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Prediction and correlation of the solubility of alkali chlorides in different solvent mixtures and temperatures

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Based on the Pitzer model modified by Wu et al. for polymer-salt-aqueous two-phase ternary systems at ambient temperature, this work aims to extend such a model to quaternary systems consisting of a polymer, two salts, and water at different temperatures. This new model is applied to the correlation and prediction of the liquid-solid equilibrium (LSE) of the quaternary systems NaCl+KCl+PEG4000+H_2O at 298 K and NaCl+KCl+C_2H_5OH+H_2O at 298 and 313 K. The model contains six binary parameters and ten mixture parameters. The binary parameters are estimated from the liquid-vapor equilibrium (LVE) data of the corresponding salt-water binary systems, while the mixture parameters are obtained from solubility data of ternary systems. The results show that the predicted solubility values of the salt in the quaternary systems are consistent with the experimental data reported in the literature. Better agreement is obtained when the polymer-salt-salt mixture parameter is included. The influence of temperature and the solvent type on the parameters are also discussed in this work. The results provide useful information for the simulation of extractive crystallization processes of inorganic salts with a polymer or an alcohol as the solvent.

1. Introduction

The analysis of the phase equilibrium data of electrolytes insolvent mixtures using a semi-empirical thermodynamic model is useful for designing, optimizing, and simulating unit operations such as crystallization, extractive and azeotropic distillation, and liquid-liquid extraction. In addition, such analyses promote increased understanding of the chemical structure of aqueous electrolyte solutions, as well as the prediction of the properties, in the presence of solvents other than water [1].

The literature on this topic contains a substantial amount of experimental and theoretical information regarding the study of electrolyte solutions in water for binary, ternary, and quaternary systems, mainly under ambient conditions. However, thermodynamic and experimental information for quaternary systems that contain electrolytes in a solvent mixture at different temperatures is limited. Typically, the correlation and prediction of electrolyte properties in multi-component systems is not a straightforward task, because it requires accurate mathematical models and a basis in the molecular thermodynamic of the phase equilibrium to obtain reliable results. In addition, under saturated conditions, the adjustment of the predictive capacity of a specific thermodynamic model is a complex task, since the model parameters are not really known, and calculations are based on extrapolations [2].

The well-known Pitzer model [3], which is based on thermodynamic principles and has been successfully used for the prediction of the solubility of inorganic salts in water, is the most general and widely utilized model. Several authors have applied this model or modified versions of it, such as the Pitzer-Simonson-Clegg model [4] and the Pitzer mole-fraction-based equations, to different systems. This last model, which was formulated to describe the activity coefficients of electrolytes in water-alcohol mixtures, was used by Farelo [5] to correlate the solubility of sodium chloride and potassium chloride in the quaternary NaCl+KCl+H_2O+C_2H_5OH system. Farelo's results were graphically represented as solubility curves for 0, 10, and 20 mass % of ethanol in the solvent mixture at 298 and 323 K. In order to properly fit the calculated and experimental solubility data, the solubility was adjusted, and an interaction parameter ($Q_{\text{ethanol,NaCl,KCl}}$) was estimated. The LIQUAC model,

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which has been broadly used in the prediction of the thermodynamic properties of electrolytes in alcohol+water mixtures, was successfully applied by Yangzheng et al. [6] to predict the solubility of KCl in ethanol+water mixtures. They found that the predictions of the LIQUAC model were better than those obtained using the NRTL, UNIQUAC, or UNIFAC models for these types of mixtures. A similar model was applied by Perez-Salado Kamps [7] to describe the solubility of NaCl and a simple gas (CO_2) in a methanol+water solvent mixture. Nevertheless, applications of these models to aqueous electrolyte solutions containing a high molecular weight polymer, such as polyethylene glycol (PEG), have not been reported. Additionally, it is important to highlight that when a polymer is treated as an organic solvent, the use of weight fraction rather than molar fraction is advised [2,8].

However, there do exist some interesting works based on thermodynamic approaches, such as that of Wu et al. [8], who developed a modification of the Pitzer model for systems containing a salt, water, and a polymer, where the last is considered as a pseudo-solvent. Their model was successfully applied to describe the liquid-liquid equilibrium of three ternary systems, PEG+$(NH_4)_2SO_4$+H_2O, PEG+Na_2SO_4+H_2O, and PEG+Na_2CO_3+H_2O, at 298 K. The binary and mixture parameters were estimated from liquid-vapor equilibrium (LVE) data of the corresponding binary and ternary systems. These parameters quantify the salt-water, polymer-water, and salt-polymer interactions within the system. The results of Wu et al. [8] indicated that the polymer parameters are independent of their chain length, and their predictions for the LLE matched the experimental data. Thus, this model has been suggested for the study of electrolytes in solvent mixtures. Recently, Lovera et al. [9] applied the Pitzer model modified by Wu et al. [8] to correlate the solid-liquid equilibrium of the ternary systems MCl+PEG4000+H_2O and MCl+Ethanol+H_2O at 298 K, where M represents Li, Na, or K. Their results were consistent with the experimental data, thus validating the approach of Wu et al. [8]. However, to date, this model has only been tested at 298 K, in liquid-liquid equilibrium (LLE) and solid-liquid equilibrium (SLE), and for a discrete number of multi-component systems. Hence, there is a need to extend its application to different systems and at multiple temperatures. Currently, there are only a few models available for systems containing a salt, water, and a polymer. Fosbøl et al. [10] used the UNIQUAC model extended to aqueous systems of electrolytes and non-electrolytes. Their work was applied to the CO_2-Na_2CO_3-$NaHCO_3$-MonoethyleneGlycol-Water system in order to investigate CO_2 gas corrosion using a thermodynamic model. It is important to note that, in this specific case, the polymer was considered as a solute. The model of Fosbøl et al. [10] was validated by comparing its prediction of excess heat capacity with experimental data from the literature; the model was also able to predict the solubility of CO_2 in that specific system.

