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ERAS modeling of the excess molar enthalpies of binary liquid mixtures of 1-pentanol and 1-hexanol with acetonitrile at atmospheric pressure and 288, 298, 313 and 323 K

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Abstract

This work reports experimental data on the excess molar enthalpy H_m^E as a function of composition of acetonitrile + 1-pentanol and acetonitrile + 1-hexanol mixtures at 288.15, 298.15, 313.15 and 323.15 K under atmospheric pressure. The data show positive values over the whole composition range for both systems and for all temperatures studied, they also increase with temperature and with alkanol chain length. The experimental curves have a parabolic shape with maximum point around 0.5 mole fraction. The extended real associated solution (ERAS) model was applied to correlate the experimental data. The ERAS model adequately described the main features of the H_m^E behavior of the mixtures.

Keywords: Excess enthalpy; Data; ERAS model; Acetonitrile; Alkanol

1. Introduction

Excess thermodynamic properties have been investigated from experimental and theoretical standpoints aiming to understand and to explain molecular interaction between molecules, as well as to test and to develop new theories and models that are able to describe the behavior of liquid mixtures. However, to develop reliable models and theories it is important to have information about the excess volume V_m^E, the excess enthalpy H_m^E and the excess Gibbs energy G_m^E. This work gives excess molar enthalpies of two binary strongly polar systems. In the literature, H_m^E [1,2], V_m^E [3–9] and G_m^E [10,11] are reported for acetonitrile + alkanol mixtures, although, there is a shortage of H_m^E data for binary mixtures. The ERAS model [12] admits the existence of two effects in the mixtures: a physical one, related to the van der Waals forces and a chemical one, related to the self association between equal molecules and the cross-association between different molecules. In this work, it is assumed that acetonitrile does not self-associate [13–15].

2. Experimental

Excess enthalpy measurements were carried out with a Parr 1455 solution calorimeter similar to that described by Venkatesulu et al. [16]. Some improvements were made to improve the performance of the apparatus; a Teflon lid was fitted on the top of the Dewar vessel to reduce the evaporation losses, a resistance wire was installed inside the Dewar vessel to perform calibration measurements, and the calorimeter was placed in a thermostatic bath to minimize heat transfer between the calorimeter and surroundings. The schematic representation of the apparatus and the operating procedure is described elsewhere [17].

Experimental excess enthalpy values were determined by the following equation:

$$H_m^E = -\left(C_p + \frac{C_v}{n}\right)\Delta T \qquad (1)$$

where C_p is the molar heat capacity of the mixture; C_v the heat capacity of the calorimeter; n is the amount of substance in the Dewar vessel after mixing and ΔT is the temperature change. C_p and C_v are calculated by reversal calorimetry where a known amount of heat flux is supplied with uncertainty of $\pm 1 \times 10^{-2}$ W. For intermediary mixture composition, it is not

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possible to determine H_m^E directly from pure reagents due to limited volume of the cell and vessel. Hence, a mixture is used in the Dewar vessel whose H_m^E is previously determined, so the value of H_m^E is calculated by

$$H_m^E = \frac{n_0}{n} H_{m_0}^E - \left(C_p + \frac{C_v}{n} \right) \Delta T \qquad (2)$$

in which n_0 and $H_{m_0}^E$ are the amount of substance in the previous mixing process inside the Dewar vessel and its excess molar enthalpy, respectively. Their values are zero when pure reagent is used.

The performance of the calorimeter was tested by measuring H_m^E of ethanol + water at 298.15 K and atmospheric pressure over the whole composition range. The data showed good agreement with those reported by Lama and Lu [18], Boyne and Williamson [19] and Costigan et al. [20]. The average standard deviation between literature data and experimental data was $\pm 5.4\,\mathrm{J\,mol^{-1}}$.

The reagent acetonitrile (purity >99.99 mol%) was supplied by EM Science-Merck (USA), ethanol (purity >99.70 mol%) by QM (Brazil), pentanol (purity >98.50 mol%) by Merck (Germany), hexanol (purity >99.00 mol%) by Sigma–Aldrich (Germany). None of the reagents used in this work received further purification.

