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Excess properties of binary alkanol–ether mixtures and the application of the ERAS model[1]

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Abstract

Experimental results are reported of excess molar volumes V^E and excess molar enthalpies H^E for binary mixtures of 1-propanol, 2-propanol, 1-butanol and 2-butanol with diisopropyl ether (DIPE) and dibutyl ether (DBE) at 298.15 K. 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 ERAS model has been investigated for describing the experimental data as well as literature data of alkanol–ether mixtures containing DBE or dipropyl ether (DPE). © 1998 Elsevier Science B.V.

Keywords: Alkanol; Binary mixtures; ERAS model; Ether; Excess properties

1. Introduction

Substituting tetraethyl-lead as gasoline additive, oxygenated compounds like alkanols or ethers are becoming evermore important because of their good anti-knocking properties. In order to design the separation processes and the synthesis of ethers properly, phase behavior and thermodynamic properties of the fluid mixtures involved needs to be known. Corresponding data are also necessary for estimating the phase behavior of gasoline mixtures containing the ethers because complete miscibility has to be guaranteed at state conditions occurring in practical use.

In previous papers, experimental H^E of binary and ternary mixtures containing MTBE, ETBE or TAME [1–4] as well as experimental V^E and C_p^E of binary, ternary and quaternary mixtures containing ETBE [5] have been published. The ERAS (**E**xtended **R**eal **A**ssociation **S**olution) model has been applied for the simultaneous description of H^E, V^E and C_p^E. Continuing these investigations in this paper, experimental results of H^E and V^E are reported for binary mixtures of 1-propanol, 2-propanol, 1-butanol and 2-butanol with diisopropyl ether (DIPE) and dibutyl ether (DBE). The experimental data and already published data of H^E and V^E [6–8] are used to test the applicability of the ERAS model for describing both properties with the same set of system-specific parameters.

2. Experimental

The substances were obtained from standard laboratory sources and were used without further purification. The purities were 99.5% for 1-propanol (Riedel de Haën), > 99.7% for 2-propanol (Merck), 99% for

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diisopropyl ether (Merck) and 99% for dibutyl ether (Merck). All substances were carefully dried with molecular sieves.

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 are measured with high accuracy ($\Delta\rho < 10^{-5}$ g cm^{-3}). From these data molar excess volumes can be determined according to the following relation:

$$V^{\mathrm{E}} = \frac{\sum_i x_i M_i}{\rho_{\mathrm{M}}} - \sum_i \frac{M_i}{\rho_i} \tag{1}$$

where ρ_i are the densities and M_i the molar masses of the pure components ($i = \mathrm{A,B}$) and x_i are the mole fractions of the mixture. ρ_{M} is the density of the mixture. V^{E}-data are obtained with an accuracy ±0.2% of the maximum of the V^{E} curve considered and the error of the mole fraction is $< \pm 0.0001$.

Molar excess enthalpies were measured using a modified TRONAC 1250 calorimeter. This quasi-isothermal flow calorimeter and the operating procedure have been described elsewhere in detail [9]. The accuracy of the H^{E} data obtained is estimated to be $< \pm 0.01\,H^{\mathrm{E}}$ (but at least ± 1 J/mol). The mole fraction x is accurate to the third decimal place.

3. Theory

The ERAS model is used to correlate the experimental results for the mixtures investigated. As this model has been described in detail several times [10–13], only a brief summary is given here.

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

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

$$\begin{aligned} H^{\mathrm{E}}_{\mathrm{chem}} = {} & x_{\mathrm{A}} \Delta h^*_{\mathrm{A}} K_{\mathrm{A}} (\phi_{\mathrm{A1}} - \phi^0_{\mathrm{A1}}) \\ & + x_{\mathrm{B}} \Delta h^*_{\mathrm{B}} K_{\mathrm{B}} (\phi_{\mathrm{B1}} - \phi^0_{\mathrm{B1}}) + x_{\mathrm{A}} \Delta h^*_{\mathrm{AB}} K_{\mathrm{AB}} \\ & \cdot \frac{\phi_{\mathrm{B1}}(1 - K_{\mathrm{A}}\phi_{\mathrm{A1}})}{(V^{\mathrm{mol}}_{\mathrm{B}}/V^{\mathrm{mol}}_{\mathrm{A}})(1 - K_{\mathrm{B}}\phi_{\mathrm{B1}}) + K_{\mathrm{AB}}\phi_{\mathrm{B1}}} \\ & - \frac{P^*_{\mathrm{M}} V^{\mathrm{E}}_{\mathrm{chem}}}{\tilde{V}^2_{\mathrm{M}}} \end{aligned} \tag{3}$$