The solubility values of ternary and quaternary systems at different temperatures have been reported in the literature, but they were not thermodynamically modelled. Zhou et al. [11] and Zhou et al. [12] reported experimental data for the solubility values of the ternary MCl+Ethylene Glycol+H_2O (M=Na, K, Rb, and Cs) system at 288, 298, and 308 K. Galleguilloset al. [13] and Taboada et al. [14] measured the solubility values of the quaternary systems NaCl+KCl+Ethanol+H_2O at 298 and 313 K and NaCl+KCl+PEG 4000+H_2O at 298 K, respectively. The main motivation of the present work is to extend the application of the Pitzer model modified by Wu et al. [8] to other temperature conditions, types of organic solvent, and numbers of mixture components. For this purpose, a model of the mean activity coefficients and solubility values of a univalent salt in a quaternary system will be developed. The formulated model will be applied to correlate the LSE of the experimentally studied systems previously mentioned, and the LVE of the salt+H_2O subsystems involved.

2. Thermodynamics treatment

Following the procedure of Wu et al. [8], this section describe show to calculate the solubility values for ternary and quaternary systems at 288, 298, 308, and 313 K. The studied ternary systems are NaCl+KCl+H_2O, NaCl+EG+H_2O, NaCl+C_2H_5OH+H_2O, KCl+EG+H_2O, KCl+C_2H_5OH+H_2O, RbCl+EG+H_2O, and CsCl+EG+H_2O (EG = ethylene glycol); while the quaternary systems are NaCl+KCl+PEG4000+H_2O, NaCl+KCl+C_2H_5OH+H_2O. Section 2.1 describes the approach formulated by Wu et al. [8] to obtain the activity coefficient functions for univalent salts. Section 2.2 contains the description of the approach to calculate the solubility values to be used in the activity coefficient functions obtained in the previous section. Lastly, Section 2.3 presents the model parametrization method. The combination of these three sections constitutes the model described in this work, which is useful to predict the solubility values of quaternary systems at different temperatures.

2.1. Activity coefficient functions

A general expression for the Gibbs free energy of a homogenous mixture composed of electrolytes, polymers, and water was given by Wu et al. [8], and is presented as Eq. (1), as follows:

$$G^E \Big/ RT = -(N_a k/3D)\sum_{i=1}^{N} n_i Z_i^2 e^2 \tau(ka) + (1/n_w)\sum_{i\neq w}^{N}\sum_{j\neq w}^{N}\lambda_{ij} r_i r_j n_i n_j + \left(1\Big/n_w^2\right)\sum_{i\neq w}^{N}\sum_{j\neq w}^{N}\sum_{k\neq w}^{N}\mu_{ijk} r_i r_j r_k n_i n_j n_k \tag{1}$$

where N_a is the Avogadro constant, k is the Debye inverse length, D is the dielectric constant, Z is the relative valence, e is the electron charge, the subscripts i, j, and k denote the solute species, n_i is the number of moles of the ith-solute species, n_w is the mass of water in kilograms, and N is the total number of species (ionic and non-ionic). Eq. (2) shows the function for the reduced Debye length (ka), τ, given by Wu et al. [8].

$$\tau(ka) = 3(ka)^{-3}\left[\ln(1+ka) - ka + (ka)^2/2\right] \tag{2}$$

According to Wu et al. [8], the first term on the right-hand side in Eq. (1) represents the long-range electrostatic contribution, which is given using the expression of Fowler and Guggenheim instead of the Debye–Hückel modified term in the original Pitzer model [3]. The second and third terms are the short-range virial contributions, where λ_{ij} and μ_{ijk} are the second and third virial coefficients, respectively. These coefficients represent the short-range forces between the ions and/or the polymer segments.

Extending the summations in Eq. (1) to N=3 and deriving with respect to the number of moles of each of the components of a ternary system formed by a polymer, a salt, and water, Wu et al. [8] obtained the activity equations of these components. In this work, extending the same approach to a quaternary system formed by a polymer (1), two univalent salts, MX(2) and NX(3), and H_2O(4), the activity equation of any saline component is obtained. Note that the salts MX and NX have a common anion X and the symbols M and N represent cations. As an illustration, the corresponding mean activity coefficient for the salt MX(2) is: