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Application of the extended real associated solution theory to excess molar enthalpies and excess molar volumes of binary mixtures of (benzene or 1-alkanol+quinoline)

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Abstract

Excess molar enthalpies and excess molar volumes of binary mixtures of (benzene or methanol or ethanol or 1-propanol or 1-butanol+quinoline) as a function of composition at a pressure of 1 atm and a temperature of 298.15 K have been used to test the Extended Real Solution Theory, ERAS, of nonelectrolyte solutions.

The ERAS theory accounts for free volume effects according to the Flory–Patterson theory and for association effects: self and cross-association between the molecules involved. The ERAS theory results for the binary mixtures (benzene or an alkanol+quinoline) indicates strong hydrogen bonding effects between unlike molecules given by the predicted hydrogen bonding energy between two dissimilar compounds. Comparison is also made between the chemical and physical contribution to the ERAS theory.

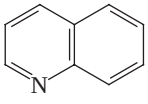
The Extended Real Associated Solution theory describes the published V_m^E data better than the published H_m^E data.

Keywords: Excess molar enthalpy; Excess molar volume; Alkanols; ERAS

1. Introduction

The excess molar enthalpies H_m^E of binary mixtures of (benzene or methanol or ethanol or 1-propanol or 1-butanol+quinoline) as a function of composition at 1 atm and 298.15 K have been reported previously by our research group [1]. The excess molar volumes, V_m^E for the alkanols and quinoline have also been reported in the literature [2].

The chemical formula for quinoline is C_9H_7N and the structure is given below



quinoline (C_9H_7N)

The experimental results were used to test the Extended Real Associated Solution (ERAS) theory of solutions. The ERAS theory is a combination of the real associated solution model of Kretschmer and Wiebe [3], Renon and Prausnitz [4], Kehiaian [5], Kehiaian and Treszczanowicz [6] and Flory's [7–10] equation of state.

The ERAS theory combines the association effects arising from hydrogen bonding with free volume effects and the differences in the van der Waals interactions between unlike molecules in the mixture. It is assumed that the associating molecules build up linear chains. The derivation of the ERAS model is based upon the partition function of a mixture of self associated (A) and inert molecules (B) as described by Heintz [11] and is expressed as the sum of a physical and a chemical contribution. In its original form, any excess property (F^E) of a binary mixture containing a self-associating liquid A and an inert component B is expressed as the sum of a physical and a chemical contribution, i.e.

$$F^E = F^E_{phys} + F^E_{chem} \quad (1)$$

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The physical part arises from van der Waals interactions, and the chemical part from hydrogen bonding.

Excess enthalpy

$$H^{E}_{ERAS} = H^{E}_{chem} + H^{E}_{phys} \tag{2}$$

with

$$H^{E}_{chem} = x_A K_A \Delta h^*_A (\varphi_{1A} - \varphi^0_{1A}) + x_B \Delta h^*_B K_B (\varphi_{1B} - \varphi^0_{1B}) + x_A \Delta h^*_{AB} K_{AB} \frac{\varphi_{1B}(1 - K_A \varphi_{1A})}{\frac{V_B}{V_A}(1 - K_B \varphi_{1B}) + K_{AB} \varphi_{1B}} - \frac{P^*_M V^E_{chem}}{\tilde{V}^2_M} \tag{3}$$

and

$$H^{E}_{phys} = (x_A V^*_A + x_B V^*_B)\left(\frac{\Phi_A P^*_A}{\tilde{V}_A} + \frac{\Phi_B P^*_B}{\tilde{V}_B} - \frac{P^*_M}{\tilde{V}_M}\right) \tag{4}$$

Excess volume

$$V^{E}_{ERAS} = V^{E}_{chem} + V^{E}_{phys} \tag{5}$$

with

$$V^{E}_{chem} = x_A \tilde{V}_M \Delta v^*_A K_A (\varphi_{1A} - \varphi^0_{1A}) \tag{6}$$

and

$$V^{E}_{phys} = (x_A V^*_A + x_B V^*_B)(\tilde{V}_M - \Phi_A \tilde{V}_A - \Phi_B \tilde{V}_B) \tag{7}$$

This work reports the applicability of the ERAS theory to predict simultaneously the excess molar enthalpies and the excess molar volumes for polarizable or polar mixtures at atmospheric pressure and at 298.15 K.

