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Excess Properties of Binary Alkanol + Diisopropyl Ether (DIPE) or + Dibutyl Ether (DBE) Mixtures and the Application of the Extended Real Associated Solution Model

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Experimental results are reported at 298.15 K for excess molar volumes V^E and excess molar enthalpies H^E for binary mixtures of methanol, ethanol, 2-propanol, 1-butanol, and 2-butanol with diisopropyl ether (DIPE) and/or with dibutyl ether (DBE). A vibrating-tube densitometer was used to determine V^E, and H^E was measured using a quasi-isothermal flow calorimeter. The applicability of the extended real associated solution model has been investigated for describing the experimental excess properties presented as well as literature data of alkanol−ether mixtures containing DIPE and DBE.

Introduction

Oxygenates (alcohols and tertiary ethers) have become important gasoline additives over the past decade. At first oxygenates were used as octane-enhancing components, but then it was noticed that they also improve the combustion of gasoline and reduce emissions. For proper design of synthesis and separation processes of ethers, the phase behavior and thermodynamic properties of the fluid mixtures involved need to be known.

In previous papers, the experimental H^E values of binary and ternary mixtures containing methyl *tert*-butyl ether (MTBE) (Tusel-Langer et al., 1991; Tusel-Langer and Lichtenthaler, 1991), ethyl *tert*-butyl ether (ETBE) (Martín et al., 1995), or *tert*-amyl methyl ether (TAME) (Kammerer and Lichtenthaler, 1996; Kammerer et al., submitted) as well as experimental V^E values and excess heat capacities $C_p{}^E$ of binary, ternary, and quaternary mixtures containing ETBE (Mier et al., 1994; 1995) have been published. Kammerer and Lichtenthaler (1998) have reported experimental results of H^E and V^E for binary mixtures of 1-propanol or 2-propanol with DIPE and for 1-butanol or 2-butanol with DBE at 298.15 K. The ERAS (extended real associated solution) model has been applied for the simultaneous description of the thermodynamic excess properties. Continuing these investigations in this paper, experimental results of H^E and V^E are reported at 298.15 K for binary mixtures of methanol, ethanol, 2-propanol, 1-butanol, or 2-butanol with diisopropyl ether (DIPE) and/or with dibutyl ether (DBE). The experimental data and published data of H^E and V^E (Letcher and Govender, 1995; Serna et al., 1995; Villamañan et al., 1982) are used to test the applicability of the ERAS model for describing all excess properties while using one particular set of system-specific parameters for each system.

Experimental Section

Materials. The substances were obtained from standard laboratory sources and were used without further purification. The purities were 99.8% for methanol (Merck), 99.7% for absolute ethanol (Riedel de Haën), >99.7% for 2-propanol (Merck), >99.4% for 1-butanol (Baker Analyzed), >99% for 2-butanol (Merck), >99% for diisopropyl ether (Merck), and >99% for dibutyl ether (Merck). All substances were carefully dried with molecular sieves and degassed.

Apparatus and Procedures. Excess molar volumes were measured using an Anton Paar DMA 60 vibrating-tube densitometer with a DMA 602 HT measuring cell. The densities of the pure components and the binary mixtures were measured with high accuracy ($\Delta\rho < \pm 10^{-5}$ g·cm^{-3}). From these data, excess molar volumes were determined according to the following relation:

$$V^E = \frac{\sum_i x_i M_i}{\rho_M} - \sum_i \frac{M_i}{\rho_i} x_i \qquad (1)$$

where ρ_i are the densities and M_i the molar masses of the pure components (i = A, B) and x_i are the mole fractions of the mixture and ρ_m is the density of the mixture. V^E data are obtained with an accuracy of ±0.2% of the maximum of the V^E curve considered, and the uncertainty of the mole fraction is less than ±0.0001.

Excess molar enthalpies were measured using a modified TRONAC 1250 calorimeter. This quasi-isothermal flow calorimeter and the operating procedure have been described in detail (Heintz and Lichtenthaler, 1979). The accuracy of the H^E data obtained is estimated to be less than $\pm 0.01 H^E$ (but at least ±1 J·mol^{-1}). The mole fraction x is accurate to the third decimal place.

