A model for excess volumes of salty water–acetonitrile mixtures at 298.15 K

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ABSTRACT

A model for salty water–acetonitrile mixtures at 298.15 K was proposed based on three different contributions: chemical, physical and electrostatical. The first two were accomplished by ERAS model and the third was achieved by analyzing several proposals: Debye–Hückel, Hepler and a modified ERAS model. In order to test the model values, densities for the mixtures were measured with a vibrating-tube densimeter and the excess molar volumes were determined. The salts molar concentrations varied from 0.001 to 0.004, covering the entire composition range for water–acetonitrile. For each system, the three model approaches was applied. The modified ERAS model provides the best results.

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1. Introduction

The dissolution of a salt in a liquid solution modifies the activities of its components because of ion–component interactions known as salt effect. Once this effect alters vapour pressures of volatile components, it is possible to apply it in separation processes, which use salt as an extractive agent.

Solution theories calculate solution properties as molar excess enthalpies, molar excess free energy and molar excess volumes considering both physical and chemical component characteristics in conjunction with intermolecular forces present in a solution. However, there are few studies, mostly in aqueous solutions, which deal with salt effect in these solution properties [1–3].

Molar excess volumes are commonly used to test solution models due to its relation to structural aspects of the components and solution and easiness for experimental measurements. Different salts (calcium acetate, potassium acetate, tetraethylammonium bromide, lithium chloride, sodium tetraphenylborate) were added to water–acetonitrile solutions. The system water–acetonitrile was chosen because of the distinction in the chemical nature of its polar components and the fact that it forms a homogeneous mixture at room temperature and pressure. The criteria applied to salt selection were: affinity for one of the mixture components (water or acetonitrile), ionic radius, salt nature, anionic or cationic effects in the same periodical group.

Besides the experimental data, a model based on ERAS model [4] was proposed to represent the chemical, physical and electrostatical contributions to excess volumes. Both chemical and physical contributions were strictly the same as those proposed by Heintz. The electrostatical contributions were achieved by testing three different approaches: the first one using a Debye–Hückel term [5]; the second, applying electrostriction concept [6] and the last, a modification on ERAS model.

2. Experimental

Density measures of pure liquids and mixtures were performed at atmospheric pressure at 298.15 K by an Anton-Paar DMA 55 vibrating-tube densimeter (resolution 1×10^{-5} g cm^{-3}). The temperature was measured with an Ahlborn therm type 3280 digital platinum resistance thermometer, which was previous calibrated with a Guildline Model 9540 digital platinum resistance thermometer (resolution 1×10^{-3} K). The temperature was kept constant using a water thermostatic bath to ±0.01 K. The mixtures were prepared by weighing and mixing in 10 cm^3 bottles. Before each series of measurements, the densimeter was calibrated with distilled water and air. The densimeter was tested by measuring the densities of water–acetonitrile mixtures and the results of their excess molar volumes were compared to those, at about the same mole fractions x_A of water, reported by Handa and Benson [7], Moreau and Douhéret [8] and Meurs and Somsen [9] with good agreement as shown in Table 1.

Uncertainties in density measurements were about ±0.00002 g cm^{-3}, in temperature was ±0.05 K and in molar

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Table 1
Comparison of measured values of V_m^E (cm^3 mol^{-1}) to those in the literature for system (x_A water + (1 − x_A) acetonitrile).

x_A	Measured	Handa and Benson	Moreau and Douhéret	Meurs and Somsen
0.5970	−0.561	−0.5527	−0.541	−0.554
0.6510	−0.581	−0.5605	−0.545	−0.570
0.7080	−0.566	−0.5621	−0.538	−0.568
0.7570	−0.558	−0.5512	−0.519	−0.559
0.8540	−0.489	−0.4787	−0.430	−0.491
0.8990	−0.413	−0.3923	−0.342	−0.405

Table 2
Samples purities in mass basis.

Reactants	Purities
Acetonitrile	>99.8% (Merck)
Calcium acetate	>99% (Sigma)
Potassium acetate	>99% (Merck)
Tetraethylammonium bromide	>99% (Merck)
Lithium chloride	>99% (Merck)
Sodium tetraphenylborate	>99.5% (Aldrich)

fractions about ±0.0001. The uncertainty in excess molar volume values caused by the above uncertainties is ±1.5% of V_m^E values for the composition central range.

Salt quantities were added to these mixtures in mole fractions that varied from 0.001 to 0.004. Table 2 presents some properties of water–acetonitrile. All substances were used without further purification (Table 3).