2. Results and discussion

The excess molar volumes for the binary mixtures were taken from the literature and used to determine the ERAS theory parameters. The ERAS pure component parameters needed for the ERAS correlation are given in Tables 1 and 2.

The ERAS fitted properties, ΔK^*_{AB}, ΔX^*_{AB}, Δh^*_{AB} and Δv^*_{AB}, where ΔK^*_{AB} is the cross association constant, ΔX^*_{AB} is the interchange energy due to the van der Waal's interaction, Δh^*_{AB} the hydrogen bonding energy between two dissimilar compounds and Δv^*_{AB} the reaction volume of the hydrogen bonding, respectively and is given in Table 3.

The ERAS model accounts for free volume effects according to the Flory–Patterson model and for association effects, self and cross-association between the molecules involved. Pure component molar volume, V_i* and vapour pressure, P^*_i are obtained by adjusting the ERAS equation of state to density, ρ_i, the thermal expansion coefficient, α and the compressibility, κ of the pure liquids.

The parameters adjusted to the mixture properties are Δh^*_{AB}, Δv^*_{AB} ΔK^*_{AB} and ΔX^*_{AB}. These parameters were determined by a fitting procedure applied simultaneously to the experimental H^E_m and V^E_m data for the binary mixtures (benzene or methanol or ethanol or 1-propanol or 1-butanol + quinoline).

The ΔK^*_{AB} values decrease for the binary mixtures (methanol or ethanol or 1-propanol or 1-butanol + quinoline), as the carbon number increases. There is therefore greater cross association for methanol and quinoline than for 1-butanol and quinoline.

The ERAS prediction is $H^E_m > 0$ for the binary mixture (benzene + quinoline) which indicates that the breakdown of π–π and N–H interactions due to self-dissociation of the benzene molecules and quinoline molecules, respectively are greater than any cross-association effects. The ERAS prediction is $V^E_m < 0$ which is due to a packing effect.

The results reveal strong negative values of Δh^*_{AB} and Δv^*_{AB} for the binary solution (an alkanol + quino-

Table 1
Pure component parameters needed for ERAS theory calculations

Compound	K_{298}	Δh^*	Thermal expansion coefficient (α)	Isothermal compressibility (κ)
		J mol^{-1}	10^{-4}/K	10^{-4}/MPa
Benzene	0.6 [13]	−15.0 [13]	12.18 [15]	9.66 [12]
Methanol	986 [14]	−25.1 [15]	11.89 [14]	12.48 [14]
Ethanol	317 [11]	−25.11 [15]	11.20 [11]	11.53 [11]
1-Propanol	197 [11]	−25.1 [15]	10.20 [14]	10.06 [14]
1-Butanol	175 [14]	−25.1 [14]	9.32 [14]	9.42 [14]
Quinoline			7.32 [12]	7.93 [12,16]

Table 2
Pure component parameters needed for ERAS calculations

Compound	V_m	P^*	V^*
	cm^3 mol^{-1}	J cm^{-3}	cm^3 mol^{-1}
Benzene	89.40	626.3	69.26
Methanol	40.73	443.6	31.70
Ethanol	58.67	426.4	46.14
1-Propanol	75.15	433.9	60.04
1-Butanol	91.97	451.6	74.53
Quinoline	118.52	389.7	99.59

Table 3
The ERAS fitted properties ΔK^*_{AB}, ΔX^*_{AB}, Δh^*_{AB} and Δv^*_{AB} for the binary mixtures (benzene or methanol or ethanol or 1-propanol or 1-butanol + quinoline)

Binary mixture	ΔK^*_{AB}	ΔX^*_{AB}	Δh^*_{AB}	Δv^*_{AB}
		J cm^{-3}	J mol^{-1}	cm^3 mol^{-1}
Benzene + quinoline	20.0	1.90	−6100	−20
Methanol + quinoline	11.5	0.90	−20,500	−29
Ethanol + quinoline	8.0	0.85	−9200	−22
1-Propanol + quinoline	6.1	0.84	−6570	−20
1-Butanol + quinoline	5.5	0.01	−4920	−20