importance in the thermodynamics of electrolyte solutions. Excess thermodynamic properties of electrolyte solutions arise from various intermolecular interactions, especially those involving charged particles. Quantitative description of the electrostatic properties of the medium in which the charges are immersed is necessary for modeling the charge interactions that contribute to excess properties. Accurate modeling of the dielectric constant and its derivatives with respect to density and composition is important for the representation of chemical and phase equilibria in electrolyte solutions. Correlations of the dielectric constant for the most commonly used solvent, water, have been extensively studied in [1–4]. Successful models for the dielectric constant of liquid mixtures have also been reported [5–8], but these studies are limited to nonelectrolyte mixtures. While the concentration

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dependence of the dielectric constant of ionic systems has been recognized from experimental evidence, few attempts have been made to take this effect into account when modeling electrolyte solutions. At the same time, a substantial body of experimental data has been accumulated in the literature, thus making it possible to study compositional effects for systems with or without ionic components. Experimental data for the dielectric constant of liquid mixtures and electrolyte solutions have been published since the early 1900s. Akhadov [9] has compiled data for binary mixtures published prior to 1980. More data have been reported since then [10–21].

This paper describes the development of a model for the representation of the dielectric constant for mixed solvents and electrolyte solutions as a function of temperature, pressure and concentrations of both nonionic and ionic components. The expressions obtained in this work are intended to be used in a comprehensive mixed-solvent electrolyte thermodynamic model, which accounts for not only phase equilibria, but also speciation effects.

The dielectric constant model is developed in two steps. In the first step, a formalism is established for predicting dielectric constants of solvent mixtures. In the second step, a correction for the presence of ions and ion pairs is introduced.

## 2. Dielectric constant of solvent mixtures

In this section, we first describe a simple method for predicting the dielectric constant of a fluid mixture using only pure-component data. Then, an extended form is developed that introduces a binary parameter and accounts for any deviations of the experimental dielectric constant from the regularities implied by the simple model.

Based on the Kirkwood theory [22] for a pure fluid, the dielectric constant,  $\epsilon$ , is related to intermolecular interactions by

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} = \frac{4\pi N_A}{3v} \left( \alpha + \frac{\mu^2 g}{3kT} \right) \quad (1)$$

where  $\alpha$  is the molecular polarizability,  $\mu$  the dipole moment of the molecule,  $N_A$  the Avogadro's constant,  $v$  the molar volume, and  $g$  is a correlation factor that characterizes the relative orientations between neighboring molecules. Eq. (1) can also be rewritten to explicitly relate the polarization per unit volume of the fluid,  $p$ , to the dielectric constant:

$$p = \frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} \quad (2)$$

For a fluid mixture, complications arise due to the change of orientation among various polar species upon mixing. A rigorous extension of Kirkwood theory to mixtures is not practical because of the complexities of orientational correlations. A commonly used approximation is to assume that the orientation  $g$ -factor for each component in the mixture remains unchanged when mixing at constant temperature and pressure. In this case, Oster's rule [6] applies and the polarization of a mixture of  $n$ -component can be expressed as

$$p_m = \frac{\sum_{i=1}^n x_i v_i p_i}{\sum_{i=1}^n x_i v_i} \quad (3)$$

where  $p_m$  is the polarization per unit volume of the mixture,  $x_i$  the mole fraction of component  $i$ , and  $v_i$  and  $p_i$  the molar volume and polarization of pure component  $i$ . The values of  $v_i$  and  $p_i$  are calculated at the temperature and pressure of interest. Eq. (3) also assumes a zero volume change upon mixing. Computation of the dielectric constant of a fluid mixture becomes then equivalent to the calculation of polarization,  $p_m$  and  $p_i$ .

Dielectric constant data have been reported as a function of temperature for a number of pure liquids [23,24,25]. The reported data at saturation pressure for each pure liquid have been found to conform to a simple equation, i.e.

$$\epsilon_i = e_i^{(0)} + \frac{e_i^{(1)}}{T} \tag{4}$$

where  $T$  is the temperature in Kelvin, and  $e_i^{(0)}$  and  $e_i^{(1)}$  the parameters determined from the experimental dielectric constants. The accuracy of this correlation is demonstrated in Fig. 1 for several pure organic and inorganic liquids. The average deviation from experimental data is 1.7% for 12 organic and six inorganic liquids, which have been tested.

There are cases when the dielectric constant for a pure liquid is available only at a single temperature ( $T^0$ ) and pressure ( $P^0$ ). Then, the variation of the dielectric constant with changing temperature and pressure needs to be predicted. For polar and associating liquids, Franck and Deul [26] and Harvey and Prausnitz [5] reported using water as a model for describing the temperature and pressure dependence of the dielectric constant. The dielectric constant of water is well known in wide ranges of temperature and pressure. Therefore, we use the following rescaled equation for water to calculate the polarization of an associating or polar liquid  $i$  at a temperature  $T$  and a pressure  $P$ :

$$p_i(T, P) = p_i(T^0, P^0) \frac{p_{H_2O}(T_r, P_r)}{p_{H_2O}(T_r^0, P_r^0)} \tag{5a}$$

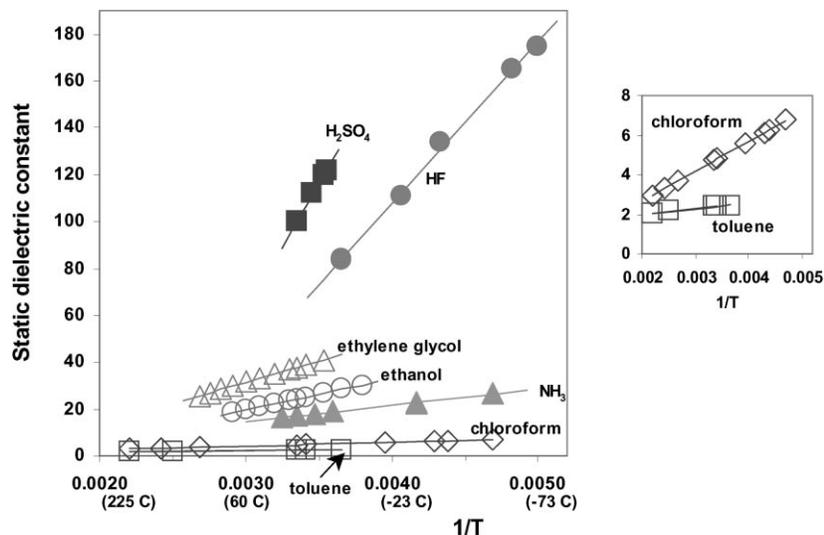


Fig. 1. Static dielectric constants for selected pure liquids. Details for the chloroform and toluene are shown in the insert. Data were taken from Weast and Lide [24], Buckley and Maryott [23], and Åkerlöf [25].

where  $p_i(T^0, P^0)$  is calculated from the known dielectric constant value based on Eq. (2). The rescaled temperatures  $T_r$ ,  $T_r^0$  and pressures  $P_r$ ,  $P_r^0$  are

$$T_r = \frac{T}{T_{C,i}/T_{C,H_2O}}; \quad T_r^0 = \frac{T^0}{T_{C,i}/T_{C,H_2O}} \quad (5b)$$

and

$$P_r = \frac{P}{P_{C,i}/P_{C,H_2O}}; \quad P_r^0 = \frac{P^0}{P_{C,i}/P_{C,H_2O}} \quad (5c)$$

where  $T_{C,i}$  and  $P_{C,i}$  are the critical temperature and pressure, respectively, of pure liquid  $i$ , and  $T_{C,H_2O}$  and  $P_{C,H_2O}$  are those for water. In case the rescaled pressure  $P_r$  (or  $P_r^0$ ) falls below the vapor pressure of water at the rescaled temperature  $T_r$  or  $T_r^0$  (which may happen depending on the  $T_C$ ,  $P_C$  characteristics of certain liquids), the water dielectric constant is calculated at the saturation pressure for water at the temperature of interest.

