



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



André Zuber<sup>a,b</sup>, Lúcio Cardozo-Filho<sup>b</sup>, Vladimir Ferreira Cabral<sup>c</sup>,  
Ricardo Figueiredo Checoni<sup>a</sup>, Marcelo Castier<sup>a,\*</sup>

<sup>a</sup> Chemical Engineering Program, Texas A&M University at Qatar, PO Box 23874, Doha, Qatar

<sup>b</sup> Departamento de Engenharia Química, Universidade Estadual de Maringá, Paraná, Brazil

<sup>c</sup> Departamento de Engenharia de Alimentos, Universidade Estadual de Maringá, Paraná, Brazil

## ARTICLE INFO

### Article history:

Received 19 March 2014

Received in revised form 25 May 2014

Accepted 27 May 2014

Available online 4 June 2014

### Keywords:

Dielectric constant

Electrolyte solutions

Water

Alkanols

Acetone

## 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.

© 2014 Elsevier B.V. All rights reserved.

## 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<sub>2</sub>, KI, NaF, LaCl<sub>3</sub>, KF, NaI, MgCl<sub>2</sub>, and Na<sub>2</sub>SO<sub>4</sub>. 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 Akhadvov [18] also compiled excellent data sources of both electrolyte and nonelectrolyte systems.

\* Corresponding author at: 326C Texas A&M Engineering Building, Education City, PO Box 23874, Doha, Qatar. Tel.: +974 4423 0534.

E-mail addresses: [marcelo.castier@qatar.tamu.edu](mailto:marcelo.castier@qatar.tamu.edu), [mcastier@gmail.com](mailto:mcastier@gmail.com) (M. Castier).

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:

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

in which  $D$  is the dielectric constant of the solvent in the presence of electrolytes,  $D_S$  is the pure solvent dielectric constant, and  $\xi_3''$  is a variable defined as:

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

in which  $N_a$  is the Avogadro number,  $n_i$  is the number of moles of a ion  $i$ ,  $\sigma_i$  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 consequence of parameter fitting strategy, model oversimplifications or incapability of describing 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:

$$D = \frac{D_S}{1 + \alpha C} \quad (3)$$

in which  $D_S$  is equal to 78.38, which is the dielectric constant of water at 298.15 K,  $\alpha$  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  $\alpha$  parameter in Eq. (3) specific for the salt present in

Download English Version:

<https://daneshyari.com/en/article/202214>

Download Persian Version:

<https://daneshyari.com/article/202214>

[Daneshyari.com](https://daneshyari.com)