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Excess Enthalpies and Volumes of Ternary Mixtures Containing 1-Propanol or 1-Butanol, an Ether (Diisopropyl Ether or Dibutyl Ether), and Heptane

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Experimental data are reported at 298.15 K of excess molar volumes V^E and of excess molar enthalpies H^E for binary and ternary mixtures of an alkanol (1-propanol or 1-butanol), an ether (diisopropyl ether or dibutyl ether), and an alkane (heptane). A vibrating-tube densitometer was used to determine V^E. H^E was measured using a quasi-isothermal flow calorimeter. The experimental results are used to test the applicability of the modified UNIFAC model for correlating H^E and of the ERAS model for describing both V^E and H^E of binary mixtures as well as for predicting the excess properties of ternary mixtures containing an alkanol, an ether, and an alkane. For all investigated binary systems, a better description of the experimental data was achieved with the ERAS model in comparison with the modified UNIFAC model.

Introduction

Proper design of synthesis and separation processes of chemical substances requires reliable knowledge of the phase behavior and thermodynamic excess properties of the usually multicomponent fluid mixtures involved. Experimental determination of all of these properties is time-consuming and involves great expense especially if the data have to be known at various state conditions and compositions. Therefore, the properties of multicomponent mixtures are often estimated from the corresponding data of the constituting binary mixtures, but the reliability of such an estimation is always questionable and has to be tested. Because the excess properties of ternary mixtures are reflecting differences in the molecular size, shape, and interaction of three components, it is of interest and significance to use ternary data for testing models for the prediction and correlation of the excess properties of multicomponent systems. An attractive but not always accurate method for estimating multicomponent properties is provided by equations based on the group-contribution concept. From the many different models proposed, UNIFAC has the widest practical interest (Fredenslund et al., 1975, 1977). Another model which has successfully been used for correlating excess properties is the ERAS model (extended real associated solution) developed by Heintz (1985) for mixtures containing molecules which are able to associate. In the present paper experimental results are reported and used to test the applicability of the UNIFAC model for correlating H^E and of the ERAS model for describing both V^E and H^E of binary mixtures as well as for predicting the excess properties of ternary mixtures containing an alkanol, an ether, and an alkane.

Tertiary ethers are nontoxic, nonpolluting, high octane number blending agents for gasoline; therefore, they are of great industrial interest, and mixtures containing such ethers have been investigated extensively (see the review by Marsh et al. (1999)). Experimental H^E of binary and ternary mixtures have been published containing major members of the ether oxygenate family: 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., 1999) as well as experimental V^E and excess heat capacities $C_p{}^E$ of binary, ternary, and quaternary mixtutes containing ETBE (Mier et al., 1994, 1995). Kammerer and Lichtenthaler (1998) and Rezanova et al. (1999) have reported experimental results of H^E and V^E for binary mixtures of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol with diisopropyl ether (DIPE) and dibutyl ether (DBE) at 298.15 K. The ERAS model has been applied for the simultaneous description of thermodynamic properties. We have continued these investigations in this paper, and experimental results of H^E and V^E are reported for ternary alkanol (1-propanol or 1-butanol) + ether (DIPE or DBE) + alkane (heptane) mixtures at 298.15 K. The two ethers are suitable as gasoline additives, heptane is a major component of gasoline, and the alkanols are basic components in the synthesis of ethers and therefore are always contained as an impurity. The experimental results are used to compare the applicability of both the UNIFAC and ERAS models for describing excess molar enthalpies of binary systems as well as to test the applicability of the ERAS model for describing and predicting both excess properties of ternary mixtures containing an alkanol, an ether, and heptane using only binary parameters.

Experimental Section

Materials. The substances were obtained from Merck. The purity was at least 99.5%, and all substances were used without further purification, but they were carefully dried with molecular sieves and degassed. The densities at 298.15 K of the pure components used in this investiga-

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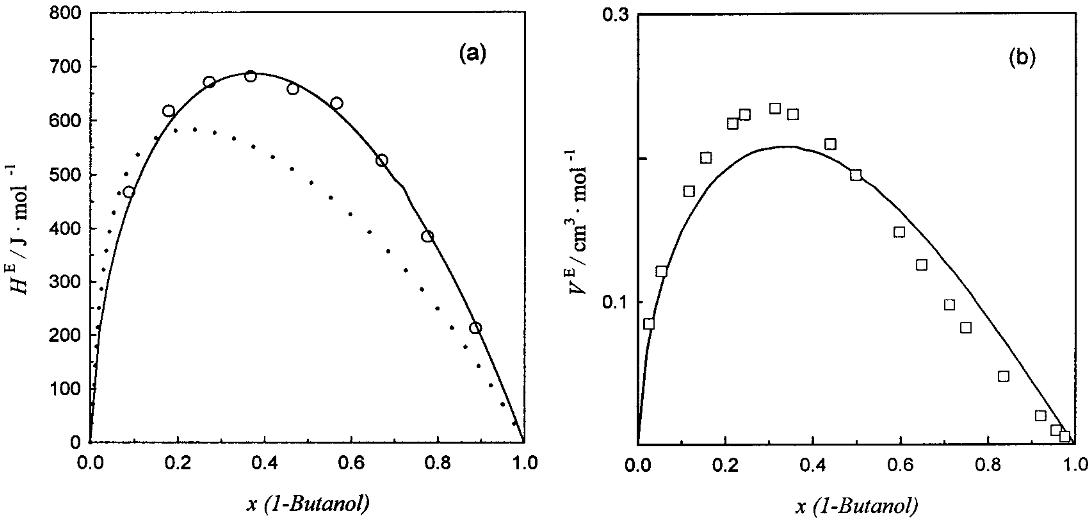