For nonpolar liquids, the dielectric constants are usually small and much less dependent on temperature compared to those for polar liquids (cf. Fig. 1). Based on Eqs. (1) and (2), the polarization of a non-polar liquid ( $\mu = 0$ ) is proportional to the reciprocal of its molar volume. Thus, the polarization at temperature  $T$  and pressure  $P$  can be estimated from

$$p_i(T, P) = \frac{v_i(T^0, P^0)}{v_i(T, P)} p_i(T^0, P^0) \quad (6)$$

where  $v_i(T^0, P^0)$  and  $v_i(T, P)$  are the molar volumes of the liquid at  $(T^0, P^0)$  and at  $(T, P)$ , respectively. For example, using the values of the liquid molar volume for  $\text{CCl}_4$  at 20 and 60°C and its dielectric constant at 20°C, the estimated dielectric constant at 60°C is 2.173, which is close to the experimental value of 2.167 [23]. Similarly, the dielectric constant for benzene at 129°C under saturated conditions is estimated to be 2.092 using the value of the dielectric constant at 20°C and molar volume values at these two temperatures. The experimental value is 2.073 [24]. A similar scheme for estimating dielectric constants at the temperature and pressure of interest using those at other conditions was used by Harvey and Prausnitz [5]. However, there is a difference in the selection of independent variables for rescaling the dielectric constant (cf. Eqs. (5a)–(5c)). In Harvey and Prausnitz's model [5], a density dependence is used in the rescaled equation (Eq. (10) in [5]), whereas pressure is selected as an independent variable in our model (Eqs. (5a)–(5c)). The dielectric constant is much more sensitive to changes in density than in pressure because a small change in density may correspond to a large change in pressure and temperature. For example, when the rescaled density ( $\rho_r$ ) is based on the critical volume of the liquid, the value of  $\rho_r$  may be very small due to a large critical volume of many organic liquids. Such small density values, when applied to water, might not correspond to the usual ranges of rescaled temperature for some applications. In such cases, pressure becomes a more convenient variable.

It has been found [5,27] that when a linear mixing rule, such as Eq. (3), is used to predict the dielectric constant in polar-nonpolar mixtures, large deviation may occur. This has been attributed to the possible existence of aggregates of associated polar molecules in the nonpolar component [27]. To account for the change of correlation between neighboring molecules due to mixing, a quadratic mixing rule is proposed to extend Eq. (3). This mixing rule has been selected on the basis of analyzing the accuracy of the

correlation using various possible mixing rules.

$$p_m = \frac{\sum_i^n \sum_j^n x_i x_j (vp)_{ij}}{\sum_{i=1}^n x_i v_i} \quad (7a)$$

where

$$(vp)_{ij} = \frac{1}{2}(v_i p_i + v_j p_j)(1 + k_{ij}) \quad (7b)$$

and  $k_{ij}$  is a parameter determined from the dielectric constant data for the binary system  $i$ – $j$ . When  $k_{ij} = 0$  for all components  $i$  and  $j$ , Eqs. (7a) and (7b) reduce to Eq. (3).

### 3. Effect of electrolyte on the dielectric constant

The dielectric behavior of electrolyte solutions is more complicated in comparison to that of solvent mixtures because of ion solvation and association. Depending on the solvent's properties and the extent of ion association or dissociation, the values of  $\epsilon_s$  for the electrolyte solution may increase or decrease with rising electrolyte concentration. For example, addition of alkali and alkaline-earth halides to water and methanol results in a decrease in the dielectric constant of the solution [10,14,18,20,28]. On the other hand, solutions of onium salts (e.g.  $\text{Bu}_4\text{NBr}$ ,  $\text{Bu}_4\text{NClO}_4$ , and  $i\text{-Pen}_4\text{NNO}_3$ ) in solvents of low and medium permittivity have dielectric constants that increase with the salt concentration [15–17,29–32]. The decrease in  $\epsilon_s$  with increasing ionic concentration is primarily due to ion-solvation effects [28]. Interactions between ions and solvent dipoles lead to dielectric saturation of solvent molecules in the electric field of the ions by inhibiting the free rotation of the solvent molecules [33,34]. For aqueous solutions, the formation of hydration shells around ions prevents the “bound” water molecules from being oriented in the external field. These water molecules are excluded from creating the effective dipole moment of the system, thus causing a decrease of polarization and the dielectric constant. In the initial concentration range, a sharp decrease in  $\epsilon_s$  is due to the availability of sufficient water molecules for the formation of hydration layers. A further increase in salt concentration leads to a water deficit and to a redistribution of water molecules in the hydration layers of the ions. This levels off the decrease, as is observed in experimental measurements [12,13]. In relatively low-dielectric-constant media, such as benzene ( $\epsilon = 2.3$ ) and acetone ( $\epsilon = 20.7$ ), ions may associate to form ion pairs. An increase in the static dielectric constant is anticipated in such solutions since the dipole moments of the ion pairs are much larger than those of the solvent molecules [30]. Assuming that the salt exists entirely as ion pairs, the increase in  $\epsilon_s$  with solute concentration can be expressed by Onsager's equation in which  $d\epsilon_s/dc$  is proportional to  $\mu^2$ , where  $\mu$  is the mean dipole moment of the solute species [35]. The increase in  $\epsilon_s$  has been observed to level off to an asymptotic value of  $\epsilon_s$  when the salt becomes more concentrated [15–17]. This leveling off has been explained as the result of the formation, in concentrated solutions, of quadrupoles and larger aggregates, which have negligible dipole moments and thus have little influence on the permittivity of the solution [15–17]. The asymptotic values of  $\epsilon_s$  are dependent on the solvent and the dissolved salt and are found to be a few units higher than the values for pure solvents. In the actual solutions, the salt is partially dissociated in media of intermediate dielectric constant, and the association constant is a function of the static dielectric constant of the solution [36]. A comprehensive treatment of the static dielectric properties in associating electrolyte solutions requires the knowledge of speciation equilibria. Such treatment is possible only when an appropriate speciation model is established. The development of a comprehensive

thermodynamic model for mixed-solvent electrolyte systems that accounts for the speciation effects in addition to the phase equilibrium will be discussed in a separate paper. Using the speciation approach, the dielectric constant model is generalized in this study to represent the effect of ions and ion pairs.