ERAS Model

The ERAS model was used to correlate the experimental results for the mixtures investigated. As this model has been described in detail several times (Heintz, 1985; Funke et al., 1989), only a brief summary of the relevant equations will be presented here. The ERAS model combines association effects arising from hydrogen bonding with free volume effects arising from differences of the van der Waals interactions between like and unlike molecules in the

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mixture. Excess properties are split into a chemical and a physical contribution to take into account the different intermolecular interactions between molecules in the mixture.

The equations for the excess molar enthalpy H^E and the excess molar volume V^E of binary mixtures (A + B) with A = alkanol and B = ether are

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

where

$$H^E_{chem} = x_A \Delta h^*_A K_A(\phi_{A1} - \phi^\circ_{A1}) + x_B \Delta h^*_B K_B(\phi_{B1} - \phi^\circ_{B1}) + x_A \Delta h^*_{AB} K_{AB} \frac{\phi_{B1}(1 - K_A\phi_{A1})}{(V_B^{mol}/V_A^{mol})(1 - K_B\phi_{B1}) + K_{AB}\phi_{B1}} - \frac{P^*_M V^E_{chem}}{\tilde{V}_M{}^2} \tag{3}$$

and

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

and also

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

where

$$V^E_{chem} = \tilde{V}_M\left\{x_A \Delta v^*_A K_A(\phi_{A1} - \phi^\circ_{A1}) + x_B \Delta v^*_B K_B(\phi_{B1} - \phi^\circ_{B1}) + x_A \Delta v^*_{AB} \frac{K_{AB}\phi_{B1}(1 - K_A\phi_{A1})}{(V_B^{mol}/V_A^{mol})(1 - K_B\phi_{B1}) + K_{AB}\phi_{B1}}\right\} \tag{6}$$

and

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

The physical contribution is derived from Flory's equation of state, which holds both for the pure components (subscripts A or B) and for the mixtures (subscript M)

$$\frac{\tilde{P}_i \tilde{V}_i}{\tilde{T}_i} = \frac{\tilde{V}_i^{1/3}}{\tilde{V}_i^{1/3} - 1} - \frac{1}{\tilde{V}_i \tilde{T}_i}, \quad i = \text{A, B, M} \tag{8}$$

where

$$\tilde{V}_i = V_i^{mol}/V^*_i,\ \tilde{P}_i = P_i/P^*_i, \text{ and } \tilde{T}_i = T_i/T^*_i$$

are the reduced pressure, volume, and temperature, respectively. Φ_A and Φ_B are the hard-core volume fractions, defined as

$$\Phi_i = \frac{x_i V^*_i}{x_A V^*_A + x_B V^*_B}, \quad i = \text{A, B} \tag{9}$$

The pure component reduction parameters are determined by fitting the Flory equation of state to experimental PVT data of the pure components. The reduction parameters P^*_M and T^*_M are obtained using the following mixing rules:

$$P^*_M = \Phi_A P^*_A + \Phi_B P^*_B - \Phi_A \theta_B X_{AB}$$

$$T^*_M = \frac{P^*_M}{P^*_A \Phi_A / T^*_A + P^*_B \Phi_B / T^*_B} \tag{10}$$

θ_B is the surface fraction of component B in the mixture, defined as

$$\theta_B \equiv 1 - \theta_A = \frac{(s_B/s_A)\Phi_B}{\Phi_A + (s_B/s_A)\Phi_B} \tag{11}$$

where s_A and s_B are the surface-to-volume ratios of molecules A and B calculated using the Bondi method of molecular group contributions (Bondi, 1968). X_{AB} in eq 10 (the only adjustable parameter of the physical part) is the energetic interaction parameter characterizing the differences of dispersive intermolecular interactions between molecules A and B in the mixture and in the pure components. To use eqs 3, 4, 6, and 7, $\tilde{V}_M$ has to be first obtained from eq 8 with $\tilde{P}_M$ and $\tilde{T}_M$ calculated using the mixing rules for P^*_M and T^*_M (eq 10) with X_{AB} as an adjustable parameter. It should be noticed that, for associating molecules, the procedure to obtain the reduction parameters of the physical contribution is different from the method for nonassociating molecules, as discussed by Heintz (1985) and summarized by Kammerer and Lichtenthaler (1996).