Figure 1. Excess molar enthalpies H^E (a) and excess molar volumes V^E (b) at 298.15 K for the binary system 1-butanol + heptane. experiment: (□) data from Treszczanowicz and Benson (1977); (○) present paper; (—) ERAS and (···) UNIFAC models.

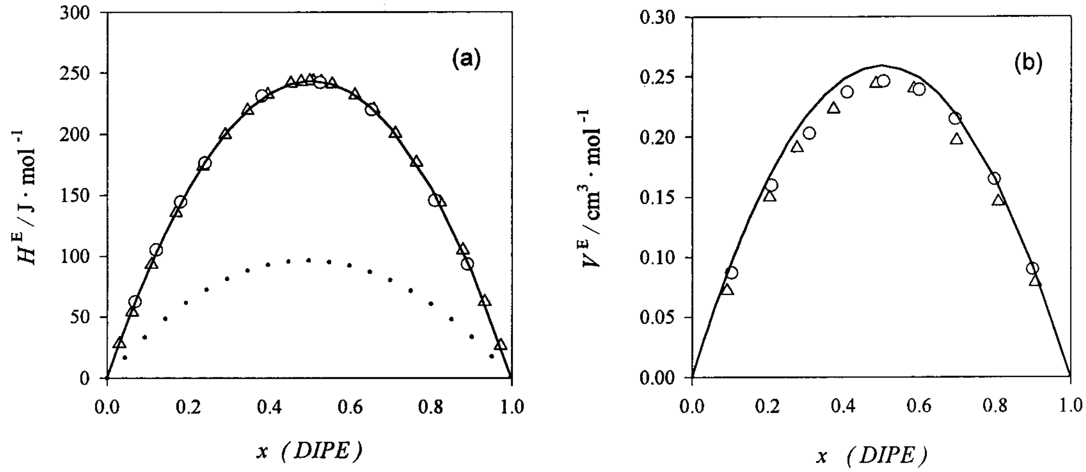

Figure 2. Excess molar enthalpies H^E (a) and excess molar volumes V^E (b) at 298.15 K for the binary system DIPE + heptane. Experiment: (○) present paper; (△) data from Oba et al. (1977); (—) ERAS and (···) UNIFAC models.

tion were 0.795 51 g·cm^{-3} (for 1-propanol), 0.805 61 g·cm^{-3} (for 1-butanol), 0.763 95 g·cm^{-3} (for DBE), 0.716 82 g·cm^{-3} (for DIPE), and 0.679 63 g·cm^{-3} (for heptane). These results agree within experimental error with literature data available.

Apparatus and Procedures. Excess molar volumes were measured using an Anton Paar DMA 60 vibrating-tube densitometer with a DMA 602 HT measuring cell calibrated with 1-propanol and water. Details of the experimental procedure have been described elsewhere (Reimann and Heintz, 1991). The densities of the pure components and the binary mixtures are measured with high accuracy ($\Delta\rho < \pm 10^{-5}$ g·cm^{-3}). From these data excess molar volumes were calculated 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), x_i are the mole fractions, and ρ_M is the density of the mixture. V^E data are determined with an error of ±0.2% of the maximum value of the V^E curve describing the dependence on composition and the error of the mole fraction is <±0.0001.