To check the purity of all reagents acquired, analyses of density and refractive index were performed at 293.15 K and the results were compared with those available in the literature as shown in Table 1 (see supplementary data file). To perform density measurements a vibrating-tube densimeter (Anton Paar, model DMA 55, uncertainty $\pm 1 \times 10^{-5}\,\mathrm{g\,cm^{-3}}$) was used. To perform refractive index measurements, a refractometer (Atago, model 3T, uncertainty $\pm 1 \times 10^{-4}$) was used.

3. Results and discussion

The excess molar enthalpy data H_m^E for the studied systems at different temperatures are shown in Table 2 (see supplementary data file). The average uncertainty for alkanol mole fraction is $\pm 5 \times 10^{-4}$.

Each set of experimental H_m^E results was fitted to the Redlich–Kister expansion of the type:

$$H_m^E = x_A(1 - x_A) \sum_{j=0}^{n} A_j (1 - 2x_A)^j \qquad (3)$$

The coefficients A_j were obtained by least square optimization and their values are shown in Table 1 as well as the standard deviation between calculated and experimental data.

The H_m^E behavior of the 1-alkanol + acetonitrile mixtures can be interpreted as the result of physical and chemical effects.

Physical interactions mainly consisting of dispersion, dipole–dipole and induction forces make an endothermic contribution to H_m^E.

Chemical interactions might be interpreted as the disruption of alkanol oligomers through the breaking of H-bonds and a cross-association between acetonitrile and alkanol molecules. The disruption of H-bonds makes an endothermic contribution to H_m^E. Possible cross-association between acetonitrile and alkanol makes an exothermic contribution to H_m^E.

As H_m^E data are positive and with high magnitude, physical interactions and H-bond breaking are the main effects in the mixing process, although, as the alkanol chain length increases the possibility of association decreases. This observation leads us to believe that, in the present case, breaking of H-bond has a minor importance to interpret the H_m^E behavior. Therefore, it is believed that physical interactions are probably dominant. This conclusion can be confirmed if further information about the mixtures studied is available such as V_m^E and G_m^E. Following the literature [6,7], the behavior of V_m^E is similar to that of H_m^E, that means, they are positive over the whole composition range and increase with temperature and with the alkanol chain length. Data of G_m^E for the studied mixtures were not found in the literature, although, positive G_m^E data of 1-propanol or 1-butanol + acetonitrile [10,11] suggest that they are also positive for the studied mixtures. The V_m^E and G_m^E behavior of 1-alkanol + acetonitrile mixtures reinforce the interpretation of H_m^E behavior in terms of physical interactions.

Since H_m^E behavior of the studied mixtures depends on physical and chemical interactions an appropriate model was applied.

Table 1
Coefficients A_j for the fitting Eq. (3), and the standard deviation σ

T (K)	A_0 (J mol^{-1})	A_1 (J mol^{-1})	A_2 (J mol^{-1})	A_3 (J mol^{-1})	A_4 (J mol^{-1})	σ (J mol^{-1})
1-Pentanol (x_A) + acetonitrile ($1 - x_A$)						
288.15	7765.4	678.4	1306.6	76.0	1430.6	15.89
298.15	8021.2	1127.4	2414.9	213.3	115.0	4.78
313.15	8531.1	930.4	1615.6	182.0	1930.1	9.58
323.15	9157.2	343.3	427.4	35.7	4406.9	26.00
1-Hexanol (x_A) + acetonitrile ($1 - x_A$)						
288.15	8345.7	771.5	−1217.5	−421.5	5766.9	26.60
298.15	9252.6	1026.6	2916.6	1758.1	−1012.6	15.42
313.15	9711.1	1316.0	789.3	234.4	3367.4	11.08
323.15	10637.0	1758.0	−2301.0	−590.0	7143.0	24.41

The ERAS model describes the excess molar enthalpy as the sum of a physical contribution and a chemical contribution.