Theories are available in the literature for the representation of the dielectric behavior of electrolyte solutions. The most notable treatments are that of Debye–Falkenhagen [37] for dilute solutions and the kinetic polarization deficiency model derived by Hubbard and Onsager [38]. The Debye–Falkenhagen effect tends to increase the permittivity of the solution with respect to the pure solvent, but the effect can only be evaluated in sufficiently dilute solutions (e.g.  $\leq 0.02 \text{ mol l}^{-1}$ ). The kinetic polarization deficiency effect predicts a permittivity decrease that is proportional to the product of the dielectric relaxation time of the solvent and the low frequency conductivity of the solution. At the same time, empirical or semiempirical equations for representing the static dielectric constant,  $\epsilon_s$ , in ionic solutions such as aqueous solutions of alkali halides have been reported in the literature. In particular, Haggis et al. [34] and Hasted and Sabeh [39] presented  $\epsilon_s$  as a linear function of salt concentration at low ionic strength. Ball et al. [40], Simon et al. [41], and Fürst and Renon [42] reported equations for the dielectric constant in an extended ionic concentration range. However, no test results were presented in these papers to evaluate the quality of the dielectric constant models and to compare the experimental and calculated static dielectric constants in electrolyte solutions. In addition, ion pairing effects are clearly not accounted for in these models. For a realistic representation of the dielectric constant of electrolyte solutions, all of the ionic effects should be taken into account. Thus, a comprehensive model for the dielectric constant in an electrolyte solution should contain contributions from not only ions, but also ion pairs. These two effects are both considered in the equations developed in this work.

The equation proposed to represent the decrease in the dielectric constant in the presence of ions is

$$\epsilon_s = \frac{\epsilon_{s0}}{1 + \sum_{\text{ions}} A_i x_i \ln(1 + B_i \sqrt{I_X})} \quad (8a)$$

where  $\epsilon_{s0}$  denotes the dielectric constant that results from the presence of all neutral species, including solvents and ion pairs and  $I_X$  is the ionic strength on the mole-fraction basis:

$$I_X = \frac{1}{2} \sum_i x_i z_i^2 \quad (8b)$$

$A_i$  and  $B_i$  are temperature-dependent parameters,

$$A_i = a_{i1} + a_{i2}T \quad (8c)$$

$$B_i = b_{i1} + b_{i2}T \quad (8d)$$

$T$  is the temperature in Kelvin, and  $a_{i1}$ ,  $a_{i2}$ ,  $b_{i1}$ ,  $b_{i2}$  the parameters determined from experimental dielectric constant data for electrolyte solutions. Although the dielectric constant decrement can be predicted from the Hubbard–Onsager model [38], the required parameters, e.g. the dielectric relaxation time of the solvent, the low frequency conductivity of the solution and the limiting value of  $\epsilon_s$  at high electrical field frequency, are not always available. Eq. (8a) was found to represent  $\epsilon_s$  data accurately for most of the tested electrolyte solutions, with the parameters  $A_i$  and  $B_i$  evaluated by fitting Eq. (8a) to the experimental  $\epsilon_s$  results. It has been found by analyzing experimental data that constant values of the parameters  $b_{i1}$  and  $b_{i2}$  can be used for any of the ionic species in all of the aqueous solutions studied here. These values are  $b_{i1} = 1441674$  and  $b_{i2} = -1389 \text{ K}^{-1}$ .

The following equation for polarization is proposed to represent the effects of ion pairing on the dielectric constant:

$$p_{s0} = p_{s0}^* \left( 1 + \frac{\sum_{k=1}^{\text{ip}} q_k x_k^{s_k}}{1 + \sum_{k=1}^{\text{ip}} h_k x_k^{t_k}} \right) \quad (9)$$

where  $p_{s0}^*$  is calculated from the general equation for the polarization of mixtures of neutral molecules (Eqs. (7a) and (7b) or (3)) and the index  $k$  denotes all ion pairs. The parameters  $q_k$ ,  $s_k$ ,  $h_k$ , and  $t_k$  are determined from the experimental data for  $\epsilon_s$ . The value of polarization determined from Eq. (9) is then converted to  $\epsilon_{s0}$  using Eq. (2) and is used in Eqs. (8a)–(8d) to account for ion pairing effects. It should be noted that ion pairs are included in the leading term ( $p_{s0}^*$ ), i.e. the ion pair is treated as a molecule. This assures the applicability of the model in the limit of fused salts where the only possible neutral species are ion pairs. The values of the polarization,  $p$  (or the dielectric constant,  $\epsilon$ ) and the molar volume ( $v$ ) of the ion pair have been fixed in the equation in all cases. For the dielectric constant of the ion pair, a value is arbitrarily assumed equal to that of water, i.e. 78.38 at 25°C. The molar volume has been set equal to 30 cm<sup>3</sup> mol<sup>-1</sup>. These values are selected based on the relatively large dielectric constant of water compared to most organic solvents and on the published standard partial molar volumes for a number of neutral species in aqueous solutions [43]. In the case of systems without any ion pairs, the neutral-species contribution to the dielectric constant,  $\epsilon_{s0}$ , reduces to that of the solvent, as shown by Eqs. (2) and (3) or (7a) and (7b).

For a mixed-solvent electrolyte system, when the types of species and their concentrations are determined from a speciation model, Eqs. (8) and (9) can be used to calculate the value of  $\epsilon_s$  at the conditions of interest.

#### 4. Results and discussion

Using Eqs. (2)–(5c) and appropriate thermophysical property data for pure components (e.g.  $\epsilon_{\text{H}_2\text{O}}$ ,  $v_i$ ,  $T_c$  and  $P_c$  for water and organic solvents) [2,44], dielectric constants of selected binary and ternary mixtures have been predicted and compared with the published experimental results. Table 1 gives results for the prediction of the static dielectric constant for 15 binary and six ternary systems, along with binary parameters in Eqs. (7a) and (7b) and the average relative deviations ( $\Delta\epsilon\%$ ) from experimental data for Eqs. (3), (7a) and (7b). For the systems studied by Harvey and Prausnitz [5], the percent average absolute deviations given by these authors are also listed in Table 1. As expected, when Eq. (3) is used, the deviations are large for mixtures containing both polar and nonpolar components, such as water–dioxane, 1-propanol–benzene, 1-propanol–CCl<sub>4</sub>, 1-propanol–water–CCl<sub>4</sub> and 1-propanol–water–benzene. Introduction of a binary parameter in Eqs. (7a) and (7b) significantly improves the results for these systems. Figs. 2–5 show results (lines) obtained on the basis of Eq. (3) using only pure-component properties. Fig. 2 shows that experimental data for binary mixtures of water–acetone, methanol–acetone, and carbon disulfide–acetone at 25°C [25,45] can be very well reproduced. The variation of dielectric constants with temperature for binary mixtures is shown in Fig. 3 for the ethylene glycol–water system, together with experimental data [25]. Results of predictions for ternary mixtures are shown in Fig. 4 for the methanol–acetone–carbon disulfide system [45] and in Fig. 5 for the 2-propanol–water–nitromethane system [27]. No binary parameters were introduced for the above calculations. In all cases, good agreement is observed between the predicted and experimental results.

