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Fluid Phase Equilibria 235 (2005) 42–49

FLUID PHASE EQUILIBRIA

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Topological and thermodynamic investigations of molecular interactions in binary mixtures: Molar excess volumes and molar excess enthalpies

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Received 18 November 2003; received in revised form 8 June 2005; accepted 22 June 2005

Abstract

Molar excess volumes and molar excess enthalpies of butyl acetate (i) with cyclohexane or benzene or toluene or *o*-, *m*- or *p*-xylene (j) binary mixtures have been measured dilatometrically and calorimetrically over the entire composition range at 308.15 K. The observed data have also been analyzed in terms of graph theoretical approach. The analysis of V^E data by graph theoretical approach suggests that butyl acetate in pure state exists as associated entity and $(i+j)$ mixtures are characterized by the presence of $(i\text{–}j)$ molecular entity. It has further been observed that V^E and H^E values calculated by this approach agree well with the corresponding experimental values. The presence of molecular entity is further confirmed by IR study of $(i+j)$ mixture.

Keywords: Molar excess volume; Molar excess enthalpy; Butyl acetate; Aromatics; Graph theoretical approach

1. Introduction

A number of experimental as well as theoretical studies on thermodynamic properties for alkyl ester with alkanes [1–9], aromatic hydrocarbons [8–17], alcohols [18,19], chloroalkane [20] and acetonitrile [16,21] have been reported in literature. Among them, systemic data for alkyl ester + aromatic polar solvent are relatively rare [10–17]. Alkyl esters are characterized by dipole–dipole interactions in the pure state [1–3]. The degree and strength of dipole–dipole interactions decreases with the increasing size of alkyl group in the esters. The additions of inert solvents like alkane generally break the orientation order of pure alkyl esters to give the positive value of excess thermodynamic functions like excess molar volume, V^E, excess molar enthalpy, H^E, and excess molar Gibb's free energy, G^E [4,5]. However, these values become very less and even negative in the mixtures of alkyl esters + aromatic hydrocarbons [10,11,14,15]. Specific interactions of dipole–induce dipole type are postulated to account for such behavior [14,15].

Moreover, it has been revealed [22–26] that that graph theoretical approach, based on molecular connectivity parameter [27] of third degree, could be of great use not only in evaluating their V^E and H^E but also in understanding the nature of molecular interactions between the components of binary mixtures. These considerations prompted us to carry out a systemic study on the thermodynamic properties of alkyl esters with aromatic hydrocarbons. In first paper of this series, we report the measured V^E and H^E data for butyl

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doi:10.1016/j.fluid.2005.06.011

Table 1
Densities, ρ, and refractive indices, n_D, of the pure components at 308.15 K

Substance	ρ (kg m^{-3})		n_D	
	This work	Literature	This work	Literature
Butyl acetate	865.45	865.4[a]	1.3908	1.3910[a]
Cyclohexane	764.43	764.46[b]	1.4205	1.4201[c]
Benzene	862.93	862.95[b]	1.4921	1.49170[d]
Toluene	852.80	852.85[b]	1.4885	1.48870[d]
o-Xylene	867.41	867.38[b]	1.5031	1.50295[e,f]
m-Xylene	851.53	851.57[b]	1.4946	1.49464[e,f]
p-Xylene	847.91	847.87[b]	1.4879	1.4881[d]

[a] Ref. [21].
[b] Ref. [31].
[c] Ref. [32].
[d] Ref. [33].
[e] Ref. [28].
[f] At 298.15 K.

acetate + cyclohexane or benzene or toluene or *o*-, *m*- or *p*-xylene at 308.15 K and their interpretation in terms of graph theoretical approach.

2. Experimental

Butyl acetate (BA) (Merck) was dried over anhydrous magnesium sulphate and then fractionally distilled [28]. The middle fraction of distilled BA was then dried over type 0.3 nm molecular sieves (Merck) in an amber colored bottle for several days before use. Cyclohexane, benzene, toluene and xylenes (Merck) were purified with standard procedure [28,29]. The purities of the purified samples were checked by measuring their densities and refractive indices at 308.15 K as described earlier [30] and these compared well with the literature values [21,28,31–33] as shown in Table 1.

