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An empirical equation for the dielectric constant in aqueous and nonaqueous electrolyte mixtures

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ABSTRACT

This work develops an empirical model to evaluate the dielectric constant of single or multi-solvents containing multiple ions, using only one adjustable parameter per ion. Correlations are performed for 35 salts in water, 9 in methanol, and 3 in ethanol. The dielectric constant of 9 two-solvent solutions (containing water, methanol, ethanol, 1-propanol, 2-propanol, or acetone) is predicted. In addition, predictions of the dielectric constant of a mixture containing water, methanol, and NaCl are presented. Besides the specific parameter for each ion, a general parameter for cations and another for anions, specific to the each solvent, are obtained. They are recommended for calculating the dielectric constant in solutions whose experimental data are unavailable in the literature.

1. Introduction

The dielectric constant is a property that plays an important role in many equations of state applied to electrolyte solutions. This property can be interpreted as a measure of the solvent's capability in shielding charged particles, as ions, present in solution. This feature is directly associated to the solvation phenomenon, which takes place in a solution because of the presence of cations and anions. The polar solvent molecules organize themselves around the ions, in structures called solvation shells, in order to reduce the number of free charged particles. The strong electrolyte field disturbs the arrangement of the solvent molecules, decreasing the dielectric constant of the solvent [1].

Usually, the dielectric constant is found in expressions based on the McMillan-Mayer approach, which considers the solvent as a continuum. Some examples are the Debye–Hückel [2], MSA (mean spherical approximation), and Born expressions [3]. The literature contains many theoretical and empirical equations for calculating the dielectric constant of pure or mixed solvents, in the presence or absence of electrolytes. However, according to Maribo-Mogensen et al. [4], there is no consensus on what expressions to use when modeling these systems.

The literature presents an extensive amount of dielectric constant data related to pure and mixed solvents. However, dielectric constant data of the solvent in aqueous and nonaqueous electrolyte solutions are rather scarce. Hasted et al. [5] published one of the first papers that present experimental data of dielectric constant of water in electrolyte solutions. The investigated systems include the following salts: LiCl, RbCl, KCl, $BaCl_2$, KI, NaF, $LaCl_3$, KF, NaI, $MgCl_2$, and Na_2SO_4. The authors observed that the dielectric constant decreases linearly for very dilute solutions, at concentrations generally lower than 1.5 M. Above this limit, the dielectric constant deviates considerably from linearity, leaning towards a constant value at high concentration. Later, experimental work showed similar behavior for more salts in aqueous solutions, such as those reported by Haggis et al. [6], Hasted and Elsabeh [7], Harris and Okonski [8], Giese et al. [9], Wei and Sridhar [10], Nortemann et al. [11], Chen et al. [12], and Loginova et al. [13]. Experimental data for nonaqueous solvents with low dielectric constant, such as methanol and ethanol in the presence of salts, are also reported in the literature by Winsor and Cole [14], Winsor and Cole [15], and Hasted and Roderick [16]. Barthel et al. [17] and Akhadov [18] also compiled excellent data sources of both electrolyte and nonelectrolyte systems.

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Based on these experimental results, many empirical and semi-empirical equations have been developed in order to model experimental dielectric constant data. Giese et al. [9] proposed an equation currently known as Pottel's model. This equation computes the dielectric constant of the solvent in an electrolyte solution considering the amount of salt present in it. Its advantage is the absence of adjustable parameters making it applicable to any system. Such feature has made the Pottel model popular and many equations of state applied to electrolytes incorporate it. Some examples are the models developed by Ball et al. [19], Fürst and Renon [20], Inchekel et al. [21], Zuber et al. [22,23], and Rozmus et al. [24].

Another model applied to electrolyte solutions was developed by Simonin et al. [25] whose equation computes the dielectric constant of the solvent in electrolyte solutions using one adjustable parameter specific for the salt present in solution. Simonin et al. [25] applied this equation to the MSA model in order to calculate thermodynamic properties of 18 aqueous salt solutions. Many other research groups incorporated Simonin's model into their equations of state, such as Mortazavi-Manesh et al. [26], Inchekel et al. [21], Torres-Arenas et al. [27], and Memarnejad and Dehghani [28].

Wang and Anderko [29] developed an equation to compute the dielectric constant in mixed-solvent electrolyte solutions. In their work, the dielectric constant of solvent mixtures – in absence of electrolytes – is obtained using a modification of the empirical Kirkwood equation. It requires as inputs the polarizability and the dipole moment of the solvent molecule. Additionally, the model takes into account the presence of charged species and depends on temperature, mole fraction of electrolytes, and two adjustable parameters per ion in solution. The model was applied to electrolyte systems in various solvents over wide ranges of temperature and composition [29], but the number of water and alcohol electrolyte solutions considered in their work is limited.

Maribo-Mogensen et al. [4] developed an equation based on the Onsager, Kirkwood, and Fröhlich framework to calculate the dielectric constant of mixed solvents in electrolyte solutions. However, the work addresses only aqueous electrolyte solutions – 13 single salt solutions at 298.15 K. The authors also compare how their dielectric constant equation and empirical models perform when coupled to the Debye–Hückel equation.