The chemical contribution to the excess properties arises from chemical interactions between the molecules, in particular, hydrogen bonding. Assuming equilibrium of linear chain association of the components A and B and the possibility of cross association, the following reactions occur:

$$\begin{gathered} A_m + A \xleftrightarrow{K_A} A_{m+1} \\ B_n + B \xleftrightarrow{K_B} B_{n+1} \\ A_m + B_n \xleftrightarrow{K_{AB}} A_m B_n \end{gathered} \tag{12}$$

The association constants K_i are assumed to be independent of the chain lengths m and n. Their temperature dependence is given by the following equation:

$$K_i \equiv K_{i0} \exp\left\{-\frac{\Delta h^*_i}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right\}, \quad i = \text{A, B, AB} \tag{13}$$

where Δh^*_i is the association energy per mole of hydrogen bonds. Correspondingly, the reaction volume Δv^*_i in eq 6 is related to the formation of linear chains. ϕ_{i1} and ϕ°_{i1} (i = A, B) are the volume fractions of the monomeric species A_1 (alkanol) and B_1 (ether) in the mixture and in the pure components, respectively. They can be determined by solving the following nonlinear equations:

$$\begin{gathered} \Phi_A = \frac{\phi_{A1}}{(1 - K_A\phi_{A1})^2}\left\{1 + \frac{V_A^{mol} K_{AB}\phi_{B1}}{V_B^{mol}(1 - K_B\phi_{B1})}\right\} \\ \Phi_B = \frac{\phi_{B1}}{(1 - K_B\phi_{B1})^2}\left\{1 + \frac{K_{AB}\phi_{B1}}{(1 - K_A\phi_{A1})}\right\} \end{gathered} \tag{14}$$

with ϕ_{i1} equal to ϕ°_{i1} if $\Phi_i = 1$.

Results and Discussion

Experimental data of the excess molar volumes V^E and the excess molar enthalpy H^E at 298.15 K of the binary

Table 1. Experimental Excess Molar Volumes V^E at 298.15 K

x	V^E/cm^3·mol^{-1}	x	V^E/cm^3·mol^{-1}	x	V^E/cm^3·mol^{-1}
(x)methanol + (1 − x)DIPE					
0.1336	−0.557	0.4055	−1.015	0.6963	−0.849
0.2154	−0.755	0.5057	−1.007	0.7996	−0.662
0.2773	−0.892	0.6172	−0.943	0.8851	−0.424
(x)ethanol + (1 − x)DIPE					
0.1024	−0.415	0.4139	−0.837	0.6965	−0.710
0.2186	−0.674	0.5136	−0.851	0.7954	−0.547
0.3091	−0.782	0.5923	−0.807	0.8922	−0.325
(x)1-butanol + (1 − x)DIPE					
0.1191	−0.599	0.4095	−1.132	0.6979	−0.920
0.2274	−0.898	0.5122	−1.107	0.7886	−0.720
0.3041	−1.045	0.6038	−1.057	0.8848	−0.457
(x)2-butanol + (1 − x)DIPE					
0.1076	−0.306	0.4144	−0.631	0.6934	−0.543
0.2279	−0.522	0.4987	−0.641	0.7912	−0.427
0.3029	−0.578	0.6078	−0.603	0.8733	−0.293
(x)methanol + (1 − x)DBE					
0.0800	−0.056	0.3910	−0.170	0.6980	−0.175
0.1010	−0.068	0.4155	−0.181	0.7131	−0.162
0.1318	−0.099	0.4890	−0.183	0.8000	−0.145
0.1940	−0.113	0.5430	−0.189	0.8137	−0.129
0.2513	−0.149	0.6020	−0.186	0.8990	−0.091
0.2940	−0.147	0.6274	−0.179	0.9241	−0.043
(x)ethanol + (1 − x) DBE					
0.0759	−0.058	0.4006	−0.147	0.6672	−0.135
0.0950	−0.068	0.4091	−0.150	0.6922	−0.132
0.1426	−0.098	0.4979	−0.151	0.7687	−0.109
0.1842	−0.108	0.5204	−0.148	0.7954	−0.106
0.2619	−0.127	0.5975	−0.146	0.8029	−0.101
0.2856	−0.134	0.5978	−0.143	0.8901	−0.069
0.3634	−0.144	0.6116	−0.144	0.9441	−0.047
(x)2-propanol + (1 − x)DBE					
0.0606	0.055	0.4163	0.136	0.6951	0.084
0.1538	0.095	0.5107	0.129	0.7945	0.059
0.2304	0.119	0.6069	0.108	0.8949	0.029
0.3154	0.131				