$$H^{\mathrm{E}}_{\mathrm{phys}} = (x_{\mathrm{A}} V^*_{\mathrm{A}} + x_{\mathrm{B}} V^*_{\mathrm{B}}) \left\{ \frac{\phi_{\mathrm{A}} P^*_{\mathrm{A}}}{\tilde{V}_{\mathrm{A}}} + \frac{\phi_{\mathrm{B}} P^*_{\mathrm{B}}}{\tilde{V}_{\mathrm{B}}} - \frac{P^*_{\mathrm{M}}}{\tilde{V}_{\mathrm{M}}} \right\} \tag{4}$$

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

$$\begin{aligned} V^{\mathrm{E}}_{\mathrm{chem}} = {} & \tilde{V}_{\mathrm{M}} \\ & \cdot \Big\{ x_{\mathrm{A}} \Delta v^*_{\mathrm{A}} K_{\mathrm{A}} (\phi_{\mathrm{A1}} - \phi^0_{\mathrm{A1}}) + x_{\mathrm{B}} \Delta v^*_{\mathrm{B}} K_{\mathrm{B}} (\phi_{\mathrm{B1}} - \phi^0_{\mathrm{B1}}) \\ & + x_{\mathrm{A}} \Delta v^*_{\mathrm{AB}} K_{\mathrm{AB}} \frac{\phi_{\mathrm{B1}}(1 - K_{\mathrm{A}}\phi_{\mathrm{A1}})}{(V^{\mathrm{mol}}_{\mathrm{B}}/V^{\mathrm{mol}}_{\mathrm{A}})(1 - K_{\mathrm{B}}\phi_{\mathrm{B1}}) + K_{\mathrm{AB}}\phi_{\mathrm{B1}}} \Big\} \end{aligned} \tag{6}$$

$$V^{\mathrm{E}}_{\mathrm{phys}} = (x_{\mathrm{A}} V^*_{\mathrm{A}} + x_{\mathrm{B}} V^*_{\mathrm{B}})(\tilde{V}_{\mathrm{M}} - \Phi_{\mathrm{A}} \tilde{V}_{\mathrm{A}} - \Phi_{\mathrm{B}} \tilde{V}_{\mathrm{B}}) \tag{7}$$

The physical contribution is derived from Flory's equation of state, which holds not only for the pure components (subscripts A or B) but also for the mixture (subscript M):

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

with $\tilde{V}_i = V^{\mathrm{mol}}_i / V^*_i$, $\tilde{P}_i = P/P^*_i$, $\tilde{T}_i = T/T^*_i$ being the reduced pressure, volume and temperature, respectively. Φ_{A} and Φ_{B} are the hard-core volume fractions defined as:

$$\Phi_i = \frac{x_i V^*_i}{x_{\mathrm{A}} V^*_{\mathrm{A}} + x_{\mathrm{B}} V^*_{\mathrm{B}}} \quad i = \mathrm{A,\ B} \tag{9}$$

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:

$$P^*_{\mathrm{M}} = \Phi_{\mathrm{A}} P^*_{\mathrm{A}} + \Phi_{\mathrm{B}} P^*_{\mathrm{B}} - \Phi_{\mathrm{A}} \vartheta_{\mathrm{B}} X_{\mathrm{AB}} \tag{10}$$

$$T^*_{\mathrm{M}} = \frac{P^*_{\mathrm{M}}}{P_{\mathrm{A}} \Phi_{\mathrm{A}} / T^*_{\mathrm{A}} + P_{\mathrm{B}} \Phi_{\mathrm{B}} / T^*_{\mathrm{B}}} \tag{11}$$

V^*_{M} and also V_{M} need not to be explicitly known because, in order to use Eqs. (3), (4) and (7), only $\tilde{V}_{\mathrm{M}}$ has to be known which is obtained from Eq. (8) with $\tilde{P}_{\mathrm{M}}$ and $\tilde{T}_{\mathrm{M}}$ from the mixing rules for P^*_{M} and T^*_{M}.