As mentioned, many empirical equations in the literature compute the variation of solvent's dielectric constant due to the presence of electrolytes; however, some authors prefer to neglect this effect in their models and only consider the dielectric constant of the pure solvent. Some equations of state that adopt this approximation were developed by Myers et al. [3] and Held et al. [30]. Such simplification may affect considerably the value of thermodynamic properties of electrolyte solutions at high concentration, as shown by Maribo-Mogensen et al. [4].

Many applications, as in pharmaceutical and fertilizer industries, deal with aqueous and nonaqueous electrolyte solutions, usually formed by alcohols such as methanol and ethanol. Therefore, there is a need for models to evaluate the dielectric constant of mixed solvents in the presence of multiple ions. This work proposes an original empirical model for the dielectric constant applicable, in principle, to mixed solvent solutions with multiple ions. However, it was not possible to find experimental dielectric constant data for water + alcohol solvents with electrolytes, which are the focus of this work. Thus, it has been possible to apply it to obtain the dielectric constant as a: (a) correlation for single solvents (water, methanol, or ethanol) in single salt solutions, using a data base larger than those of related publications; (b) prediction for binary solvents in the absence of electrolytes; (c) prediction for water + methanol in the presence of NaCl. As consequence of the scarcity of experimental data, apart from Wang and Anderko [29], most of the publications reviewed here apply their equations to aqueous electrolyte solutions only.

2. Model development

Zuber et al. [23] have investigated the correlation and prediction of many thermodynamic properties of aqueous single and multiple salt solutions, using the Q-electrolattice equation of state (EOS). In that work, the dielectric constant in electrolyte solutions is computed using the Pottel model as follows:

$$D = 1 + (D_S - 1)\left[\frac{1-\xi_3''}{1+(\xi_3''/2)}\right] \tag{1}$$

in which D is the dielectric constant of the solvent in the presence of electrolytes, D_S is the pure solvent dielectric constant, and ξ_3'' is a variable defined as:

$$\xi_3'' = \frac{N_a \pi}{6}\sum_{i}^{\text{ions}} \frac{n_i(\sigma_i)^3}{V} \tag{2}$$

in which N_a is the Avogadro number, n_i is the number of moles of a ion i, σ_i is the diameter of ion i, and V is the solution volume.

As many other EOS applied to electrolyte solutions, the Q-electrolattice EOS exhibits increasing deviations for some thermodynamic properties at high salt concentrations. This trend may be a consequece of parameter fitting strategy, model oversimplifications or incapability of drescribing properties at such conditions, among many others. However, Maribo-Mogensen et al. [4] observed a major impact of the dielectric constant value on EOS predictions for electrolyte systems.

Liszi et al. [31] points out that the Pottel model poorly represents experimental dielectric constant data. Despite being unable to describe the behavior of the dielectric constant over wide ranges of concentration, such model has been used in many publications, as mentioned previously. Wang and Anderko [29] emphasize that many equations, developed to calculate the dielectric constant in electrolyte solutions, have not been tested against experimental data. In fact, some calculations using the Pottel model have shown that the dielectric constant deviates considerably from the experimental data. Fig. 1 presents evidence of this deviation for CsCl or NaCl in aqueous solution at 298.15 K. In these calculations, the solution volume that appears in Eq. (2) was determined using the Q-electrolattice EOS. At 4.5 mol/kg of CsCl, the deviation between the molar volume calculated with the Q-electrolattice EOS and the experimental value is approximately equal to 2%, whereas the deviation of the dielectric constant is 60%. At 1.0 mol/kg of NaCl, the corresponding deviations are 0.3% and 23%. This performance of the Pottel model confirms the observations of Liszi et al. [31].

Better agreement between Pottel's model and experimental data was observed by Inchekel et al. [21] when using their EOS, which includes fitted values of ionic diameters. However, these authors recommend using Simonin's model to compute the dielectric constant in electrolyte solutions for better EOS performance. This model is as follows:

$$D = \frac{D_S}{1 + \alpha C} \tag{3}$$

in which D_S is equal to 78.38, which is the dielectric constant of water at 298.15 K, α is an adjustable parameter specific for a given salt, and C is its molar concentration.

In fact, due to the presence of the adjustable parameter, Simonin's model may be more accurate than Pottel's. However, there seems to be no published work that compares experimental dielectric constant data directly to the results of Simonin's model. Its development focuses only on aqueous electrolyte solutions, considering the α parameter in Eq. (3) specific for the salt present in

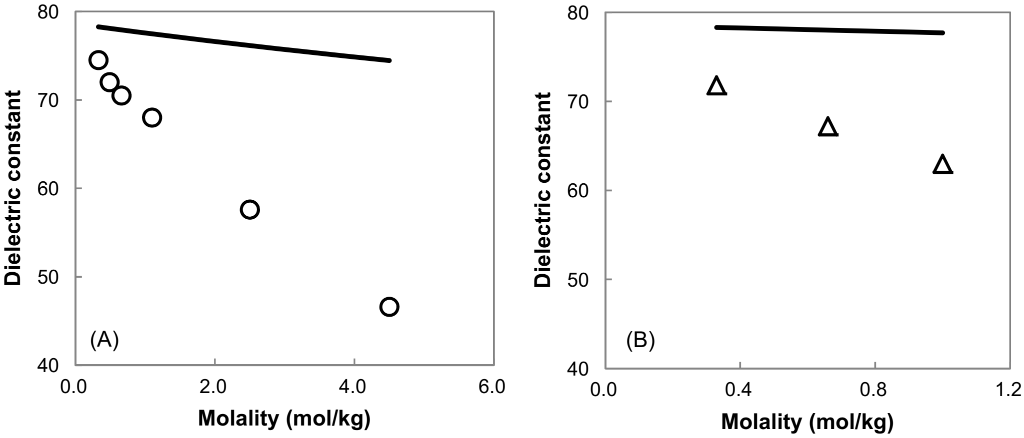

Fig. 1. Dielectric constant of water in (A) CsCl or (B) NaCl solutions computed using the Pottel model (—) at 298.15 K. Experimental data (○) from Wei et al. [44] and (△) Haggis et al. [6].

solution. Nonetheless, the general current trend in modeling electrolyte solutions is to adopt ion-based parameters, as opposed to salt-based ones.