Molar excess volumes, V^E, for the binary mixtures have been measured dilatometrically at 308.15 K in the manner described elsewhere [34]. The temperature of the thermostat was controlled within ±0.01 K. The uncertainties in the measured V^E values are ±0.5%.

Molar excess enthalpies (H^E) were determined with a heat flux calorimeter (model C-80, Setaram, France) at 308.15 K as described elsewhere [35]. The uncertainties in the measured H^E values are about ±0.1 J mol^{-1}.

3. Results and discussion

The V^E and H^E for BA + cyclohexane or benzene or toluene or *o*-, *m*-, *p*-xylene as a function of mole fraction, x_i, at 308.15 K are reported in Tables 2 and 3 and shown in Figs. 1 and 2. The results were fitted to the Redlick-Kister equation

$$X^E(X = V \text{ or } H) = x_i(1 - x_i)\sum_{n=0}^{3} X_n(1 - 2x_i)^n \qquad (1)$$

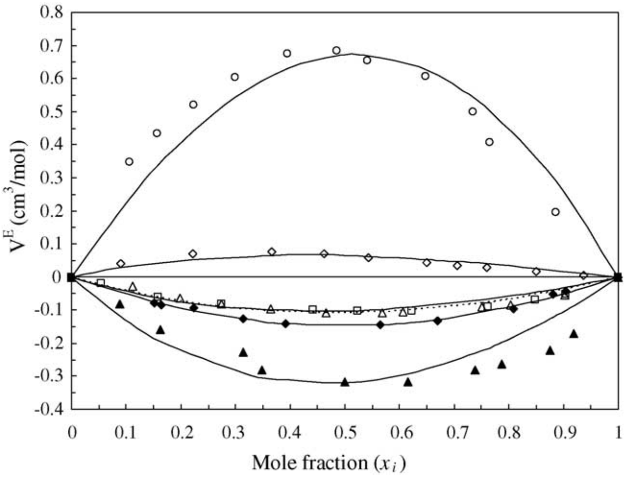

Fig. 1. Excess volumes (V^E) for butyl acetate (i) + benzene (j) (◇) or toluene (□) or *o*-xylene (△) or *m*-xylene (◆) or *p*-xylene (▲) or cyclohexane (○) at 308.15 K as a function of mole fraction of butyl acetate (x_i). The curves represent the values calculated from Eq. (1).

where x_i is the mole fraction of BA and X_n (n = 0–3) are adjustable parameters. These parameters were evaluated by method of least squares and are given along with standard deviations, $\sigma(X)$, in Table 4. The V^E values for BA + benzene at 308.15 K have been reported by Oswal [14]. Our experimental curve for BA + benzene system is in agreement with that reported by him. V^E values of *o*-, *m*- or *p*-xylene systems at 303.15 K have also been reported by Ramachandran et al. [15]. Our experimental values for these systems are lower than their values at each mole fraction because reported values are at lower temperature. However, the general shape of the curves is same. We are unaware of any previously published H^E data for the present systems at 308.15 K with which to compare our results. The H^E values for all the binary systems are negative over the entire composition range except

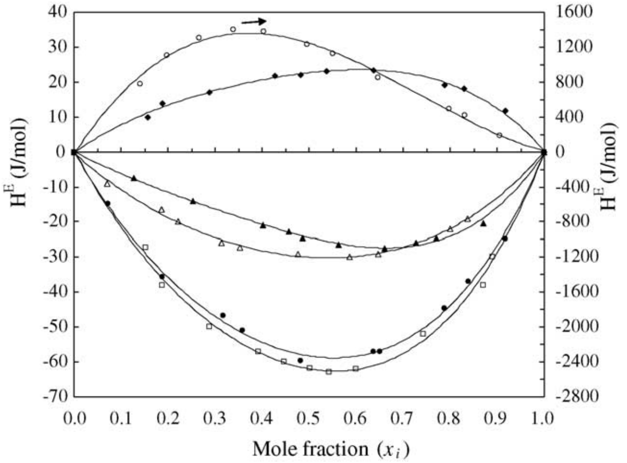

Fig. 2. Excess enthalpies, H^E, of butyl acetate (i) + benzene (j) (▲), toluene (□), *o*-xylene (△), *m*-xylene (◆), *p*-xylene (●) or cyclohexane (○) at 308.15 K as a function of mole fraction of butyl acetate (x_i). The curves represent the values calculated from Eq. (1).