$$H_{\mathrm{m}}^{\mathrm{E}} = H_{\mathrm{m}}^{\mathrm{E}}(\mathrm{phys}) + H_{\mathrm{m}}^{\mathrm{E}}(\mathrm{chem}) \tag{4}$$

The physical contribution is given by the following equation:

$$H_{\mathrm{m}}^{\mathrm{E}}(\mathrm{phys}) = (x_{\mathrm{A}} V_{\mathrm{A}}^{*} + x_{\mathrm{B}} V_{\mathrm{B}}^{*}) \left(\frac{\phi_{\mathrm{A}} P_{\mathrm{A}}^{*}}{\tilde{V}_{\mathrm{A}}} + \frac{\phi_{\mathrm{B}} P_{\mathrm{B}}^{*}}{\tilde{V}_{\mathrm{B}}} - \frac{P_{\mathrm{M}}^{*}}{\tilde{V}_{\mathrm{M}}} \right) \tag{5}$$

This work assumes that acetonitrile does not self-associate ($K_{\mathrm{B}} = 0$). That assumption leads the chemical contribution of the ERAS model to have the follow form:

$$H_{\mathrm{m}}^{\mathrm{E}}(\mathrm{chem}) = x_{\mathrm{A}} K_{\mathrm{A}} \Delta h_{\mathrm{A}}^{*} (\phi_{\mathrm{A}_1} - \phi_{\mathrm{A}_1}^{0}) + x_{\mathrm{A}} K_{\mathrm{AB}} \Delta h_{\mathrm{AB}}^{*} \times \frac{\phi_{\mathrm{B}_1}(1 - K_{\mathrm{A}} \phi_{\mathrm{A}_1})}{(v_{\mathrm{B}}/v_{\mathrm{A}}) + K_{\mathrm{AB}} \phi_{\mathrm{B}_1}} - \frac{P_{\mathrm{M}}^{*} V_{\mathrm{m}}^{\mathrm{E}}(\mathrm{chem})}{\tilde{V}_{\mathrm{M}}^{2}} \tag{6}$$

The variables involved in equations above are: mole fraction of each component x_i, characteristic volume V_i^*, characteristic pressure P_i^*, reduced volume $\tilde{V}_i$, volumetric fraction of components in mixture ϕ_i, characteristic pressure of mixture P_{M}^*, reduced volume of mixture $\tilde{V}_{\mathrm{M}}$, volumetric fraction of monomers in solution ϕ_{i_1}, volumetric fraction of monomers in pure component $\phi_{i_1}^0$ and chemical contribution of the excess molar volume $V_{\mathrm{m}}^{\mathrm{E}}(\mathrm{chem})$.

The chemical contribution to the excess molar volume is calculated in accordance with the ERAS model by the following equation:

$$V_{\mathrm{m}}^{\mathrm{E}}(\mathrm{chem}) = x_{\mathrm{A}} K_{\mathrm{A}} \Delta v_{\mathrm{A}}^{*} \tilde{V}_{\mathrm{M}} (\phi_{\mathrm{A}_1} - \phi_{\mathrm{A}_1}^{0}) + x_{\mathrm{A}} K_{\mathrm{AB}} \Delta v_{\mathrm{AB}}^{*} \tilde{V}_{\mathrm{M}} \times \frac{\phi_{\mathrm{B}_1}(1 - K_{\mathrm{A}} \phi_{\mathrm{A}_1})}{(v_{\mathrm{B}}/v_{\mathrm{A}}) + K_{\mathrm{AB}} \phi_{\mathrm{B}_1}} \tag{7}$$

The model requires information from pure components, thermal expansion coefficient α_i, isothermal compressibility β_i, molar mass M_i, molar volume v_i, association constant K, molar volume of association Δv_i^* and molar enthalpy of association Δh_i^*. These values are presented in Table 2.

The characteristic and reduced properties calculated by the model for each component are shown in Table 3.