The model developed by Wang and Anderko [29] is restricted to a few ions but there is little information about how to extend it to other ionic systems. Maribo-Mogensen et al. [4] carry out an elaborated investigation of 13 aqueous electrolyte systems. However, their equation is more appropriate for use with association models such as the statistical association fluid theory (SAFT). Moreover, results for pure solvents other than water and for mixed solvents are not presented.

The equation proposed here is a modification of Simonin's expression, applicable to calculate the dielectric constant of pure or mixed solvents in the presence or absence of electrolytes. Its evaluation involves a series of steps, which are outlined in this section.

The first step is to compute the dielectric constant of pure solvents using the following empirical equation proposed by Zuo and Fürst [32]:

$$D_S = d_1 + \frac{d_2}{T} + d_3T + d_4T^2 + d_5T^3 \quad (4)$$

in which d_1–d_5 are adjustable parameters.

In the second step, the dielectric constant of mixed solvents (D_{mix}) is computed by weighing the pure solvent dielectric constants with their volume fractions, following the suggestion of Michelsen and Mollerup [33], i.e.:

$$D_{\text{mix}} = \sum_{\text{s}} D_{\text{s}}\phi_{\text{s}} \quad (5)$$

in which the volume fraction ϕ_{s} of solvent s is:

$$\phi_{\text{s}} = \frac{x_{\text{s}}v_{\text{s}}}{\sum_j^{\text{solvent}} x_j v_j} \quad (6)$$

where x_{s} and v_{s} are the mole fraction and the molar volume of solvent s, respectively. In this equation, v_{s} is calculated for each solvent using the Rackett expression for the molar volume of saturated liquids, as presented by Poling et al. [34]:

$$v_{\text{s}} = v_{\text{c}}(0.29056 - 0.08775\omega)^{(1-T/T_{\text{c}})^{2/7}} \quad (7)$$

in which v_{c} is the critical volume, ω is the acentric factor, T is the temperature, and T_{c} is the critical temperature of the solvent. The calculations of dielectric constant for mixed solvents, in this work, are performed at 101.32 kPa and temperatures from 288 to 353 K. At such conditions, the solutions are liquid, and the difference between the system pressure and the saturation pressure of each solvent has negligible effect on the molar volumes. Thus, the Rackett expression (Eq. (7)) is suitable for these calculations.

The third and final step is to evaluate the joint effect of multiple solvents and electrolytes on the dielectric constant:

$$D = \frac{D_{\text{mix}}}{1 + \sum_i^{\text{ion}} \left[x_i \sum_j^{\text{solvent}} \alpha_{i,j}\phi_j\right]} \quad (8)$$

in which $\alpha_{i,j}$ is the adjustable parameter of ion i in solvent j, and ϕ_j is calculated on an ion-free basis. Eq. (8) is original and is the general expression of the model proposed here.

In the particular case of single-solvent solutions, Eq. (8) simplifies to:

$$D = \frac{D_{\text{s}}}{1 + \sum_i^{\text{ion}} \alpha_i x_i} \quad (9)$$

Eq. (9) is useful to correlate experimental dielectric constant data available in the literature for such systems.

In comparison with the Simonin model (Eq. (3)), the new equation depends on temperature because D_{s} is calculated with Zuo and Fürst [32] equation and the adjustable parameter is specific to each ion, meaning that it is applicable to any electrolyte solution that contains it.

Another difference is the use of ion mole fractions. It is conventional to use them as variables in equations of state, even in those for electrolyte systems. Since the dielectric constant model has been developed with the long-term goal of incorporating it into an equation of state, mole fractions are adopted.

3. Parameter fitting

Proposed by Zuo and Fürst [32] to calculate the dielectric constant of pure solvents, Eq. (4) has five adjustable parameters (d_1–d_5), which have been used as published, for water, ethanol, 1-propanol, and 2-propanol. On the other hand, those authors [32] fitted methanol parameters with a different equation. In order to use Eq. (4) for all pure solvents, new parameters for methanol were obtained, using experimental data from Davidson [35] and Shirke et al. [36] at temperatures from 176.60 to 323.15 K, and, for acetone, using Akerlof [37] at temperatures from 293.15 to 323.15 K. Table 1 presents the new methanol and acetone parameters.

In order to calculate the molar volume of saturated liquid solvents, the parameters of Rackett equation (Eq. (7)) for water, methanol, ethanol, 1-propanol, 2-propanol, and acetone were obtained from Poling et al. [34].

Table 1
Fitted methanol and acetone parameters of Eq. (4).

