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Solvation-based modeling vapor pressures of (solvent + salt) systems with the application of Cox equation

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ABSTRACT

A solvation model framework, based on the LSER (linear solvation energy relationship) principles, is proposed for correlating vapor pressures of (solvent + salt) systems. The LSER method basely uses a linear combination of several solvatochromic indices of solvents to describe their physical properties. The assumption inherent in the solvation-based vapor pressure approach is attributed to an additional effect of several physical quantities, i.e. the vapor pressure of a pure solvent estimated by the Cox equation, the salt concentration, the solvatochromic indicators of the solvent and the physical properties of the ionic salt species. It has been performed independently two structural forms of the generalized solvation model, i.e. the integrated property-basis model using nine physical descriptors USMIP (the unified solvation model with the integrated properties) and the reduced property-basis one. Also, a simplified concentration-dependent vapor pressure model is presented. The observed vapor pressure data of fifteen (solvent + salt) and two (solvent (1) + solvent (2) + salt) systems have been processed to establish the basis for the model reliability analysis using a log-ratio objective function. The proposed vapor pressure approaches reproduce the observed performance relatively accurately, yielding the overall design factors of 1.065 and 1.072 for the solvation-based models with the integrated and reduced properties and 1.017 for the concentration-based model, respectively. Both the integrated property-basis and reduced property-basis solvation models were able to simulate satisfactorily the vapor pressure data of a binary solvent mixture involving a salt, yielding an overall mean error of 5.7%.

1. Introduction

Increasing concern about environmental issues has recently directed the attention of the scientific community to greener industrial processes with the interactive salt effect. The effect of the ionic salt species on the phase equilibrium finds an applicable field in many separation processes such as distillation, crystallization, liquid–liquid extraction, salt precipitation from mixed solvents, etc. [1]. In many areas of industry, solvent mixtures accumulate due to recycling difficulties. Typically, biofuel processes produce fermented products such as esters, ethers and alcohols that form azeotropes with water which is abundant in the fermentator. The extractive distillation with the interactive salt effect has emerged as the most common and environmentally beneficial method for separating the azeotropic or close-boiling binary solvent systems. The ionic salt is basely used as an extractive agent (entrainer) to alter the relative volatility of the liquid mixture, so that the components can be more easily separated from the system and reused [1–12]. Regarding the azeotropic mixtures, the salting-in or salting-out effect has been employed by several workers to design a distillation operation for shifting or breaking an azeotrope through a salt as the entrainer. Experimental findings have shown that azeotropes can be entirely eliminated by using a salt or ionic liquid in a mixture of polar solvents [7–13]. The synthesis of a water-free organic solvent is another example for such a separation process. Typically, the dewatering of some organic solvents is carried out by adding soluble electrolytes to the aqueous solutions being capable of affecting dramatically the volatility range of components [5]. However, the experimental results of Apelblat and Korin [6] exhibit that the salting-out effect of ionic salts could modify reasonably the molar enthalpies and vapor pressures of saturated aqueous solutions. The technical details and thermodynamic aspects of a separation process with the interactive salt effect have been excellently reviewed by many researches [1,12–16]. Particularly frustrating aspects of using an inorganic salt as the entrainer are insufficient solubility in nonaqueous solvents and corrosion. Nevertheless, the ionic salt becomes favorably potential alternative to the commonly-used liquid as a separation agent in the azeotropic or extractive distillation [12,13,17].

In the context of many chemical processes it is important to determine and interpret the precise effect of dissolved salts on the phase behavior of solvent mixtures. There are several complexities

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in describing the salt interaction with the volatile components that generally arise out of the selective interactive effect due to a specific salt on the volatilities of liquid components [13]. It is presumed that the salt would likely induce the formation of different associated complexes or clusters of molecules of the volatile component about its ions. The salt effect is thought to be a complex function of the salt and solvent interaction and self-interaction among all the components of the system [12–17].

The usual approach to quantify the efficiency of a salt-based separation process is to specify the properties of the equilibrium system due to a thermodynamic criterion being obeyed. Typically, the thermodynamic criterion of (vapor + liquid) equilibrium implies that the equality of fugacities of component *i* in both phases is reached regarding each of (solvent + salt) binary system as a pseudo-component, and is given by Eq. (1) [14–19]