Table 2. Experimental Excess Molar Enthalpy H^E at 298.15 K

x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}
(x)2-propanol + (1 − x)DBE					
0.0538	318.4	0.5709	1009.0	0.8693	383.2
0.2406	903.5	0.6892	846.5	0.9395	194.5
0.4250	1063.5	0.7871	574.9	0.9768	88.5
(x)1-butanol + (1 − x)DIPE					
0.0754	255.3	0.4272	480.9	0.7208	275.6
0.1116	338.1	0.5338	427.9	0.8229	173.4
0.2147	458.1	0.6007	369.9	0.9156	79.9
0.3102	494.9	0.6770	462.6		
(x)2-butanol + (1 − x)DIPE					
0.1112	468.6	0.5328	780.9	0.7200	554.7
0.2140	691.6	0.6067	711.7	0.8223	372.5
0.3094	791.9	0.6761	611.1	0.9153	186.2
0.4262	826.6				

systems investigated are listed in Tables 1 and 2; the dependence on mole fraction is shown in Figures 1−4 together with the results of the model calculations. Figures 1−4 also show data available from the literature. The excess molar volumes reported by Blanco et al. (1994) for methanol + DIPE and ethanol + DIPE agree with the new results of this work within experimental accuracy.

Each mixture contains one strong self-associating component (an alkanol) and a non-self-associating component (an ether) which, however, can form associates with the alkanol through hydrogen bonding. The chemical part of the excess properties is the combination of two contributions of opposite signs, namely, a positive term due to the destruction of alkanol−alkanol hydrogen bonds upon mixing and a negative term due to the formation of alkanol−ethers complexes in the mixture. For DIPE (a branched ether) + alkanol systems the absolute values of the excess volumes are significantly larger (the excess enthalpies are smaller) compared to the values of the corresponding binary mixtures with DBE (a linear ether) (Figures 1−3). For DIPE the values of V^E significantly increase going from 1-butanol to 2-butanol (Figure 4), which is similar to the behavior of this ether with two isomeric propyl alcohols (Kammerer and Lichtenthaler, 1998). This is due to the fact that the formation of alkanol−ether cross-associates is more pronounced in mixtures with linear alkanols. With DBE even a change from negative to positive values of V^E is observed going from 1-propanol to 2-propanol (Figure 3), which is similar to the behavior of this ether with two isomeric butyl alkanols (Kammerer and Lichtenthaler, 1998). The same tendency is observed for the excess molar enthalpies of these systems. For the mixtures of DIPE and DBE with linear alkanols (Figures 2−4) the values of H^E do not change very much when going from ethanol to 1-butanol, but the excess molar volumes V^E do become more negative. For the systems with methanol the values of H^E are less positive and the values of V^E are more positive due to the strong association of this alkanol.