Solvent	d_1	d_2	d_3	d_4	d_5	T (K)
Methanol	1.0462×10^2	1.0000×10^3	9.0184×10^{-2}	-2.5998×10^{-3}	4.8503×10^{-6}	176.60–323.15
Acetone	1.0922×10^1	5.2827×10^3	1.2961×10^{-1}	-1.0541×10^{-3}	1.7175×10^{-6}	293.15–323.15

Table 2
Fitted ion parameters for electrolytes in water.

Ion	α_i	Ion	α_i	Ion	α_i	Ion	α_i
H^+	9.55	Mg^{2+}	6.69	F^-	5.88	$NO_3{}^-$	6.75
Li^+	6.59	Ca^{2+}	−0.53	Cl^-	6.80	$ClO_4{}^-$	8.48
Na^+	3.62	Ba^{2+}	0.75	Br^-	7.31	$SO_4{}^{2-}$	−0.66
K^+	2.43	Al^{3+}	2.87	I^-	7.65	OH^-	13.96
Rb^+	2.08						
Cs^+	2.23						

Table 3
Fitted ion parameters for electrolytes in methanol.

Ion	α_i	Ion	α_i	Ion	α_i
Li^+	13.48	Cl^-	13.29	$NO_3{}^-$	4.56
Na^+	17.78	Br^-	14.58	$ClO_4{}^-$	4.08
K^+	8.02	I^-	19.66		

Table 4
Fitted ion parameters for electrolytes in ethanol.

Ion	α_i	Ion	α_i
Li^+	2.06	Cl^-	2.28
Na^+	20.03	I^-	31.20

Equation (9) is used to correlate the experimental dielectric constant in single salt solutions in water, methanol, or ethanol. All data for single salt solutions in a given solvent were used simultaneously to fit the α parameters of the ions present in these solutions. The parameter fitting minimizes an objective function (OF) defined as follows:

$$OF = \sum_{k=1}^{N_p} \left(\frac{D_k^{calc} - D_k^{exp}}{D_k^{calc}} \right)^2 \quad (10)$$

in which N_p is the number of data points, and D_k^{calc} and D_k^{exp} denote the calculated and experimental dielectric constant values, respectively. This objective function was minimized using the generalized reduced gradient algorithm as implemented in Microsoft Excel. The fitted ion-specific parameters of single salts in water, methanol, or ethanol are shown in Tables 2–4, respectively.

Table 2 shows that the fitted parameters of alkali ions in water decrease as ionic diameters increase, except for cesium. The halogen ion parameters follow the opposite trend. Also, it can be observed that the ion parameters for alkalis have greater change than those of halogens. No regular pattern is observed for cations with charge greater than 1 and polyatomic anions.

The trends presented by some parameter groups, such as alkali and halogen ions, may be associated to ion diameters and, consequently, to the hydration phenomenon. For example, as mentioned by Wang and Anderko [29], alkali ions with small diameters can contribute to a stronger dielectric constant decrement than those with large diameters. It happens because a small ion such as Li^+, with a high charge density, can disrupt many water-water interactions in order to form a hydration shell. Therefore, the water dielectric constant strongly decreases due to the presence of this ion. One may relate this physical phenomenon to the parameters presented in Table 2, assuming that Li^+, whose parameter is 6.59, is much more capable of disrupting interactions between water molecules than K^+, whose parameter is 2.43. In addition, when these parameters are applied to Eq. (9), it is possible to observe that, at a given temperature and mole fraction, the lithium parameter results in a larger denominator. Therefore, it results in a lower dielectric constant value. Additionally, it is know that halogen ions weakly interact with water molecules. It means that these ions have weak influence on the disruption of water molecule interactions and, consequently, weak influence on the dielectric constant of water. This physical phenomenon may be related to the parameter values for halogen ions, which are very close to one another and follow a trend opposite to that of alkali ions.

The dielectric constant decreases when the ion concentrations increase for the vast majority of the systems whose data were used to fit the alpha-parameters. Eq. (9) captures this trend if all these parameters are positive. The dielectric constant of water in the presence of $MgSO_4$ is a notable exception. It increases up to a certain ion concentration and decreases thereafter. Eq. (8) can neither correlate nor predict this seemingly uncommon behavior, which may have influenced the fitting procedure, resulting in the negative parameter value for $SO_4{}^{2-}$. However, the alpha-parameter of Mg^{2+} is positive and the net effect, using Eq. (9), is a decay of the dielectric constant of water as the concentration of $MgSO_4$ increases. The small amount of experimental data of solutions of salts containing Ca^{2+} may have contributed to obtaining a negative parameter value since the dielectric constant of water in these solutions follows the usual trend.

Table 3 presents the parameters for ions in methanol. Like the parameters for anions in water, the values for Cl^-, Br^-, and I^- increase as ionic diameters increase. On the other hand, the parameters for the cations do not follow a clear trend as those for cations in aqueous solutions. Table 4 shows the parameters for ions in ethanol, and it is possible to observe that both parameters for cations and anions increase with increasing ionic diameter.

4. Results

Fig. 2 shows the correlation of experimental dielectric constant data using Eq. (4) and the parameters from Table 1 for pure methanol and pure acetone. The average relative deviation (ARD (%)) obtained for this fitting procedure is 1.82% for methanol and 0.24% for acetone, using the following equation:

$$ARD(\%) = \frac{100}{N_p} \sum_{k=1}^{N_p} \left| \frac{D_k^{calc} - D_k^{exp}}{D_k^{calc}} \right| \quad (11)$$

Table 5
Average relative deviation (ARD (%)) of dielectric constant of mixed solvent systems using Eq. (5).