Table 2
Thermal expansion coefficient α, isothermal compressibility β, molar volume v, association constant K, molar enthalpy of association Δh^* and molar volume of association Δv^*

Component	T (K)	$\alpha \times 10^4$ (K^{-1})	$\beta \times 10^4$ (MPa^{-1})	v (cm^3 mol^{-1})	K	Δh^* (J mol^{-1})	Δv^* (cm^3 mol^{-1})
Acetonitrile	288.15	13.530[a]	9.760[a]	52.080[b]	–	–	–
	298.15	13.680[c]	10.700[c]	52.780[b]	–	–	–
	313.15	13.890[a]	12.110[a]	53.930[b]	–	–	–
	323.15	14.030[a]	13.050[a]	54.700[b]	–	–	–
1-Pentanol	288.15	8.796[a]	8.310[a]	107.565[b]	167	−25,100[d]	−5.6[d]
	298.15	9.000[e]	8.820[e]	108.681[b]	135	−25,100	−5.6
	313.15	9.480[f]	9.650[f]	110.544[b]	72	−25,100	−5.6
	323.15	9.810[a]	10.250[a]	111.814[b]	54	−25,100	−5.6
1-Hexanol	288.15	8.631[a]	7.900[a]	124.057[b]	167	−25,100	−5.6
	298.15	8.800[e]	8.390[e]	125.321[b]	135	−25,100	−5.6
	313.15	9.170[f]	9.170[f]	127.298[b]	72	−25,100	−5.6
	323.15	9.420[a]	9.730[a]	128.674[b]	54	−25,100	−5.6

[a] Extrapolated.
[b] [22].
[c] [23].
[d] [24].
[e] [7].
[f] [21].

Table 3
Characteristic volume V^*, reduced volume $\tilde{V}$, characteristic pressure P^*, characteristic temperature T^* and expansion coefficient correction α^*

Component	T (K)	V^* (cm^3 mol^{-1})	$\tilde{V}$	P^* (J cm^{-3})	T^* (K)	$\alpha^* \times 10^5$ (K^{-1})
Acetonitrile	288.15	39.8302	1.3076	682.9433	4406.3	–
	298.15	40.0278	1.3186	662.7545	4464.2	–
	313.15	40.4037	1.3348	639.9239	4554.8	–
	323.15	40.6537	1.3455	628.9631	4616.3	–
1-Pentanol	288.15	89.7171	1.1989	400.4571	5887.0	8.1213
	298.15	89.9049	1.2088	405.9111	5883.0	8.3451
	313.15	90.2490	1.2249	415.9248	5867.0	9.9886
	323.15	90.3918	1.2370	425.2195	5840.7	10.6130
1-Hexanol	288.15	103.6153	1.1973	415.9053	5922.3	7.2346
	298.15	103.8791	1.2064	419.0730	5932.1	7.4530
	313.15	104.3048	1.2204	424.2182	5948.6	8.8619
	323.15	104.5540	1.2307	429.1634	5948.9	9.4828

The model has four adjustable parameters, cross-association constant K_{AB}, molar enthalpy of cross-association Δh^*_{AB}, molar volume of cross-association Δv^*_{AB} and Flory's parameter χ_{AB}. The first three parameters are found in Eqs. (6) and (7). Flory's parameter is used to calculate the characteristic pressure of mixture.

$$P^*_M = P^*_A\phi_A + P^*_B\phi_B - \phi_A\theta_B\chi_{AB} \tag{8}$$

In the ERAS model, both physical and chemical contributions are positive over the whole composition range and the physical contribution is the larger one. The model is able to correlate the main feature of the H^E_m data in the temperature range studied. Moreover, the behavior of the chemical contribution might be interpreted as the existence of alkanol oligomers disrupted especially at high acetonitrile concentration. The four adjustable parameters of the model as well as the standard deviation between experimental data and those calculated are given in Table 4.

As the physical contribution is the main one observed and with the purpose of decreasing the number of parameters, a simplified version with just the physical contribution was considered. The model then reduces only one adjustable parameter, the Flory's parameter. The values of the parameter and the standard deviation between experimental data and those of the ERAS model in its simplified form are shown in Table 5.