3. Theory

The excess molar volumes of the ternary systems were calculated by adding three contributions: chemical, physical and electrostatical. Both chemical and physical contributions were strictly the same as those proposed by ERAS model [4]. The electrostatical contributions were achieved by testing three different approaches: the first one using a Debye–Hückel term [5]; the second, applying electrostriction concept [6] and the last, a modification on ERAS model.

ERAS model was initially applied to mixtures of alkanol-alkane [4] and its main proposal was the prediction of excess properties simultaneously. It was based on the sum of two different contributions: chemical, which was derived on the consecutive association of molecules as proposed by Kretschmer and Wiebe [10] and physical, which used Flory's [11] treatment of free volume effects of liquid mixtures with different sizes and shapes.

Kretschmer and Wiebe [10] explained the behaviour of solutions whose components formed associations by hydrogen bonding. Despite the fact that this theory describes excess enthalpy and excess free Gibbs energy well, it was not able to fit excess volumes data.

The association reaction is:

$$A + A_n \leftrightarrow A_{n+1} \tag{1}$$

Table 3
Properties of water and acetonitrile.

Property	Water		Acetonitrile	
	Literature[a]	Measured	Literature[b]	Measured
Density (g cm^{-3})	0.9984	0.9982	0.7822	0.7828
Refraction index	1.33262	1.3332	1.34423	1.3447

[a] Handbook of Chemistry and Physics, 1987.
[b] Riddick et al. [18].

The association constant K_A is:

$$K_A = \frac{c_{An+1}}{C_{An}c_A} \tag{2}$$

where c_i are the molar concentration of the i-mer.

When crossed association between solvents occur, the crossed association constant, regarding the above definition, is:

$$K_{AB} = \frac{c_{A_nB}}{c_{A_n}c_B} \tag{3}$$

where A is the solvent with higher association.

Flory's equation of state presents very good results for excess properties of hydrocarbon mixtures. Later it was applied to liquid mixtures in general, where the volumetric variations were derived on free volumes of the compounds [12]. Flory established that pure liquids have different free volumes, i.e., different degrees of thermal expansions, which are more important when large differences in shapes and sizes of the components exist. The equation of state proposed is:

$$\frac{\tilde{p}\tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{1/3}}{\tilde{V}^{1/3} - 1} - \frac{1}{\tilde{V}\tilde{T}} \tag{4}$$

where $\tilde{p} = p/p^*$ is the reduced pressure of the solution, $\tilde{T} = T/T^*$ is the reduced temperature of the solution and $\tilde{V} = V/V^*$ is the reduced volume of the solution. The properties p^*, T^* and V^* are the characteristic properties of the solution and can be calculated from p–V–T data.

The characteristic properties are calculated by:

$$p^* = p_A^*\Phi_A + p_B^*\Phi_B - \Phi_A\theta_B\chi_{AB} \tag{5}$$

$$\theta_B = \frac{\Phi_B S_B}{\Phi_A S_A + \Phi_B S_B} \tag{6}$$

$$T^* = \frac{p^*}{\Phi_A p_A^* T_A^{*-1} + \Phi_B p_B^* T_B^{*-1}} \tag{7}$$

where θ_B is the segment fraction of B and χ_{AB} is Flory's physical interaction parameter.

Writing the physical, V_p^E, and chemical, V_c^E, contributions of ERAS model for a binary mixture of A and B:

$$V_p^E = (x_A V_A^* + x_B V_B^*)(\tilde{V} - \Phi_A\tilde{V}_A - \Phi_B\tilde{V}_B) \tag{8}$$

$$V_c^E = x_A K_A \Delta v_A^* \tilde{V}(\phi_{A1} - \phi_{A1}^0) + \frac{x_B K_{AB}\Delta v_{AB}^* \tilde{V}\phi_{B1}(1 - K_A\phi_{A1})}{V_B/V_A + K_{AB}\phi_{B1}} \tag{9}$$

where Δv_A^* is the reaction volume of the hydrogen bonding for water and Δv_{AB}^* is the reaction volume of solvation water–acetonitrile, ϕ_i are the volumetric fraction of the monomer in solution, ϕ_i^0 are the volumetric fraction of the pure monomer, Φ_i are the volumetric fraction volumetric fraction of the component. The volumetric fractions of the are calculated by:

$$\Phi_i = \frac{x_i V_i^*}{\sum(x_i V_i^*)} \tag{10}$$

$$\Phi_A = \frac{\phi_{A1}}{(1 - K_A\phi_{A1})^2}\left[\frac{1 + V_A K_{AB}\phi_{B1}}{V_B(1 - K_B\phi_{B1})}\right] \tag{11}$$