Solvent system	N_p	T (K)	ARD (%)	Ref.
Methanol + water	55	293.15–333.15	2.1	[37]
Methanol + ethanol	105	288.15–308.15	1.0	[39]
Methanol + 1-propanol	105	288.15–308.15	1.4	[39]
Methanol + 2-propanol	105	288.15–308.15	1.9	[39]
Ethanol + water	54	293.15–353.15	3.2	[37]
1-Propanol + water	55	293.15–353.15	9.7	[37]
2-Propanol + water	55	293.15–353.15	10.7	[37]
Acetone + water	55	293.15–323.15	3.1	[37]
Acetone + methanol	11	298.15	2.2	[40]

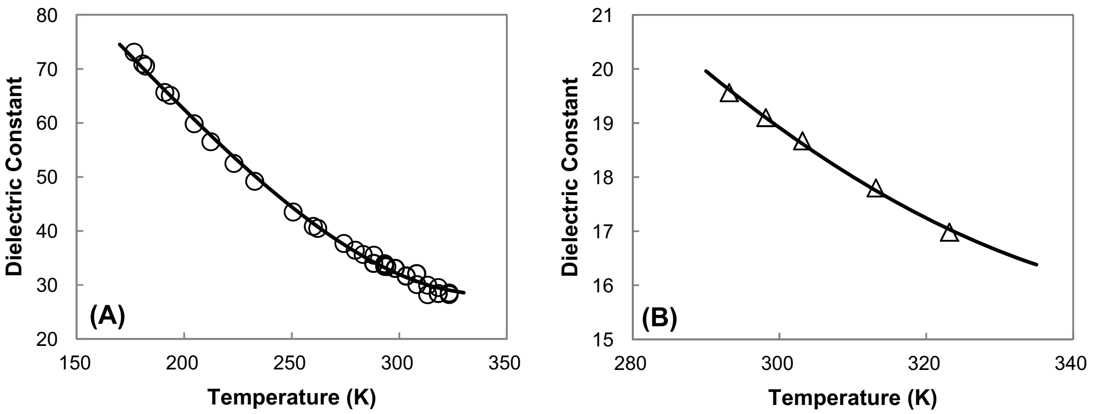

Fig. 2. Dielectric constant of (A) methanol or (B) acetone using Eq. (4) and the adjustable parameters of Table 1. Experimental data (○) from Davidson [35] and Shirke et al. [36] and (△) Campbell and Kartzmark [40].

The dielectric constant of mixed solvents can be computed by many equations, as mentioned by Jouyban et al. [38]. These models typically require one or more adjustable parameters. Eq. (5) is used in this work because it calculates the dielectric constant of mixed solvents satisfactorily without any adjustable parameter. The performance of this equation is evaluated by comparing its results to the experimental data of Akerlof [37], Chmielewska et al. [39], and Campbell and Kartzmark [40]. Table 5 shows the ARD (%) values, at different temperature ranges, of some binary solvent systems, among which the methanol + ethanol system has the lowest deviation in dielectric constant (1.0%). The deviations obtained in this work and by Wang and Anderko [29] for water in the presence of methanol, ethanol, 1-propanol, or 2-propanol increase according to this mixture sequence. Although the largest deviations occur for 1-propanol or 2-propanol in water, their deviations in dielectric constant are below 2.0% for their mixtures with methanol. The deviations between experimental values and model predictions for acetone + water (3.1%) and acetone + methanol (2.2%) are somewhat larger than the correlation of Wang and Anderko [29] (1.2% and 0.4%, respectively), who use one adjustable parameter for each binary mixture. Interestingly, the four largest ARD (%) values in Table 5 are for comparisons to the experimental data of Akerlof [37].

Fig. 3 shows the dielectric constant of methanol + water, ethanol + water, and 1-propanol + water at 293.15 K and 333.15 K.

Table 6

Average relative deviation (ARD (%)) of dielectric constant of water in single salt solutions.

Salt	N_p	m_{max} (mol/kg)	T (K)	ARD (%)	Ref.
HCl	2	0.51	298.15	0.80	[5]
LiCl	25	19.15	298.15	5.81	[5,6,8,9,17]
LiBr	11	13.84	298.15	9.36	[6,9,17]
LiI	2	1.00	298.15	3.77	[9,17]
$LiNO_3$	7	7.32	298.11	2.83	[17]
$LiClO_4$	6	3.48	298.15	1.44	[17]
NaF	6	1.00	298.15	2.23	[9,17]
NaCl	34	5.62	276.15–338.15	3.45	[8,9,11,16,17]
NaBr	6	4.48	298.15	4.34	[6,8,9]
NaI	7	11.87	298.15	5.34	[6,8,9]
$NaNO_3$	8	4.64	298.11–298.15	1.84	[8,17]
$NaClO_4$	9	6.50	298.15	2.98	[8,17]
NaOH	2	0.50	298.15	0.10	[5]
Na_2SO_4	6	1.02	298.15	4.30	[8,17]
KF	35	15.55	288.00–308.00	5.20	[8,9,13,17]
KCl	32	4.57	298.15	2.84	[5,6,8,9,12,17]
KBr	9	3.37	298.15	4.65	[8,9,17]
KI	35	4.96	288.00–323.00	5.94	[8,9,17,43]
KNO_3	4	2.19	298.15	2.69	[17]
RbF	1	1.00	298.15	2.47	[9]
RbCl	10	6.45	298.15	1.52	[5,9,17]
RbBr	1	1.00	298.15	2.77	[9]
RbI	1	1.00	298.15	1.84	[9]
$RbNO_3$	3	1.61	298.11	2.11	[17]
CsF	28	6.00	288.00–308.00	2.16	[9,17,43]
CsCl	17	5.09	298.15	2.36	[9,12,17]
CsBr	5	2.23	298.15	1.15	[9,17]
CsI	3	1.07	298.15	3.38	[9,17]
$CsNO_3$	2	1.06	298.11	3.18	[17]
$CaCl_2$	4	5.49	298.15	8.85	[8]
$CaBr_2$	2	0.96	298.15	6.98	[8]
$BaCl_2$	5	2.14	298.15	1.84	[5,8]
$MgSO_4$	7	1.11	298.15	7.29	[17]
$MgCl_2$	10	4.50	298.15	8.99	[8,17]
$Al(NO_3)_3$	1	1.06	298.15	0.00	[8]
Total	346	–	–	3.62	–