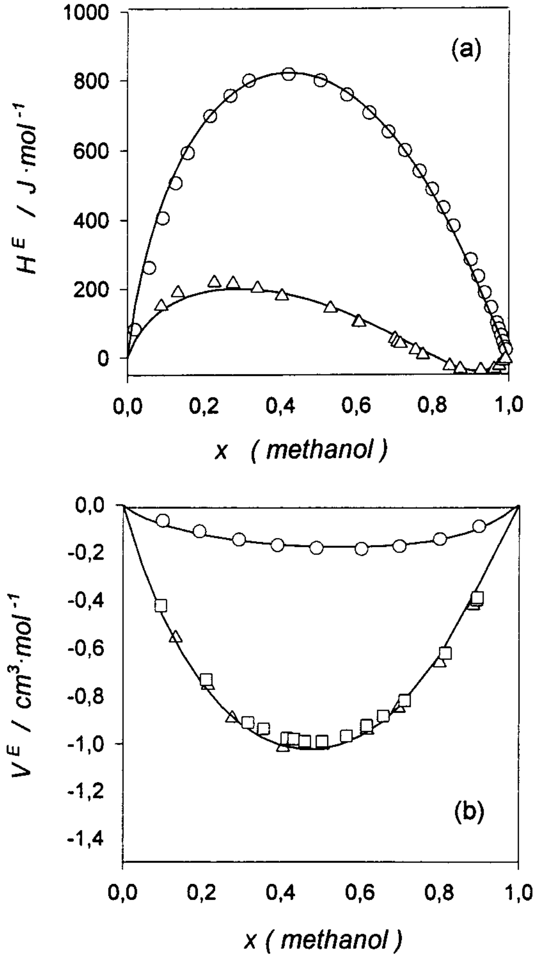

Figure 1. Excess molar enthalpy (a) and excess molar volume (b) of (○) {(x)methanol + (1 − x)DBE} (H^E from Villamañan et al., 1982) and (△) {(x)methanol + (1 − x)DIPE} (H^E from Letcher and Govender, 1995; (□) V^E from Blanco et al., 1994). (—) ERAS model calculation using parameters listed in Tables 3 and 4.

As the mixtures investigated exhibit strong hydrogen bonding, the chemical contribution dominates the excess properties. The physical contribution is described with the

Table 3. Parameters of Pure Substances Used in ERAS Calculations

substance	V_{mol} ^{298}/cm^3·mol^{-1}	K_A^{298}	P*/J·cm^{-3}	V*/cm^3·mol^{-1}	T*/K	s/nm^{-1}
methanol[a]	40.7	986	422.8	32.1	4978	16.49
ethanol[a]	58.7	328	403.7	47.1	5239	15.43
1-propanol[a]	75.2	197	412.5	61.1	5493	14.90
2-propanol[a]	77.0	131	378.2	62.3	5409	14.87
1-butanol[a]	92.0	175	425.4[b]	75.1[b]	5588[b]	14.21
2-butanol[a]	92.4	68[b]	388.7[b]	75.4[b]	5572[b]	14.07
DIPE	142.5	0	439.1[b]	109.7[b]	4641[b]	14.20
DBE	170.5	0	455.3	133.7[b]	4883	14.23

[a] The self-association parameters are assumed to be the same for all alkanols; $\Delta h_A^* = -25.1$ kJ·mol^{-1} and $\Delta v_A^* = -5.6$ cm^3·mol^{-1}. [b] Parameters were recalculated; therefore, they are different from those reported by Kammerer and Lichtenthaler (1998).