Table 4
Cross-association constant K_{AB}, Flory's parameter χ_{AB}, cross-association molar enthalpy Δh^*_{AB}, cross-association molar volume Δv^*_{AB} and standard deviation σ

T (K)	K_{AB}	χ_{AB} (J cm^{-3})	Δh^*_{AB} (J mol^{-1})	Δv^*_{AB} (cm^3 mol^{-1})	σ (J mol^{-1})
1-Pentanol + acetonitrile					
288.15	2.1	130	−6900	−1.2	±151.9
298.15	1.7	135	−6700	−2.0	±130.0
313.15	1.4	138	−7000	−1.0	±164.3
323.15	0.8	144	−6700	−2.5	±234.3
1-Hexanol + acetonitrile					
288.15	1.6	124	−4500	−1.1	±183.4
298.15	1.4	140	−3500	−1.1	±143.0
313.15	1.3	147	−6000	−1.3	±180.0
323.15	0.6	160	−6000	−1.5	±183.9

The behavior of the ERAS model with both contributions and with only one are shown in Figs. 1 and 2.

Analyzing Tables 4 and 5 as well as Figs. 1 and 2, the model in its simplified form correlates the experimental data better than the model in its complete form. Moreover, the ERAS model

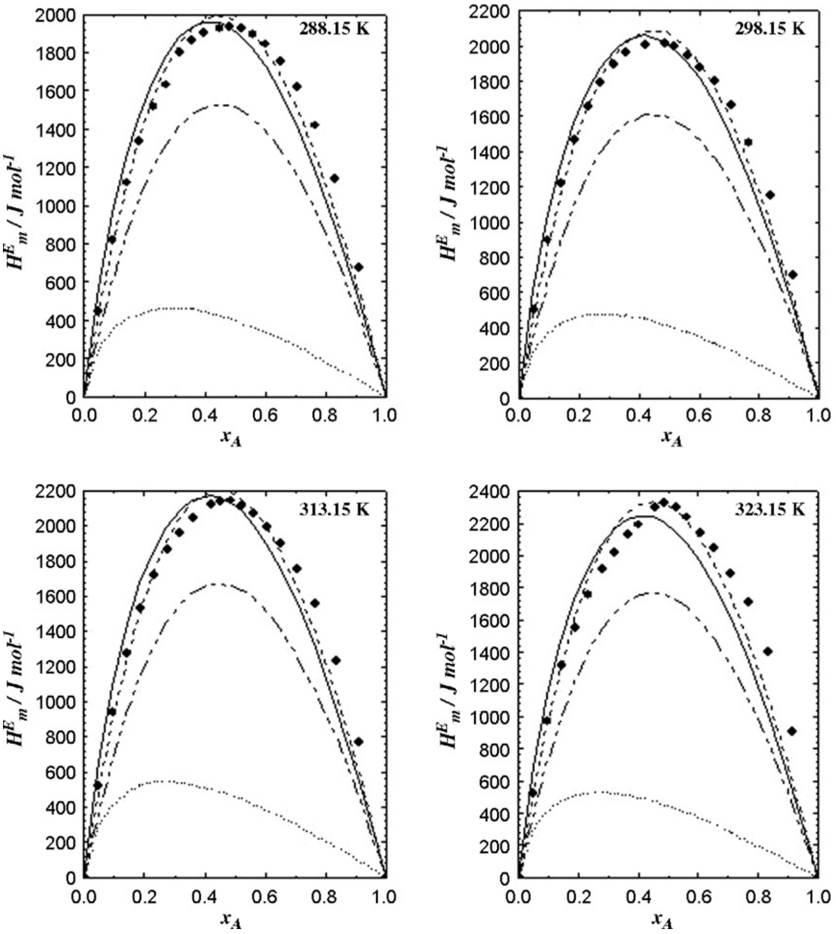

Fig. 1. Excess molar enthalpy as a function of 1-pentanol mole fraction for acetonitrile + 1-pentanol mixtures at different temperatures: (◆) experimental data; (—) ERAS full version; (····) ERAS chemical contribution; (– –) ERAS physical contribution; (- -) ERAS simplified version.