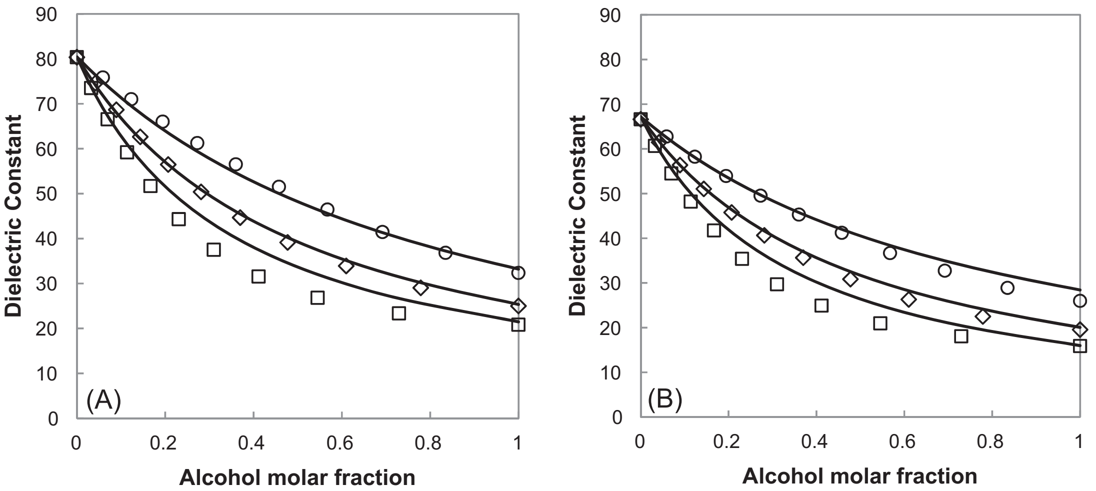

Fig. 3. Dielectric constant of mixed solvents at (A) 293.15 K and (B) 333.15 K using Eq. (5) (lines) and experimental data [37] of: methanol + water (○), ethanol + water (◊), or 1-propanol + water (□).

Eq. (5) gives higher deviations for 1-propanol systems at both temperatures; however, it can represent adequately the dielectric constant decrease in all the mixtures as the temperature increases.

Table 6 presents the ARD (%) values for dielectric constant of 35 aqueous single salt solutions, using 346 experimental data points in the parameter fitting procedure. Most of the experimental data is at 298.15 K. For NaCl, $NaNO_3$, KF, KI, and CsF, the correlation includes experimental data in different temperature ranges. All deviations obtained for electrolyte in water are below 10% and the average ARD is 3.62%. The highest deviations are observed for LiBr, $CaCl_2$, $CaBr_2$, $MgSO_4$ and $MgCl_2$.

Fig. 4 shows the correlation of dielectric constant of water in the presence of three different single salts: LiCl, KCl, and RbCl, by using Eq. (9). For these solutions, the model can correlate the experimental data behavior adequately. In addition, it can be observed that the dielectric constant data exhibit large experimental uncertainty for LiCl and KCl solutions at higher molalities. These uncertainties may have influenced the fitting procedures because all the experimental data found in the literature were taken into account. At one molal, the dielectric constant in these three chloride solutions exhibits the following sequence: $D_{LiCl} < D_{KCl} < D_{RbCl}$. Lithium has the smallest ionic diameter among the cations of these salts; thus, its charge density is the highest one. Therefore, in order to shield the cation charge, the water molecule structure is broken, creating a hydration shell [41] that lowers the dielectric constant at a given concentration.

Fig. 5 displays the: (a) experimental dielectric constant data in two aqueous single salt solutions containing NaCl or KBr at 298.15 K, whose references are shown in Table 6; (b) values calculated with the expression proposed here (Eq. (9)) and parameters from Table 2; (c) predictions of the Simonin model (Eq. (3)) with parameters based on the average hard-core diameter for the salts ($\alpha_{NaCl} = 0.0816$ L/mol and $\alpha_{KBr} = -0.0974$ L/mol) [25]; (d) predictions of the Simonin model with parameters based on the cation hard-core diameter ($\alpha_{NaCl} = 0.0818$ L/mol and $\alpha_{KBr} = 0.0651$ L/mol) [25]. The parameters of Simonin et al. [25] were fitted from mean ionic activity coefficient and osmotic coefficient data of 18 aqueous single salt solutions using the MSA equation. The Simonin equation captures that the dielectric constant in NaCl solutions decreases as the molality increases with any of the two parameters. For KBr solutions, the parameter based on the average hard-core diameter does not even capture the trend of the experimental data. In contrast, the results of dielectric constant obtained by using the equation proposed in this work are in good agreement with experimental data, for both electrolyte solutions.