Table 1  
Results of calculating dielectric constants for binary and ternary solvent mixtures<sup>a</sup>

System	Number of points	$T$ (°C)	$k_{ij}$ in Eqs. (7a) and (7b)	$\Delta\varepsilon\%$ Eq. (3)	$\Delta\varepsilon\%$ Eqs. (7a) and (7b)	%AAD <sup>b</sup> [5]	Reference
Water–methanol	103	5–60	0.1393	3.4	1.4	0.6 <sup>c</sup>	[25,51]
Water–ethanol	55	20–80	0.0096	1.6	1.6	1.3 <sup>d</sup>	[25]
Water–1-propanol	55	20–80	–0.2444	6.1	1.7	3.9	[25]
Water–2-propanol	55	20–80	–0.2784	5.8	2.5	4.4	[25]
Water–acetone	55	20–50	0.1350	3.5	2.1	1.2	[25]
Water–ethylene glycol	50	20–100	0.1094	3.0	1.1	1.0 <sup>d</sup>	[25]
Water–dioxane	20	25	–0.7628	30.9	3.2	7.9 <sup>e</sup>	[15,27]
Benzene–1-propanol	10	35	–0.5614	17.9	4.0		[27]
CCl <sub>4</sub> –1-propanol	10	35	–0.5623	22.4	3.6		[27]
Methanol–CCl <sub>4</sub>	10	35	–0.3677	10.1	6.5	12.7 <sup>e</sup>	[27]
Methanol–CS <sub>2</sub>	8	25	–0.0305	3.7	3.6		[45]
Acetone–CS <sub>2</sub>	11	25	–0.1447	4.6	2.3	3.2 <sup>f</sup>	[45]
Acetone–methanol	11	25	–0.02267	0.7	0.4	0.4 <sup>f</sup>	[45]
1-Propanol–CH <sub>3</sub> NO <sub>2</sub>	10	35	–0.1720	5.2	0.3	0.3	[27]
2-Propanol–CH <sub>3</sub> NO <sub>2</sub>	12	35	–0.2475	7.2	1.4	2.1	[27]
Acetone–methanol–CS <sub>2</sub>	11	25	<sup>g</sup>	14.7	11.7	14.2	[45]
1-Propanol–benzene–water	8	35	<sup>h</sup>	28.7	4.2		[27]
Methanol–CCl <sub>4</sub> –water	8	35	<sup>i</sup>	7.9	4.5	5.0	[27]
1-Propanol–CCl <sub>4</sub> –water	8	35	<sup>i</sup>	31.1	9.0		[27]
1-Propanol–CH <sub>3</sub> NO <sub>2</sub> –water	10	35	<sup>j</sup>	6.2	1.4	1.1	[27]
2-Propanol–CH <sub>3</sub> NO <sub>2</sub> –water	10	35	<sup>j</sup>	3.4	1.3	0.8	[27]

<sup>a</sup> Pure liquid molar volume data were taken from [44].

<sup>b</sup> Percent average absolute deviation; results obtained using quadratic mixing rule (Eq. (13) in [5]).

<sup>c</sup> Temperature range is 5–55°C; data taken only from reference [51].

<sup>d</sup> Fewer data points were used; temperature range is 20–60°C for water–ethanol and 20–80°C for water–ethylene glycol.

<sup>e</sup> Different data sources were used; temperature range is 20–35°C for water–dioxane and 25–55°C for methanol–CCl<sub>4</sub>.

<sup>f</sup> Additional data source was used; temperature range is 20–25°C.

<sup>g</sup> Using parameters determined from binary mixtures.

<sup>h</sup> Binary parameter for benzene–water ( $k_{ij} = -0.9922$ ) was determined from Deul and Franck's data [46] at 300°C and at 20, 30, and 40 MPa.

<sup>i</sup> Binary parameter for CCl<sub>4</sub>–water ( $k_{ij} = -1.0$ ) was determined from data for ternary mixtures of methanol–CCl<sub>4</sub>–water and 1-propanol–CCl<sub>4</sub>–water.

<sup>j</sup> Binary parameter for CH<sub>3</sub>NO<sub>2</sub>–water ( $k_{ij} = 0.02926$ ) was determined from data for ternary mixtures of 1-propanol–CH<sub>3</sub>NO<sub>2</sub>–water and 2-propanol–CH<sub>3</sub>NO<sub>2</sub>–water.

On the other hand, Fig. 6 shows results for systems for which the use of a binary parameter is necessary to obtain a good agreement with experimental data. In this figure, results for 1-propanol–benzene (Fig. 6(a)) and 1-propanol–benzene–water (Fig. 6(b)) are shown by using solid lines for the results obtained with the use of binary parameters (Eqs. (7a) and (7b)). For comparison, the dashed lines show the predictions based on Eq. (3).

In many cases, mixtures exist in the liquid state even though one component is in the gaseous state at the ( $P$ ,  $T$ ) conditions of interest. For example, for the ethanol–water mixtures at 80°C [25], dielectric constant data for liquid ethanol do not exist. To test the applicability of Eqs. (5a)–(5c), the value of  $\varepsilon_{\text{ethanol}}$  at 80°C was estimated based on an  $\varepsilon_{\text{ethanol}}$  value at a lower temperature and the  $\varepsilon_w$  values for water at

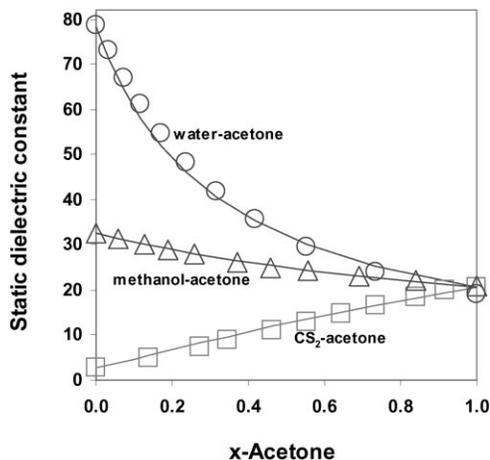


Fig. 2. Predicted and experimental static dielectric constants at 25°C for the water–acetone [25], methanol–acetone [45], and carbon disulphide–acetone [45] mixtures.

the rescaled temperatures and pressures. When the estimated  $\epsilon$  value is used in Eq. (3) with appropriate molar volumes for liquid ethanol and water, the dielectric constant for the ethanol–water mixture at this temperature is accurately reproduced, as shown in Fig. 7. Dielectric constant data for liquid mixtures at temperatures above  $\sim 100^\circ\text{C}$  are scarce. Deul and Franck [46] reported static dielectric constants for water–benzene mixtures at temperatures from 300 to 400°C and pressures to 280 MPa. These data are very valuable in the study of dielectric properties in polar/non-polar binary mixtures. However, these data were measured above the critical temperature and pressure for benzene and their treatment is beyond the scope of this study.