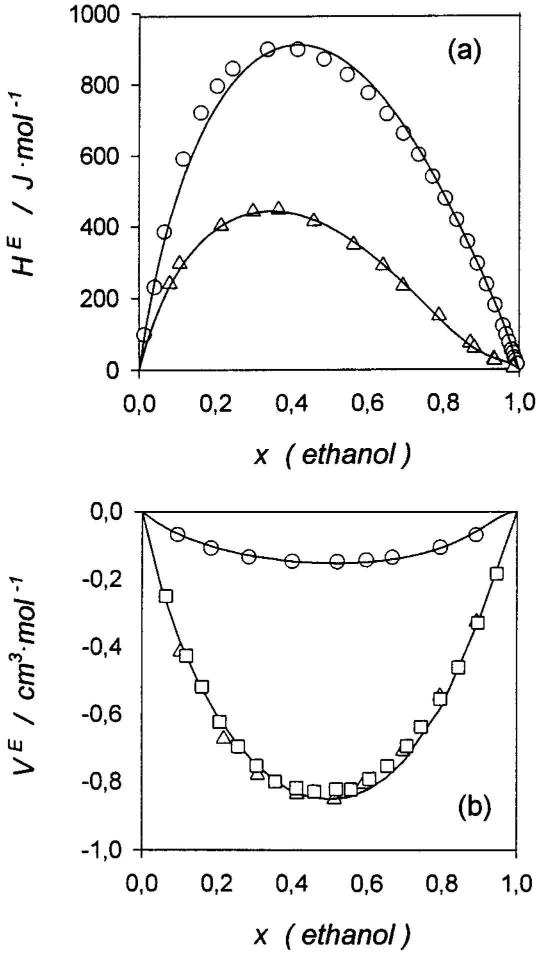

Figure 2. Excess molar enthalpy (a) and excess molar volume (b) of (○) {(x)ethanol + (1 − x)DBE} (H^E from Villamañan et al., 1982) and (△) {(x)ethanol + (1 − x)DIPE} (H^E from Letcher and Govender, 1995; (□) V^E from Blanco et al., 1994). (—) ERAS model calculation using parameters listed in Tables 3 and 4.

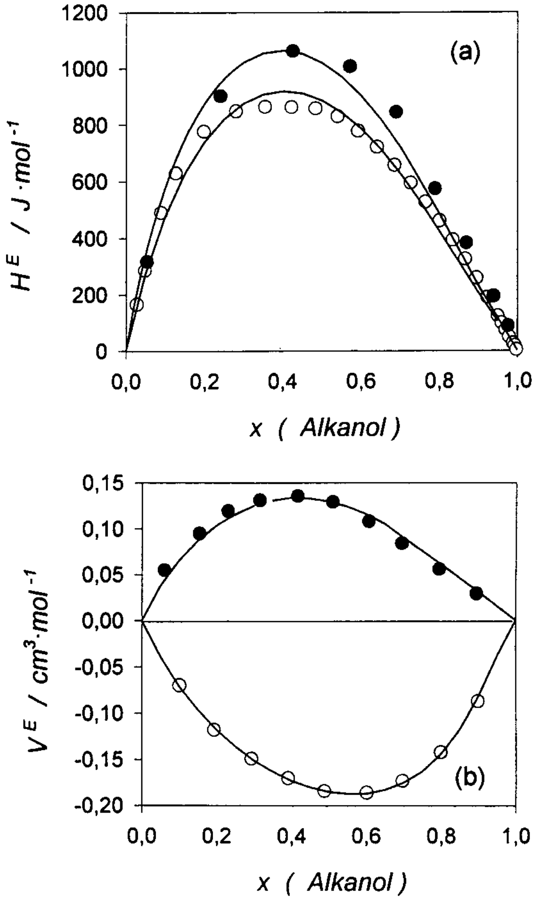

Figure 3. Excess molar enthalpy (a) and excess molar volume (b) of (○) {(x) 1-propanol + (1 − x) DBE} (H^E from Villamañan et al., 1982; V^E from Serna et al., 1995) and (●){(x)2-propanol + (1 − x)DBE}. (—) ERAS model calculation using parameters listed in Tables 3 and 4.

parameter $X_{AB} = 3$ J·cm^{-3}, which gives very good results for each system. Thus, the only binary parameters to be determined from experimental excess properties are Δh_{AB}^*, Δv_{AB}^*, and K_{AB}. These adjustable parameters were fitted simultaneously to H^E and V^E data using least-squares methods. The properties of the pure substances and the binary parameters of the mixtures are listed in Tables 3 and 4, respectively. Table 4 also contains the binary parameters for the systems 1-propanol and 2-propanol + DIPE and for 1-butanol and 2-butanol + DBE. These parameters have been calculated with the experimental data of Kammerer and Lichtenthaler (1998) and are different from those reported there because different pure component parameters have been used (see Table 3). The good agreement between experimental results and model calculations for these systems is not affected.

As shown in Figures 1−4, the ERAS model gives an almost quantitative description of H^E and V^E for each system investigated. In particular, the observed differences in excess properties between mixtures containing a linear and a branched alkanol are described with good accuracy. For the systems with the branched ether (DIPE) Δh_{AB}^* and Δv_{AB}^* have the largest values for the mixture with methanol and decrease with increasing chain length of the 1-alkanol. For the systems DIPE+2-alkanol, Δh_{AB}^* and Δv_{AB}^* have significantly smaller values than those for the systems with the corresponding 1-alkanols. The values of K_{AB} are always of the same order of magnitude. For the mixtures with the linear ether (DBE) Δh_{AB}^* slightly increases when going from methanol to 1-butanol whereas