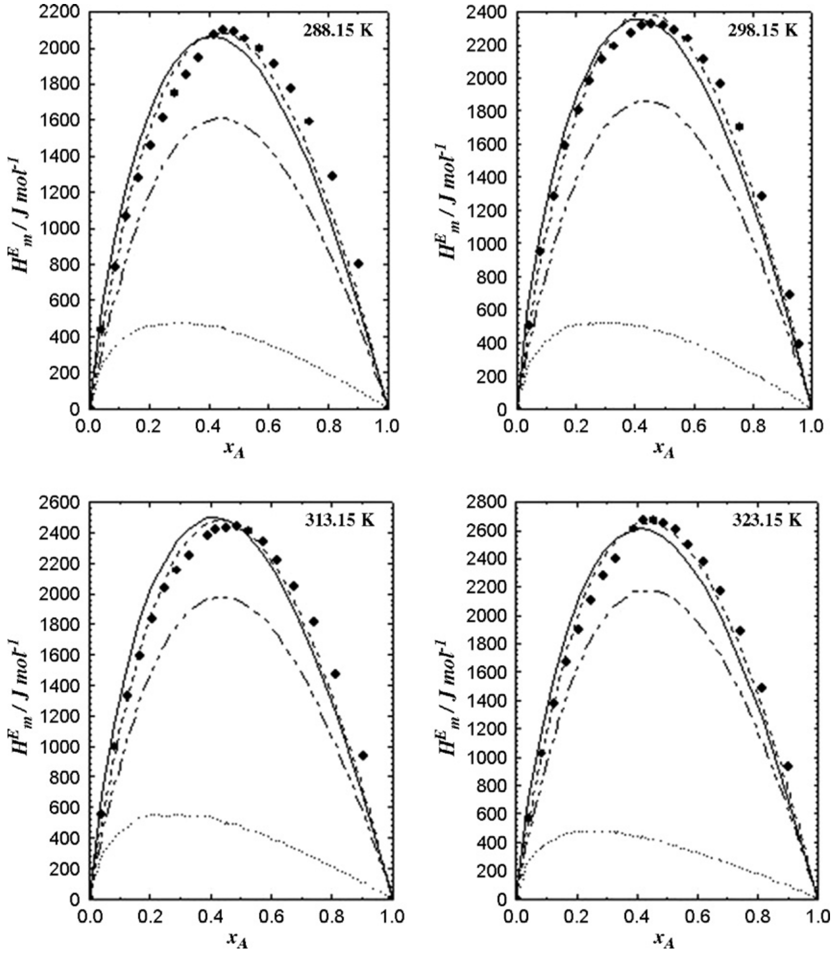

Fig. 2. Excess molar enthalpy as a function of 1-hexanol mole fraction for acetonitrile + 1-hexanol mixtures at different temperatures: (♦) experimental data; (—) ERAS full version; (····) ERAS chemical contribution; (– –) ERAS physical contribution; (- -) ERAS simplified version.

in its simplified form shows an adjustable parameter higher than that in its complete version. This behavior might be interpreted as an advantageous mathematical compensation of the neglected chemical term. The fact that one adjustable parameter correlates the data better than four adjustable parameters might be a surprise, for with empirical fits, such as Redlich–Kister expansion, more parameters lead to better fit. In semi-theoretical models, such as ERAS model, the situation might be different. An inappropriate contribution term of the model equation can be compensated, but not fully, by other contribution term. As a final remark, the performance of the ERAS model can reinforce the analysis that the physical contribution plays the major role in the behavior of H_m^E of the studied mixtures.

Table 5
Flory's parameter χ_{AB} and standard deviation σ

T (K)	χ_{AB} (J cm^{-3})	σ (J mol^{-1})
1-Pentanol + acetonitrile		
288.15	164	±80.5
298.15	171	±73.3
313.15	177	±88.5
323.15	187	±135.6
1-Hexanol + acetonitrile		
288.15	156	±105.3
298.15	176	±82.2
313.15	181	±94.6
323.15	192	±87.0

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2006.08.007.

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