In the model of Harvey and Prausnitz [5], mixture density information has been incorporated into the mixing rule Eq. (7) in [5]), while our model requires only pure component data. Our results show

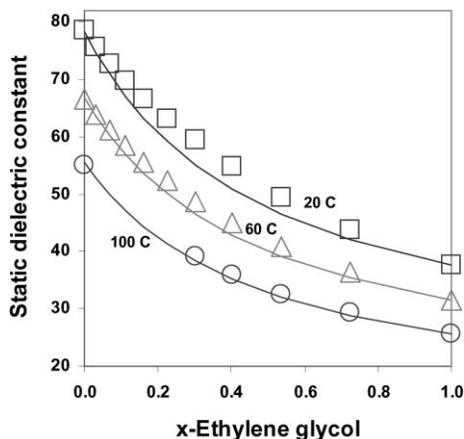


Fig. 3. Predicted and experimental static dielectric constants for the water–ethylene glycol mixture at various temperatures. The experimental data were taken from Akerlöf [25].

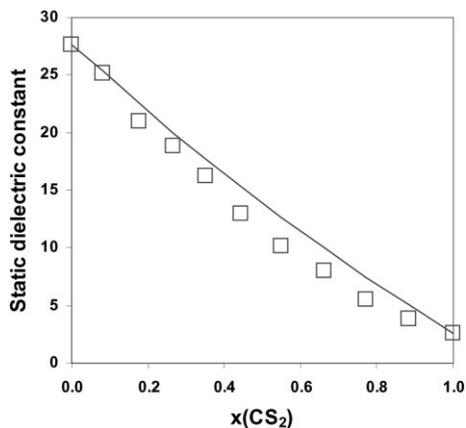


Fig. 4. Predicted and experimental static dielectric constant for the methanol–acetone–carbon disulfide mixture at 25°C. The molar ratio for methanol and acetone is  $\sim 2.7$  [45].

that a reasonable agreement with experiment can be obtained without introducing the binary parameters in many of the tested systems. Since mixture densities may not always be available, the simple model described by Eqs. (3)–(5c) should be easier to use. It is, however, necessary to use the binary parameter,  $k_{ij}$ , when association occurs and when the excess volume is large in a solvent mixture. It is also possible that the value of  $k_{ij}$  can be estimated based on excess volume data so that the dielectric constants for a mixture can be accurately predicted.

Dielectric constant data were reported in the literature for electrolyte solutions in both water [12–14,18,19,21,28,34,39,47–50] and other solvents [10,15–17,20,29–32,49]. Using Eqs. (7a)–(9), static dielectric constants for a number of electrolyte solutions can be very well reproduced by the proposed model.

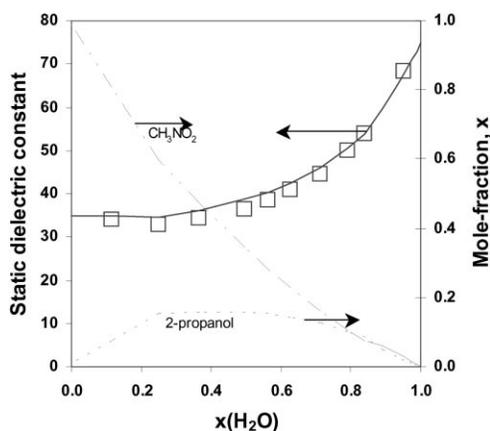


Fig. 5. Predicted and experimental static dielectric constant for 2-propanol–water–nitromethane at 35°C. The experimental data were taken from Suryanarayana and Somasundaram [27]. The liquid phase composition (mole fractions) is also shown in the figure.

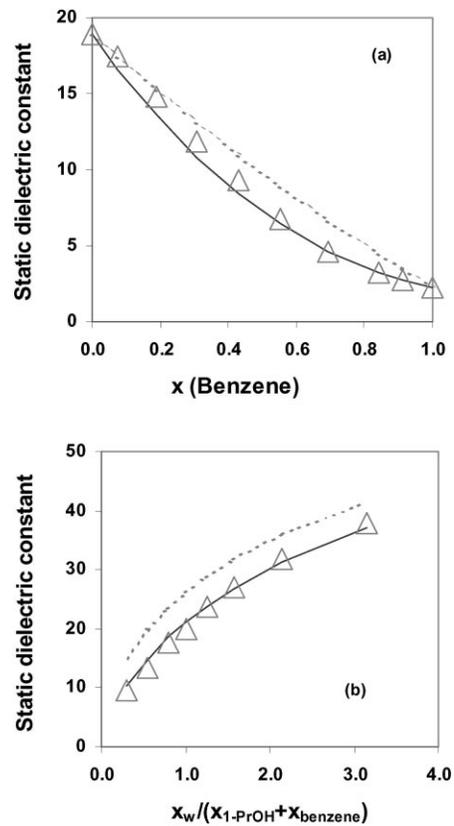


Fig. 6. Results for (a) 1-propanol–benzene and (b) 1-propanol–benzene–water mixtures at 35°C. Dashed lines were calculated using Eq. (3); solid lines were based on Eqs. (7a) and (7b) using binary parameters. The experimental data were taken from Suryanarayana and Somasundaram [27].

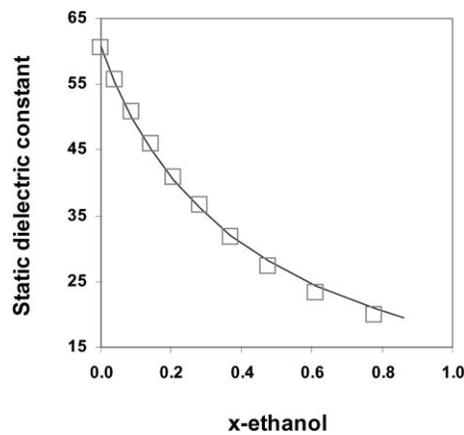


Fig. 7. Comparison of the predicted and experimental static dielectric constants for the ethanol–water mixture at 80°C. The experimental data were taken from Akerlöf [25].