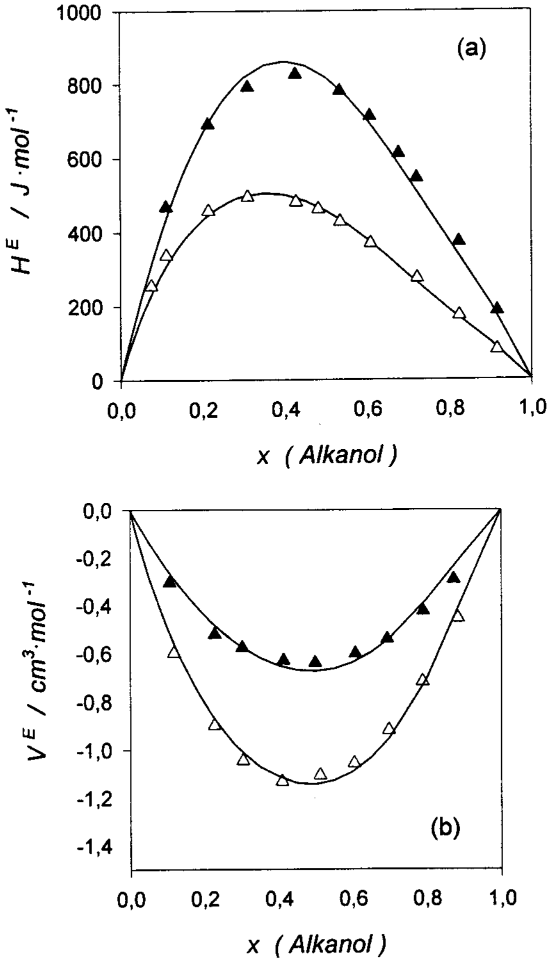

Figure 4. Excess molar enthalpy (a) and excess molar volume (b) of (△) {(*x*)1-butanol + (1 − *x*)DIPE} and (▲) {(*x*)2-butanol + (1 − *x*) DIPE }. (—) ERAS model calculation using parameters listed in Tables 3 and 4.

Table 4. ERAS Parameters for Binary Mixtures

mixture	Δh^*_{AB} kJ·mol^{-1}	Δv^*_{AB} cm^3·mol^{-1}	K^{298}_{AB}	X_{AB} J·cm^{-3}
methanol + DIPE	−25.9	−14.2	39.5	3
ethanol + DIPE	−21.8	−10.6	34.1	3
1-propanol + DIPE[a]	−22.0	−10.0	39.9	3
2-propanol + DIPE[a]	−20.2	−8.0	35.1	3
1-butanol + DIPE	−22.0	−10.2	32.7	3
2-butanol + DIPE	−19.4	−7.8	33.7	3
methanol + DBE	−17.0	−7.5	41.1	3
ethanol + DBE	−18.3	−6.8	34.8	3
1-propanol + DBE[a]	−18.3	−6.5	39.0	3
2-propanol + DBE	−17.3	−5.1	40.9	3
1-butanol + DBE[a]	−18.5	−6.4	37.4	3
2-butanol + DBE[a]	−16.5	−5.0	39.7	3

[a] Due to the different pure component parameters, binary parameters have been recalculated and differ from those reported by Kammerer and Lichtenthaler (1998).

Δv^*_{AB} shows a slight decrease. Both parameters have smaller values for the systems with 2-alkanols than for the systems with 1-alkanols. K_{AB} is very similar for all alkanol + DBE systems investigated. The difference in the behavior of parameters (Δh^*_{AB} and Δv^*_{AB}) for binary mixtures alkanol + branched or linear ether is due to structural effects. The results of the model calculations are in good agreement with the explanation given above with respect to the effect of molecular structure on the formation of alkanol−ether complexes due to hydrogen bonding.

Conclusion

Excess volumes and excess enthalpies were reported for seven binary systems containing methanol, ethanol, 2-propanol, 1-butanol, and 2-butanol with DIPE and DBE. The ERAS model provides a simultaneous description of H^E and V^E for all alkanol + ether systems investigated. The model is able to take into account various structural effects on the excess properties. In most cases, an almost qantitative description of H^E and V^E with the same set of system specific parameters is achieved.

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