ϑ_{B} is the surface fraction of the component B in the mixture, defined as:

$$\vartheta_{\mathrm{B}} \equiv 1 - \vartheta_{\mathrm{A}} = \frac{(s_{\mathrm{B}}/s_{\mathrm{A}})\Phi_{\mathrm{B}}}{\Phi_{\mathrm{A}} + (s_{\mathrm{B}}/s_{\mathrm{A}})\Phi_{\mathrm{B}}} \tag{12}$$

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 [14]. X_{AB} in Eq. (10) 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. X_{AB} is the only adjustable parameter of the physical part.

The chemical contribution to the excess properties arises from chemical interactions between the molecules, in particular, hydrogen bonding. It is assumed that there is an equilibrium of linear chain association of the components A and B and the possibility of cross-association:

$$A_i + A \overset{K_A}{\leftrightarrow} A_{i+1} \tag{13}$$

$$B_i + B \overset{K_B}{\leftrightarrow} B_{i+1} \tag{14}$$

$$A_i + B_j \overset{K_{AB}}{\leftrightarrow} A_iB_j \tag{15}$$

The association constants K_i are assumed to be independent from the chain length i and their temperature dependence is given by the following equation:

$$K_i \equiv \frac{1}{V^*_{1i}} \frac{c_i}{c_{i-1}c_1} = K_{i0}\exp\left\{-\frac{\Delta h_i^*}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right\}$$
$$i = (\mathrm{A, B, AB}) \tag{16}$$

where V^*_{1i} denotes the hard-core volume of the monomeric species, Δh_i^* the association energy and c_i the molar concentration of the i-mer. The reaction volume Δv_i^* is related to the formation of the linear chain. ϕ_{i1} and ϕ_{i1}^0 $(i = \mathrm{A,B})$ are the volume fractions of the monomeric species A_1 (alkanol) and B_1 (ether) in the mixture and in the pure components, respectively. To determine ϕ_{A1} and ϕ_{A1}^0 the following two equations have to be solved:

$$\Phi_A = \frac{\phi_{A1}}{(1-K_A\phi_{A1})}\left\{1+\frac{V_A^{mol}K_{AB}\phi_{B1}}{V_B^{mol}(1-K_B\phi_{B1})}\right\} \tag{17}$$

$$\Phi_B = \frac{\phi_{B1}}{(1-K_B\phi_{B1})^2}\left\{1+\frac{K_{AB}\phi_{B1}}{(1-K_A\phi_{A1})}\right\} \tag{18}$$

with ϕ_{i1} equal to ϕ_{i1}^0 if $\Phi_A = 1$.

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 1-propanol + $(1-x)$DIPE					
0.1025	0.429	0.4095	0.986	0.7282	0.806
0.2136	0.736	0.5277	0.976	0.7985	0.686
0.3254	0.895	0.6237	0.951	0.8807	0.452
x 2-propanol + $(1-x)$DIPE					
0.1125	0.213	0.4007	0.505	0.7025	0.433
0.2089	0.351	0.5194	0.527	0.7986	0.332
0.3158	0.456	0.6124	0.494	0.9108	0.167
x 1-butanol + $(1-x)$DBE					
0.1065	0.089	0.3995	0.213	0.7128	0.213
0.2041	0.145	0.5136	0.232	0.8166	0.163
0.3105	0.191	0.6008	0.227	0.8956	0.115
x 2-butanol + $(1-x)$DBE					
0.1034	0.041	0.4163	0.122	0.6937	0.079
0.2530	0.096	0.5032	0.120	0.8137	0.041
0.3105	0.108	0.5816	0.109	0.9028	0.015

It is important to realize that, for associating molecules, the procedure to obtain reduction parameters of the physical contribution is somewhat different from the original one described by Flory as discussed by Heintz [10] and summarized elsewhere [3].

4. Results and discussion

The experimental data for H^E and V^E, at 298.15 K, of the binary mixtures investigated are listed in Tables 1 and 2. All mixtures contain one strong self-associating component (an alkanol) and a non-self-associating component (an ether), which can form associates with the alkanol through hydrogen bonding. The excess enthalpy depends on the balance between two contributions with opposite signs: (a) a positive term due to the destruction of alkanol–alkanol hydrogen bonds and (b) a negative term due to the formation of hydrogen bonded alkanol–ether complexes. For DIPE (a branched ether) the excess enthalpy increases going from 1-propanol to 2-propanol (Fig. 1), which is similar to the behavior of DBE (a linear ether) with the two isomeric butyl alkanols (Fig. 2). This is due to the fact that the formation of alkanol–ether cross-associates is more pronounced in mixtures with linear alkanols. The same tendency is observed in the excess molar volumes of these systems. The values of V^E for DIPE are becoming less negative going from 1-propanol to 2-propanol (Fig. 1). With DBE even a change from negative to positive values of V^E is observed going from 1-butanol to 2-butanol (Fig. 2). For the mixtures of DBE and DPE with linear alkanols (Figs. 3 and 4) the values of H^E remain almost unchanged, going from ethanol or 1-propanol to 1-butanol. The excess molar volumes are becoming less negative going from 1-butanol to 1-propanol for the mixture with DBE or from 1-butanol to ethanol for the mixture with DPE.