Table 2  
Parameters in Eq. (8a)–(8d) for selected ions

Ion	$a_{i1}$	$a_{i2}$	Electrolytes used to obtain parameters	Temperature range (°C)	Reference
Na <sup>+</sup>	0.793	−0.0009031	NaCl, NaNO <sub>3</sub> , NaBr, NaI, NaF, NaOH, Na <sub>2</sub> SO <sub>4</sub>	0–50	[14,21,28,34,47–49]
Ba <sup>2+</sup>	1.20	−0.0009031	BaCl <sub>2</sub> , Ba(CHOO) <sub>2</sub>	3–40	[13,28,48,49]
Y <sup>3+</sup>	1.80	−0.0009031	Y(CHOO) <sub>3</sub> , Y(NO <sub>3</sub> ) <sub>3</sub>	15–35	[12,13]
Cl <sup>−</sup>	0.793	−0.0009031	NaCl, LiCl, KCl, RbCl, CsCl, CaCl <sub>2</sub> , MgCl <sub>2</sub> , BaCl <sub>2</sub> , LaCl <sub>3</sub> ,	0–50	[14,21,28,34,47–49]
NO <sub>3</sub> <sup>−</sup>	0.420	0.0	NaNO <sub>3</sub> , Cu(NO <sub>3</sub> ) <sub>2</sub> , Y(NO <sub>3</sub> ) <sub>3</sub>	25	[12,13,48]

Tables 2 and 3 give the parameters in Eqs. (7a)–(9) for selected ions and ion pairs. Fig. 8 shows results for phosphoric acid solutions at 25°C. While speciation treatment for the H<sub>3</sub>PO<sub>4</sub>–H<sub>2</sub>O system is necessary due to the multiple-step acid dissociation, the results shown in Fig. 8 were obtained assuming complete first dissociation of H<sub>3</sub>PO<sub>4</sub>. Here, we only intend to demonstrate that the proposed model is generalized to include contributions from all individual species if their concentrations can be accurately determined by incorporating a speciation model. The results for aqueous NaCl solutions are shown in Fig. 9 for various temperatures.

The effect of ions on the dielectric constant is illustrated in Fig. 10 for the chlorides of alkali metals, magnesium, and lanthanum and in Fig. 11 for the nitrates of sodium, copper, and yttrium. It is known that cations attract water molecules more strongly than anions, and that the cation contribution to the reduction of  $\epsilon_s$  is primarily dependent on the charge [28]. It is, thus, expected that cations in aqueous solutions have

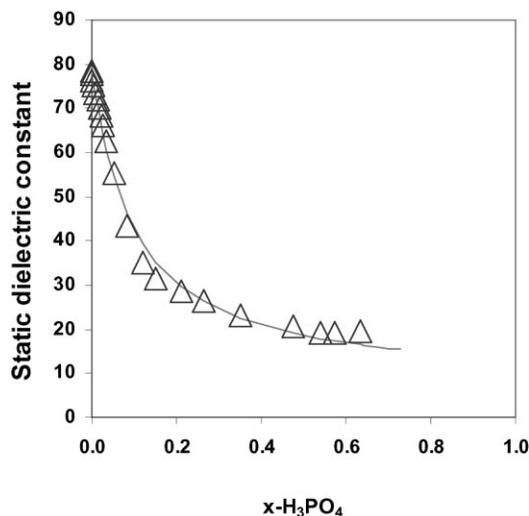


Fig. 8. Predicted and experimental static dielectric constants for phosphoric acid solutions at 25°C. The experimental data were taken from Christensen et al. [47].

Table 3  
Parameters in Eq. (9) for selected ion pairs<sup>a</sup>

Ion pair	$q_k^{(0)}$	$q_k^{(1)}$	$s_k$	$h_k^{(0)}$	$h_k^{(1)}$	$t_k$	Solvent	$T$ (°C)	Reference
Bu <sub>4</sub> NClO <sub>4</sub>	93.803	–	0.92879	896.38	–	1.6868	Propionic acid	25	[16]
Bu <sub>4</sub> NClO <sub>4</sub>	57.484	–	0.99066	966.15	–	1.5577	1,1-Dichloroethane	25	[16]
Bu <sub>4</sub> NBr	13696.9	–	2.3480	123319.0	–	2.3493	Acetone	25	[29]
Bu <sub>3</sub> NHPicrate	–344.045	1.3429	0.85	–17.3256	0.058563	0.20	Benzene	7–50	[32]

<sup>a</sup>  $q_k = q_k^{(0)} + q_k^{(1)}T$  and  $h_k = h_k^{(0)} + h_k^{(1)}T$ .

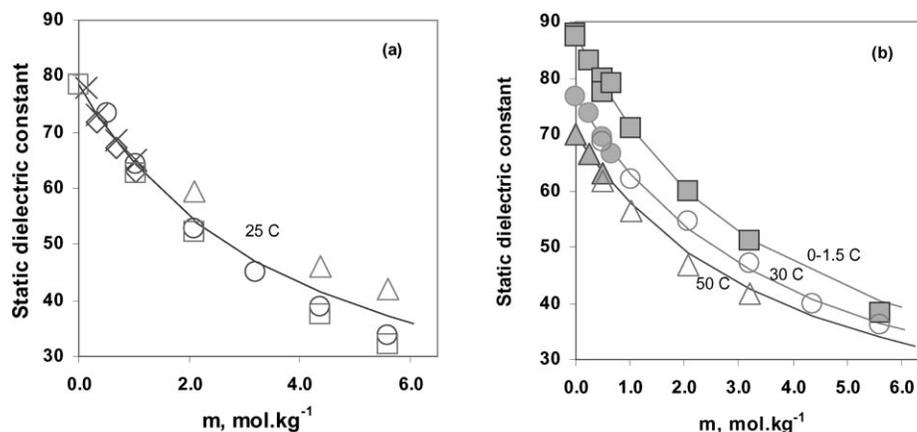


Fig. 9. Predicted and experimental static dielectric constants for aqueous NaCl solutions. (a) Results at 25°C: ( $\Delta$ ) Harris and O’Konski [48]; ( $\square$ ) Christensen et al. [47]; ( $\circ$ ) Zasetkii et al. [21]; ( $\diamond$ ) Haggis et al. [34]; ( $\times$ ) Hasted and Roderick [49]. (b) Results at 0°C ( $\square$ ); 30°C ( $\circ$ ); and 50°C ( $\Delta$ ). The solid symbols denote the data of Hasted and coworkers [28,39] and the hollow symbols were taken from Zasetkii et al. [21].

a much larger effect on the depression of the dielectric constant than anions. This behavior is very well reproduced by the model, which is in good agreement with experimental results, as shown in Figs. 10(a) and 11(a) for chlorides and nitrates. The concentration decrement of  $\epsilon_s$  becomes larger as the cation charge increases. The presence of larger quantities of the  $\text{Cl}^-$  and  $\text{NO}_3^-$  ions in the solutions of higher charged cations (i.e.  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Y}^{3+}$ , and  $\text{La}^{3+}$ ) may also contribute to “freezing” water molecules in the hydration layers of the ions, causing a greater decrease in  $\epsilon_s$  [12]. When the concentration is normalized to that of the anions, e.g.  $m_{\text{Cl}^-}$  and  $m_{\text{NO}_3^-}$ , the decrease in  $\epsilon_s$  approaches a nearly-identical relationship for all of the investigated cations, as shown in Figs. 10(b) and 11(b). The larger deviations for  $\text{MgCl}_2$  seen in Fig. 10 and the different shape of the variation of  $\epsilon_s$  versus molality may have been caused by the strong solvation of the  $\text{Mg}^{2+}$  ions. On the other hand, considering the large deviations in  $\epsilon_s$  between various data sources for other electrolytes (e.g. up to 26% for NaCl (Fig. 9(a)) and 23% for  $\text{BaCl}_2$  [28,48]), the difference in the calculated and experimental  $\epsilon_s$  for  $\text{MgCl}_2$  may be well within the experimental uncertainties. The effect of ion size on the static dielectric properties of aqueous alkali solutions has also been studied by several authors [18,28]. It is noted that cations with a smaller radius make a greater contribution to the depression of  $\epsilon_s$  than those with a larger radius. A weak correlation with the radius is observed in Fig. 10(a) for KCl, RbCl, and CsCl. However, this is somewhat obscured by experimental uncertainties, especially for KCl and RbCl.