Table 7
Average relative deviation (ARD (%)) of dielectric constant of methanol in single salt solutions.

Salt	N_p	m_{max} (mol/kg)	T (K)	ARD (%)	Ref.
LiCl	16	2.55	293.15–298.15	2.66	[15–17]
LiI	3	0.41	298.15	3.67	[17]
$LiNO_3$	3	2.67	298.15	6.67	[17]
$LiClO_4$	4	0.13	298.15	2.78	[17]
NaCl	8	0.16	298.15	1.81	[15,17]
NaBr	10	1.27	293.15–298.15	2.54	[16,17]
NaI	13	1.28	293.15–298.15	6.79	[14–17]
$NaClO_4$	13	1.38	298.15	0.79	[17]
KI	12	0.51	293.15–298.15	4.50	[15–17]
Total	82	–	–	3.58	–

Tables 7 and 8 present the ARD values for dielectric constant in 9 and 3 single salt solutions in methanol and ethanol, respectively. The number of experimental dielectric constant data points for nonaqueous electrolyte solutions is much smaller than for aqueous solutions. This may be a consequence of the low solubility of salts in these solvents. The deviations obtained for both solvents in the presence of electrolytes are lower than 8.0%, and the average ARDs are equal to 3.58% and 3.95% for methanol and ethanol, respectively.

Fig. 6 shows the correlations of dielectric constant in NaCl solutions in pure water or pure methanol, using the parameters presented in Tables 2 and 3, respectively. The correlations are in good agreement with experimental data. For both solutions, the dielectric constant decreases with salt addition. Fig. 6 also displays predictions for mixtures water + methanol + NaCl at four constant mole fractions of methanol with no use of additional parameters. The endpoints of these curves correspond to the maximum

Table 8
Average relative deviation (ARD (%)) of dielectric constant of ethanol in single salt solutions.

Salt	N_p	m_{max} (mol/kg)	T (K)	ARD (%)	Ref.
LiCl	1	2.18	293.15	0.00	[17]
LiI	4	1.03	293.15	7.05	[17]
NaCl	2	0.34	293.15	4.78	[17]
Total	7	–	–	3.95	–

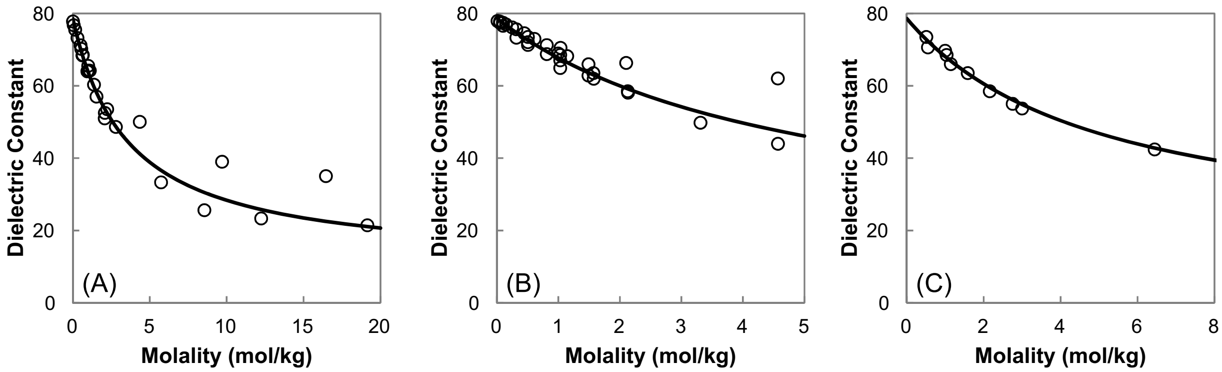

Fig. 4. Dielectric constant of water in single salt solutions formed by: (A) LiCl, (B) KCl, and (C) RbCl. Sources of the experimental data (○) are available in Table 6.