As all investigated mixtures exhibit strong hydrogen bonding the chemical contribution dominates the excess properties. In order to minimize the number of parameters to be adjusted, the parameter X_{AB} describing the physical contribution was taken to be the same for all mixtures. A value of $X_{AB} = 3\,\mathrm{J\,cm^{-3}}$ gives very good results in the description of all systems. Therefore, the only parameters to be fitted to the experi-

Table 2
Experimental excess molar enthalpies 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 1-propanol + $(1-x)$DIPE					
0.103	326.4	0.407	439.8	0.706	201.4
0.205	441.6	0.507	372.2	0.805	107.8
0.308	464.9	0.607	291.9	0.903	26.8
x 2-propanol + $(1-x)$DIPE					
0.100	400.0	0.401	683.6	0.700	455.2
0.201	593.2	0.500	645.6	0.800	314.6
0.302	670.2	0.601	564.7	0.900	130.8
x 1-butanol + $(1-x)$DBE					
0.105	385.4	0.401	875.6	0.701	618.2
0.201	722.9	0.501	840.5	0.800	442.1
0.302	853.4	0.601	754.6	0.901	221.7
x 2-butanol + $(1-x)$DBE					
0.101	619.1	0.402	1213.0	0.702	949.7
0.202	960.4	0.502	1224.0	0.801	707.3
0.303	1145.0	0.602	1128.0	0.901	366.7

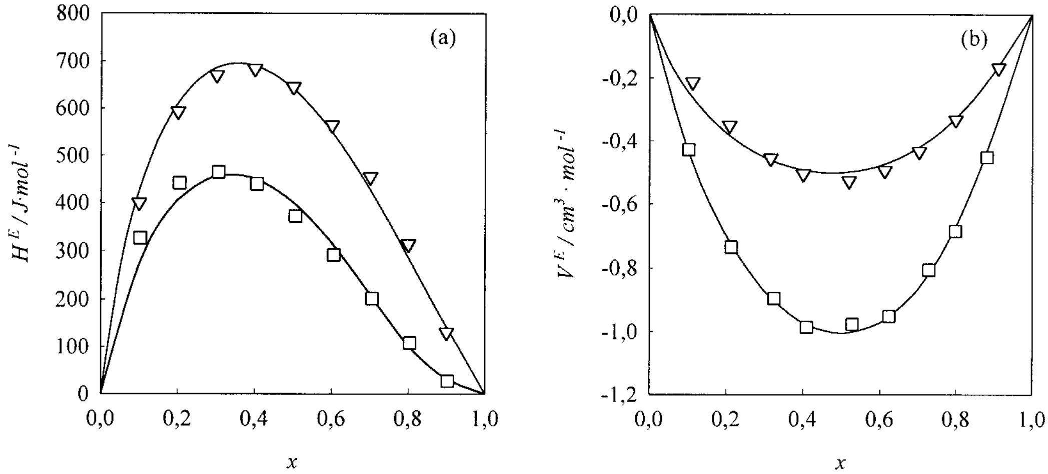

Fig. 1. Excess enthalpy (a) and excess volume (b) of (□) {x1-propanol+(1−x)DIPE} and (▽) {x2-propanol+(1−x)DIPE}; (———) ERAS model calculation using parameters listed in Tables 3 and 4.