The increase in the static dielectric constant in solutions containing ion pairs is also very well reproduced. Results for tetrabutylammonium perchlorate in several organic solvents are shown in Fig. 12. The alkyl ammonium salts are known to be strongly ion paired in solvents of low and medium permittivity [30] such as chloroform ( $\epsilon = 4.7$ ) and acetic acid ( $\epsilon = 6.2$ ). Fig. 13 shows results for tri(*n*-butyl)ammonium picrate in benzene at various temperatures. A linear function of temperature for the parameters  $q_k$  and  $h_k$  in Eq. (9) has been used to give the best fit to the experimental results.

$$f_k = f_k^{(0)} + f_k^{(1)}T \quad (f = q \text{ and } h) \quad (10)$$

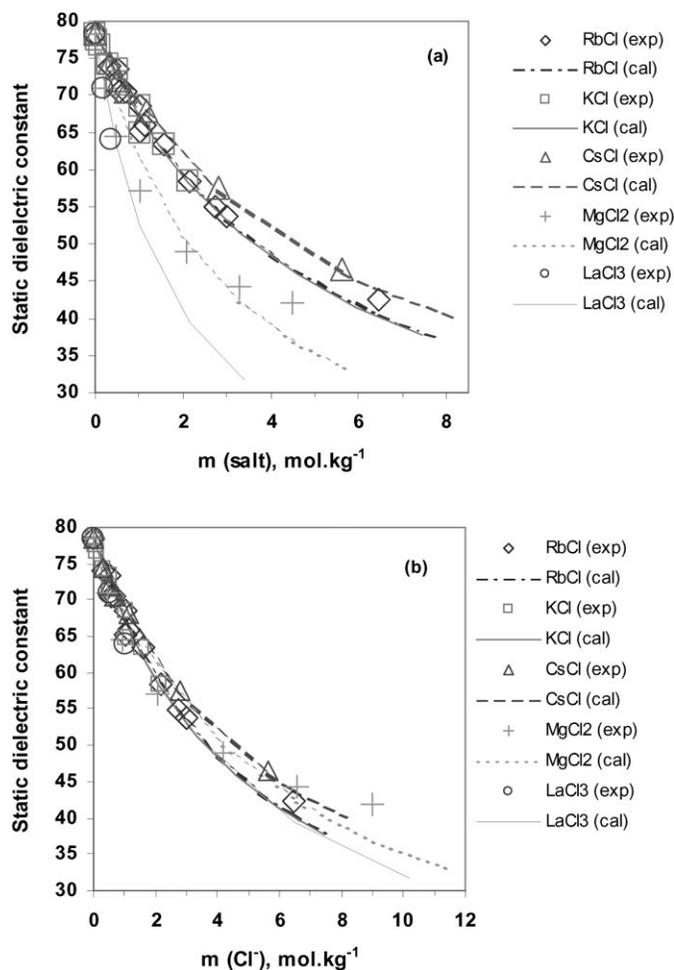


Fig. 10. The static dielectric constant at 25°C for aqueous chlorides of alkali metals, magnesium, and lanthanum as a function of the molality of (a) the salt, and (b) chloride ions. Experimental data were taken from Haggis et al. [34] (RbCl and KCl); Wei et al. [18] (RbCl and CsCl); Hasted et al. [28] (RbCl, KCl, MgCl<sub>2</sub>, and LaCl<sub>3</sub>); and Harris and O'Konski [48] (MgCl<sub>2</sub>).

It is found that parameters in Eq. (9) are strongly dependent on the solvent. For example, different parameters are obtained for tetrabutylammonium perchlorate in different solvents. This can be explained by different trends of  $\epsilon_s$  with changing salt concentration in various solvents as shown in Fig. 12. Since only few dielectric constant data sets were published for electrolyte solutions in mixed solvents, a more general equation can be established after extensive experimental data become available. Nevertheless, the parameters obtained in this study can be used as binary parameters representing interactions between ion pairs and the solvent and can be used for estimating  $\epsilon_s$  in mixed-solvent electrolyte solutions. For the data reported by Sigvartsen et al. [15] for tetra-*iso*-pentylammonium nitrate (*i*-Pen<sub>3</sub>NNO<sub>3</sub>) in dioxane–water mixtures, an equation of the form

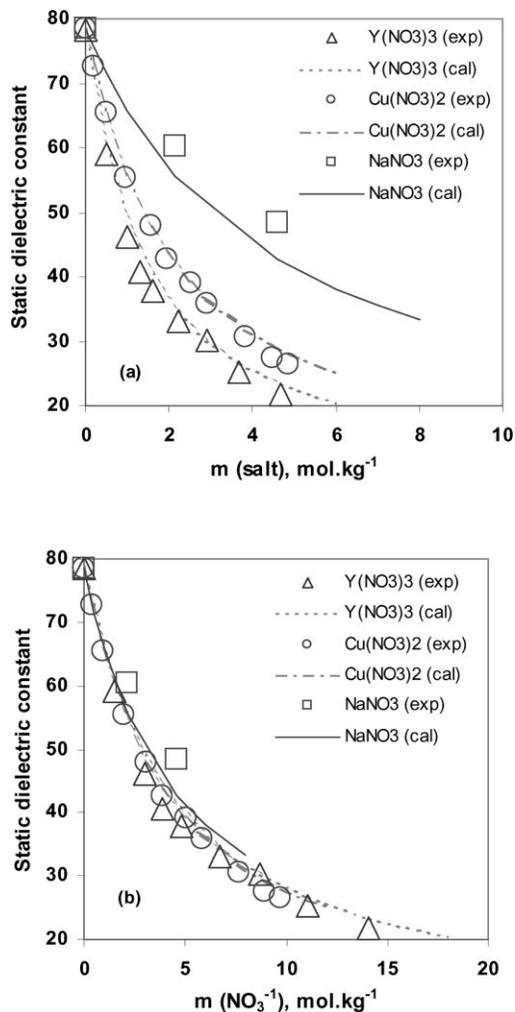


Fig. 11. The static dielectric constants at 25°C for aqueous solutions of sodium, copper, and yttrium nitrates as a function of the molality of (a) the salt, and (b) nitrate ions. Experimental data were taken from Harris and O’Konski [48] ( $\text{NaNO}_3$ ) and Lileev et al. [12] ( $\text{Y}(\text{NO}_3)_3$  and  $\text{Cu}(\text{NO}_3)_2$ ).