$$y'_i \phi_i P'_t = x'_i \gamma'_i \phi^0_i P'_i \tag{1}$$

where the prime refers to the salt system; γ'_i represents the activity coefficient of component *i* in the salt-containing system; y'_i and x'_i denote the mole fractions of component *i* in the vapor and liquid phases, respectively; P'_t is the total pressure of the system involving a salt. The P'_i stands for the saturation vapor pressure of component *i* at the system temperature and in the presence of the salt to which we shall refer hereafter to as *P*. ϕ_i and ϕ^0_i designate the fugacity coefficients of component *i* in the vapor mixture and the pure solvent at the saturated state, respectively. If the non-ideality of the vapor phase is prevalent, the fugacity coefficients ϕ_i and ϕ^0_i of component *i* can be calculated by the virial state equation truncated after the second term [14,20]. In general, since the total pressures of relevant systems involving the ionic salts are sufficiently low, all fugacity coefficient corrections are similar and can be neglected. Many attempts have been made to describe vapor–liquid equilibria of salt-containing associated mixtures using the group-contribution theory, the statistical associating fluid theory (SAFT), the associated perturbed anisotropic chain theory (APACT), the lattice quasi-chemical theory, COSMO-SAC method and the concepts of multiscale dipole–dipole association [21–25]. In the design practice, the separation efficiency due to a salt effect is usually interpreted in terms of the properties specified by Eq. (1), where the solubility range of the salt is accounted for explicitly [13–19]. Subsequently, appropriate theoretical models are required to estimate the activity coefficient and vapor pressure of the components. Kumar [13] has broadly classified activity coefficient models into two categories depending upon whether the model is derived from excess Gibbs free energy or not. The first category models are concerned with the concept of excess Gibbs free energy, i.e., Wilson, NRTL, UNIQUAC and UNIFAC models [13], and their modified versions [26,27,23]. In the second type semi-empirical in the nature equations, the presence of salt is accounted for implicitly [18,19]. The starting point is based on either the formation of a binary complex between the ionic salt species and the solvent molecules or the use of the concept of preferential solvation [13,19].

Because the determination of all required experimental vapor pressure data in a wide temperature range is almost impossible, it is a practical way to extrapolate vapor pressure prediction to the overall temperature range based on a generalized correlative model for (solvent + salt) systems. While various models, based on the critical temperature and pressure properties, exist for the vapor pressure of a pure fluid, yet only few works have focused on assessing and generating analytically an efficient equation for vapor pressures of (solvent + salt) systems relative to the solubility range of the salt. In the scope of this study, we came across the need to quantify rigorously vapor pressures of relevant systems through a solvation-based relation. The study was aimed to correlate vapor pressures of (solvent + salt) systems through the principles of linear solvation energy relationship (LSER) [28–30] using the solvatochromic indicators of the solvent and physical properties of the ionic salt species. Two structural forms of the generalized solvation model framework have been performed independently, i.e. a unified solvation approach based on an integration of the overall properties of the solvent and salt, and a reduced property-basis approach which does not account for the properties of the ionic salt species explicitly. A simplified concentration-dependent vapor pressure model is also presented and checked for consistency. The reliability of existing models has been analyzed statistically on the basis of a log-ratio objective function.

Recently, the application of LSER has been extended to correlate the tracer diffusion coefficients, the solubility of compounds and the distribution behavior of associated liquid systems [31–33]. The proposed LSER-based solvation models were able to characterize precisely different properties of associating fluids in VLE and LLE systems [33–35]. This capacity turns the LSER principles applicable to (solvent + salt) systems. In this perspective, attempts have been made to correlate vapor pressures of (solvent + salt) systems by a log-basis approach, namely, a unified solvation model with the integrated properties (USMIP). The model combines the system properties at the limiting conditions attributed to the vapor pressure of a pure solvent (or a solvent mixture) with an expansion term clarifying the complementary effect of the salt concentration, the solubility and solvatochromic parameters of the solvent and the physical properties of the ionic salt species. However, to quantify the magnitude of the salt effect, quantitative knowledge of the vapor pressure of a pure solvent is needed.

1.1. Survey of vapor pressure models for pure solvents: application of Cox equation

Numerous correlative and theoretical-based relationships for estimating saturation vapor pressures of pure fluids have been published in the literature, being excellently reviewed by many researchers [36–41]. As a result, for accurate fitting vapor pressure data of a pure solvent, the model must possess at least three parameters [37,39]. Traditionally, comprehensive studies on the vapor pressure have been fulfilled using commonly four equations of practical interest in terms of their abilities to correlate vapor pressure of a pure solvent, i.e. the three-parameters Antoine equation, four- or five-parameters Wagner equation, the SVRC model with two fluid-specific regressed parameters, and the Cox equation including at least three adjustable parameters [36–41]. Several modifications to the Wagner equation including three to six adjustable parameters and relations derived from the corresponding states or kinetic theory have found use to varying degrees [36–41]. Recently, various literature studies which use the structure property information alone to generalize the model parameters have been published [39]. As such, quantitative-structure-property relationship (QSPR) models stand out because they become powerful methods providing reliable vapor pressure estimates based solely on detailed chemical structure information covering an optimum number of structural descriptors [39]. Another approach that has gained significance over the years has been the use of the polynomial-type Cox equation with varying temperature exponent [36,42]. The Cox equation applicable to a wide temperature range has been employed frequently for data fitting, particularly in publications from NIPER (the Bartlesville Laboratory of the Bureau of Mines). Due to its reliable correlative capacity and high flexibility, the Cox equation has been incorporated into the LSER-based solvation model to account for the vapor pressure of a pure solvent.

The generalized form of the Cox equation is given by Eq. (2) [36,42,43]. The logarithm of the ratio of P_0 (kPa) to an arbitrarily selected vapor pressure, e.g. the critical pressure P_c (kPa)