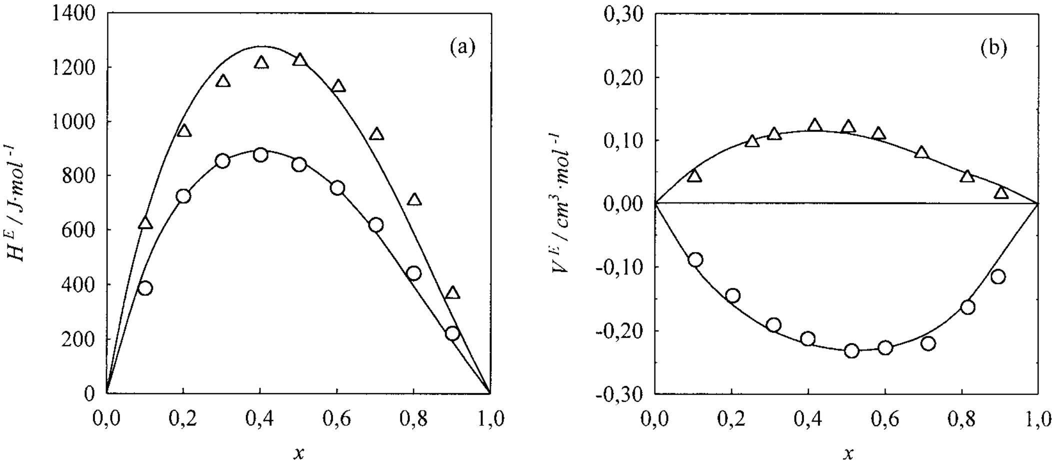

Fig. 2. Excess enthalpy (a) and excess volume (b) of (○) {x1-butanol + (1 − x)DBE} and (△) {x2-butanol + (1 − x)DBE}; (———) ERAS model calculation using parameters listed in Tables 3 and 4.

mental excess properties are Δh^*_{AB}, Δv^*_{AB} and K_{AB}. The three adjustable parameters were fitted simultaneously to H^E and V^E data using least-squares analysis. The properties and parameters of the pure substances are listed in Table 3 and the adjusted parameters are listed in Table 4.

The ERAS model is able to describe all systems very well. In most cases an almost qualitative description can be achieved. In particular, the observed changes in excess properties in going from a linear to a branched alkanol are described very well. For the systems with branched alkanols,

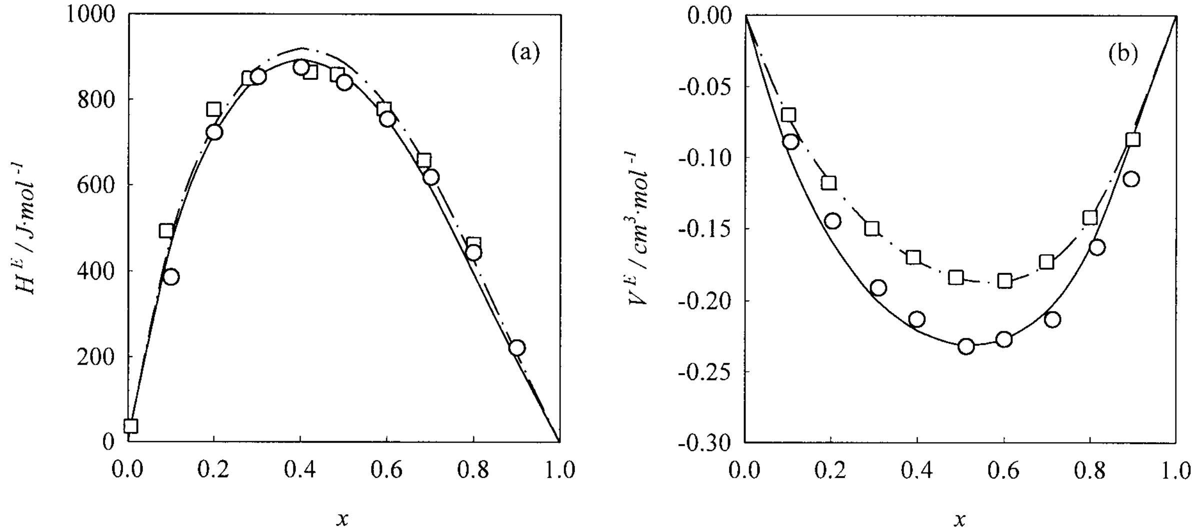

Fig. 3. Excess enthalpy (a) and excess volume (b) of (□) – $\{x1-\text{propanol}+(1-x)\text{DBE}\}$ (H^E from [8], V^E from [6]) and (○) – $\{x1-\text{butanol}+(1-x)\text{DBE}\}$; (———), (– · –) represent ERAS model calculation using parameters listed in Tables 3 and 4.