$$p_{s0} = \frac{\sum_i^n \sum_j^n x_i x_j (vp)_{ij}}{\sum_{i=1}^n x_i v_i} \left( 1 + \frac{(a_1 + a_2 x_w) x_{ip}^{a_3}}{1 + (a_4 + a_5 x_w) x_{ip}^{a_6}} \right) \quad (11)$$

is used to reproduce the dielectric constant results, as shown in Fig. 14. Eq. (11) is a somewhat generalized form of Eq. (9). In this equation,  $x_w$  is the mole fraction of water in the mixture and  $x_{ip}$  is the mole fraction of the ion pair. The parameters of Eq. (11) for  $i$ -Pen<sub>3</sub>NNO<sub>3</sub> in dioxane–water mixtures are  $a_1 = 117.821$ ,  $a_2 = -169.276$ ,  $a_3 = 0.7905$ ,  $a_4 = 1443.82$ ,  $a_5 = 2732.83$ , and  $a_6 = 1.6$ . The binary parameter for water–dioxane was taken from Table 1, and those for water–ion pair and dioxane–ion pair were set equal to zero in the calculations.

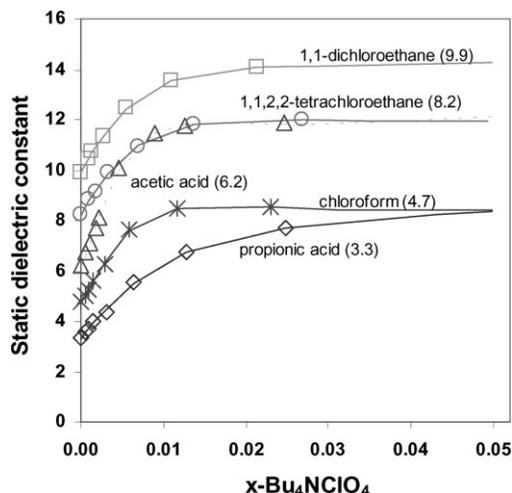


Fig. 12. The static dielectric constants at 25°C for solutions of tetrabutylammonium perchlorate in various solvents as a function of the salt concentration (as mole fraction). Experimental data were taken from Sigvartsen et al. [16]. The values in parenthesis are the dielectric constants of the pure solvent at 25°C.

It should be mentioned that the current model may be applied to systems that contain dissolved gases, as long as the solubility of the gases in the liquid phase can be determined and the pure liquid density of the dissolved component is valid at the temperature and pressure of interest. When the solubility of a gas in the liquid mixture is small (e.g.  $<10^{-3} \text{ mol l}^{-1}$ ), the effect of the dissolved gas on the dielectric constant of the mixture is expected to be negligible. When significant amounts of gases are dissolved and

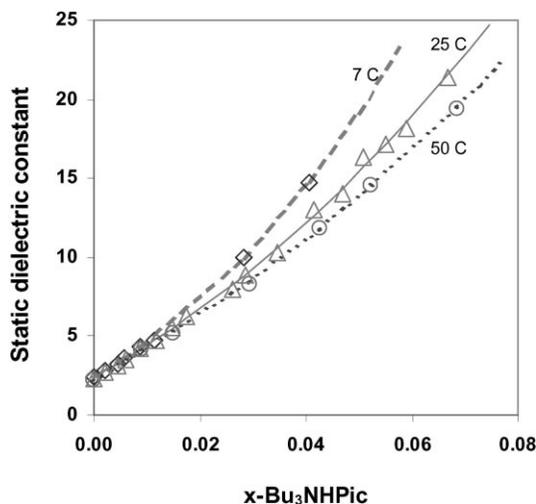


Fig. 13. The static dielectric constants for solutions of tri(*n*-butyl)ammonium picrate in benzene at various temperatures as a function of the salt concentration (as mole fractions). Experimental data were taken from Cavell and Sheikh [32].

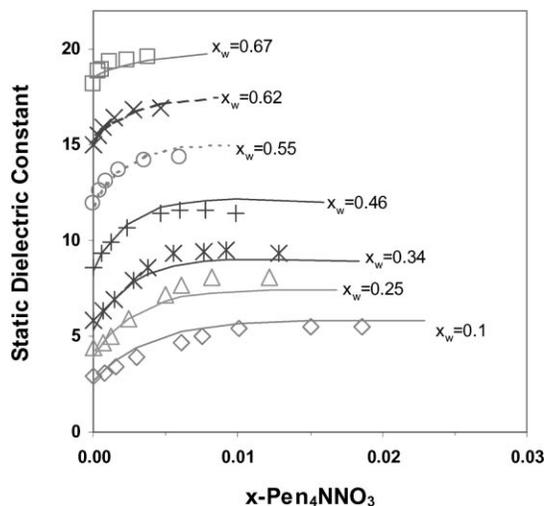


Fig. 14. The static dielectric constants for solutions of tetra-*iso*-pentylammonium nitrate in dioxane–water mixtures as a function of the mole fraction of nitrate. Experimental data were taken from Sigvartsen et al. [15].

there are chemical equilibria involving the dissolved gas in the liquid mixture, speciation effects in the liquid phase must be taken into account when the dielectric constant is calculated.

## 5. Conclusions

General equations have been developed for calculating the static dielectric constant of mixed-solvent electrolyte solutions. Dielectric constants of solvent mixtures can be reasonably predicted on the basis of only pure solvent properties. The agreement with experimental data can be further improved by adjusting a single, temperature-independent binary parameter. The effects of ions and ion pairs are taken into account using empirical functions obtained by analyzing an extensive set of experimental data. The increase in the dielectric constant due to ion pairing and its decrease due to ion dissociation and solvation can be accurately represented by the equations. These equations are of central importance for thermodynamic modeling of phase and chemical equilibria in mixed-solvent electrolyte systems.

### List of symbols

$a_{i1}, a_{i2}, b_{i1}, b_{i2}$	parameters in Eqs. (8a)–(8d) specific to ion $i$ , determined from experimental data
$A_i$ and $B_i$	parameters specific to ion $i$ , used in Eq. (8a)
$e_i^{(0)}$ and $e_i^{(1)}$	parameter in Eq. (4) for pure liquid $i$ , determined from experimental data
$I_X$	mole fraction-based ionic strength
$N_A$	Avogadro's constant
$p_i$	polarization of component $i$
$p_m$	polarization of the liquid mixture
$P$	pressure
$P_{C,i}$	critical pressure of pure liquid $i$

$q_k, s_k, h_k, t_k$	parameters in Eq. (9), specific to the ion pair $k$ , determined from experimental data
$T$	temperature
$T_{C,i}$	critical temperature of pure liquid $i$
$v_i$	molar volume of pure liquid $i$
$x_i$	mole fraction of species $i$

*Greek letters*

$\alpha$	molecular polarizability
$\epsilon_s$	static dielectric constant of the electrolyte solution
$\epsilon_{s0}$	static dielectric constant of the solvent mixture
$\mu$	dipole moment of the molecule

*Subscripts*

s	solution
s0	solvent
w	water
$i$	species index
$k$	ion pair index

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