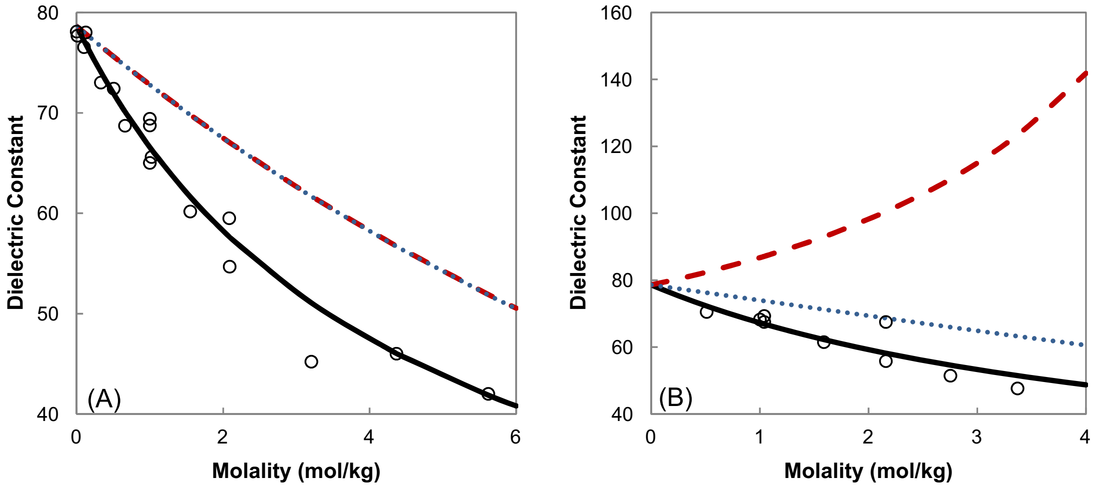

Fig. 5. Dielectric constant calculations of water in single salt solutions of (A) NaCl and (B) KBr, using the new model proposed in the work (—); Simonin's equation (▬ ▬ ▬) with the average hard-core diameter parameters; and Simonin's equation (• • • •) with the cation hard-core diameter parameters. Sources of the experimental data (○) are available in Table 6.

salt solubility in solution, as determined by Pinho and Macedo [42]. To the best of our knowledge, there are no experimental dielectric constant data available in the literature for mixtures water + alcohol + salt. Despite the missing experimental evidence, the model predicts dielectric constants whose values are intermediate between those of the two single solvent + salt solutions. This suggests that the model can be used, at least as a first approximation, for predicting the dielectric constant of mixed solvents containing electrolytes.

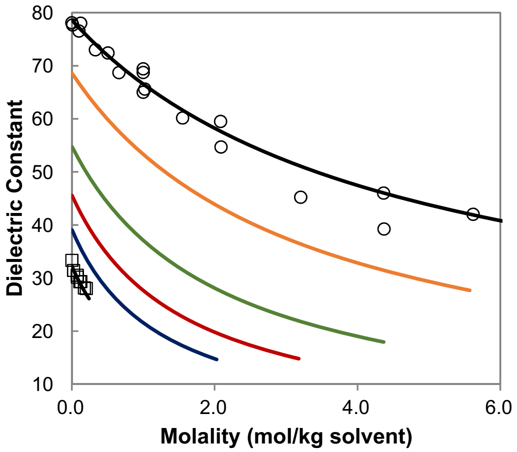

Fig. 6. Correlation of dielectric constant using Eq. (9) (black lines) in solutions containing NaCl in water (○) or methanol (□) at 298.15 K (refs. in Table 6), and predictions of dielectric constant using Eq. (8) of mixtures containing water + methanol + NaCl at constant methanol mole fractions: 0.10 (orange), 0.30 (green), 0.50 (red), and 0.70 (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

It is significant that experimental dielectric constant data of single or mixed solvents in electrolyte solutions are scarce in the literature. Thus, the application of this empirical equation in EOSs would be restricted to the electrolyte systems investigated in this work. In order to apply Eq. (8) or (9) to electrolyte solutions not addressed in this work, general parameters for any cation or any anion in each particular solvent are presented in Table 9. These parameters were fitted by using all the experimental dielectric constant data mentioned in Tables 6–8. They were determined by minimizing Eq. (10) as objective function for each solvent. The average deviations for solutions in water, methanol, and ethanol are 5.57%, 4.76%, and 28.20%, respectively. As expected, these deviations are higher than those presented in Tables 6–8. For example, using the parameters of Table 3, the minimum and the maximum

Table 9
General parameters for electrolytes in different solvents.

Solvent	α_{cation}	α_{anion}
Water	2.60	7.89
Methanol	12.41	15.91
Ethanol	9.04	21.36

ARD values for aqueous electrolyte solutions are 0% and 9.36%, for $Al(NO_3)_3$ and LiBr, respectively. Using the general parameters (Table 9), the deviations for these solutions become 3.86% and 14.35%. Thus, these parameters may be used for ions whose parameters remain unavailable because of the lack of experimental data. However, for the ions considered in this work, the parameters of Tables 2–4 are recommended.

5. Conclusion

This work proposed an equation for computing the dielectric constant of single or multi solvent mixtures containing electrolytes. This equation has one adjustable parameter per ion for each solvent. Correlations of dielectric constant in single salt solutions in water, methanol, and ethanol exhibited good agreement with experimental data for the studied solutions. The average ARD obtained for these electrolyte solutions was 3.62%, 3.58%, and 3.95%, respectively. The model usually provided better dielectric constant results than those obtained by the Pottel and Simonin expressions.

Calculations of dielectric constant for mixtures containing two solvents were performed for seven different solutions by using the parameters for pure solvents and a relation based on the volume fraction. The results are in good agreement with experimental data, except for mixtures of (1-propanol or 2-propanol) + water.

Predictions of the dielectric constant of water + methanol + NaCl mixtures were performed. Due to the absence of experimental data for multi-solvent electrolyte systems, trend curves were obtained, each of them at a constant methanol mole fraction. These curves display meaningful trends and converge adequately to the correlated dielectric constant in solutions containing NaCl in water or methanol, as a single solvent. General parameters for cations and anions in water, methanol, or ethanol were obtained as an attempt to apply our model to those electrolyte systems whose experimental data remain unavailable, or were not addressed in this work.

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