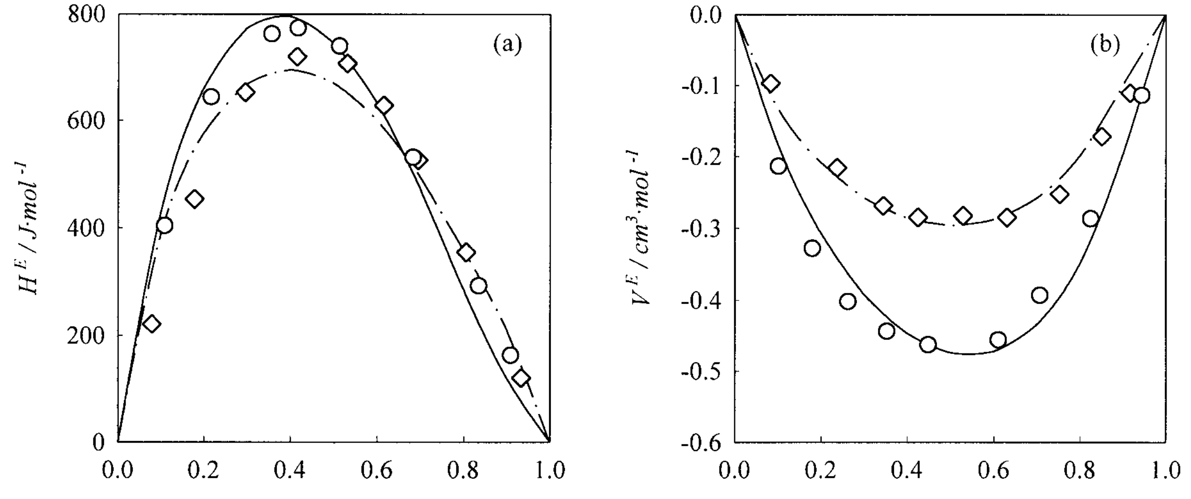

Fig. 4. Excess enthalpy (a) and excess volume (b) of (◇) – $\{x\text{ethanol}+(1-x)\text{DPE}\}$ and (○) – $\{x1\text{-butanol}+(1-x)\text{DPE}\}$ (data from [7]); (———), (– · –) represent ERAS model calculation using parameters listed in Tables 3 and 4.

i.e. $2-\text{propanol}+\text{DIPE}$ and $2-\text{butanol}+\text{DBE}$, the model calculations result in much lower values for K_{AB} and little lower values for Δh^*_{AB} than for the systems with 1-alkanols, which is in agreement with the explanation with respect to the formation of alkanol–ether complexes due to hydrogen bonding of these systems given above.

5. Conclusion

The ERAS-model allows a simultaneous description of H^E and V^E for a wide variety of alkanol–ether systems. The model is able to take into account various structural effects on the excess properties and achieves, in most cases, qualitative description

Table 3
Parameters of pure substances used in ERAS calculations

	V^{mol}/ (cm^3 mol^{-1})	K_A	T^*/ (K)	V^*/ (cm^3 mol^{-1})	P^*/ (J cm^{-3})	s/ (nm^{-1})
Ethanol	58.7	328	5239	47.1	403.7	15.43
1-Propanol	75.2	197	5493	61.1	412.5	14.90
2-Propanol	77.0	131	5409	62.3	378.2	14.87
1-Butanol	91.9	175	5196	73.5	411.3	14.21
2-Butanol	91.9	72	5360	74.1	385.9	14.07
DPE	137.7	0	4641	109.7	440.0	14.23
DIPE	142.5	0	4721	110.2	423.6	14.20
DBE	170.4	0	4883	150.8	455.3	14.23

Table 4
Parameters for the binary mixtures used in ERAS calculations

Mixture	Δh^*_{AB}/ (kJ mol^{-1})	Δv^*_{AB}/ (cm^3 mol^{-1})	K_{AB}	X_{AB}/ (J cm^{-3})
1-Propanol + DIPE	−22.1	−10.0	39.2	3
2-Propanol + DIPE	−19.4	−9.4	14.2	3
Ethanol + DPE	−19.8	−7.4	31.2	3
1-Butanol + DPE	−18.9	−7.4	40.7	3
1-Propanol + DBE	−18.5	−6.5	40.1	3
1-Butanol + DBE	−18.7	−6.9	39.3	3
2-Butanol + DBE	−15.3	−5.4	23.2	3

of H^E and V^E with system-specific parameters which are physically reasonable.

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