Table 1. Experimental Results of the Excess Molar Enthalpies H^E at 298.15 K for Binary Mixtures

x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}
		x 1-Butanol + (1 − x) Heptane			
0.0880	467.5	0.3670	681.1	0.6700	525.8
0.1790	617.4	0.4650	657.5	0.7760	384.1
0.2720	670.5	0.5660	631.1	0.8870	212.8
		x DIPE + (1 − x) Heptane			
0.0680	62.4	0.2400	176.6	0.6520	219.9
0.1200	105.2	0.3800	231.1	0.8090	145.7
0.1800	144.6	0.5240	242.1	0.8900	93.5
		x DBE + (1 − x) Heptane			
0.1100	43.7	0.3902	101.6	0.6953	91.3
0.2008	68.6	0.4640	105.2	0.8032	68.7
0.2942	89.5	0.5141	106.3	0.8583	51.4
0.3418	95.7	0.6165	102.1	0.9144	37.4

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 by Heintz and Lichtenthaler (1979). The mole fraction x is accurate to the third decimal place. To obtain H^E data of binary systems, two pure liquid components are mixed together; in the case of ternary mixtures, a binary liquid mixture of known composition is mixed with a third pure component and the resulting heat effect is measured directly. Details of calculation have been de-

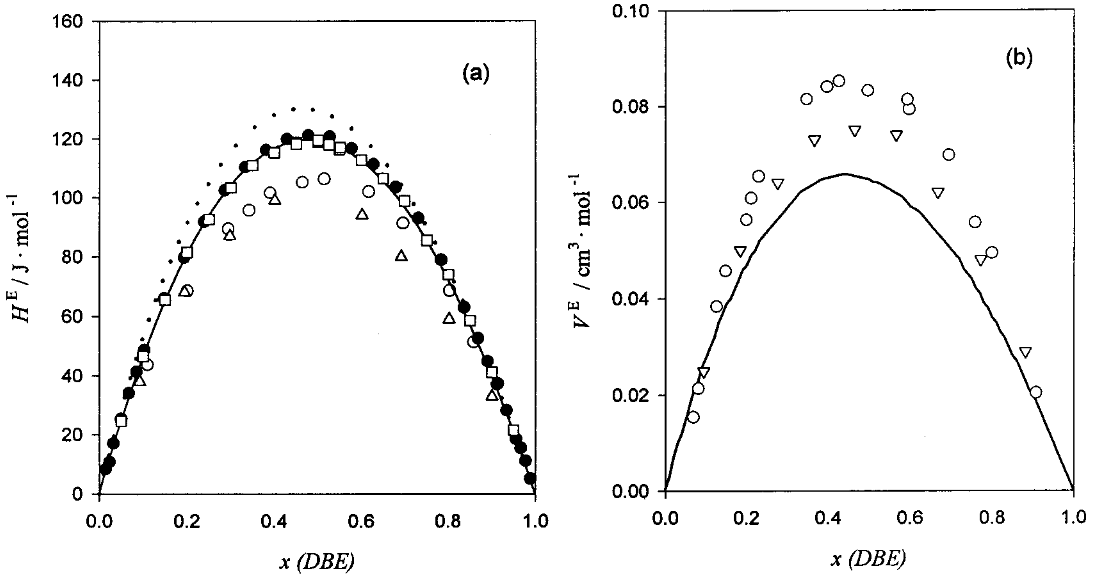

Figure 3. Excess molar enthalpies H^E (a) and excess molar volumes V^E (b) at 298.15 K for the binary system DBE + *n*-heptane. Experiment: (●) data from Villamañan et al. (1982); (□) data from Benson et al. (1988), (△) data from Marongiu et al. (1988); (▽) data from Teng and Acree (1992); (○) present paper; (—) ERAS and (···) UNIFAC model.

Table 2. Experimental Results of the Excess Molar Volumes V^E at 298.15 K for Binary Mixtures

x	V^E/cm^3·mol^{-1}	x	V^E/cm^3·mol^{-1}	x	V^E/cm^3·mol^{-1}
		x DBE + (1 − x) Heptane			
0.0691	0.015	0.2286	0.065	0.5969	0.079
0.0808	0.021	0.3472	0.081	0.6933	0.070
0.1255	0.038	0.3969	0.084	0.7576	0.056
0.1475	0.046	0.4260	0.085	0.7997	0.049
0.1982	0.056	0.4965	0.086	0.9072	0.020
0.2099	0.061	0.5929	0.081		
		x DIPE + (1 − x) Heptane			
0.1039	0.087	0.4088	0.237	0.6939	0.215
0.2093	0.160	0.5050	0.246	0.7971	0.165
0.3096	0.203	0.5991	0.239	0.8985	0.090

Table 3. Experimental Excess Molar Enthalpies H^E at 298.15 K for the Ternary Mixture $x_A = (1 - x_B - x_C)$ 1-Propanol + x_B DIPE + x_C Heptane

x_A	x_B	x_C	H^E/J·mol^{-1}	x_A	x_B	x_C	H^E/J·mol^{-1}
x_B/x_C = 0.20/0.80				x_B/x_C = 0.40/0.60			
0.1040	0.1844	0.7116	572.6	0.1040	0.3718	0.5242	557.6
0.2070	0.1632	0.6298	670.6	0.2070	0.3290	0.4640	664.7
0.3090	0.1422	0.5488	678.6	0.3090	0.2867	0.4043	676.3
0.4090	0.1216	0.4694	645.4	0.4090	0.2452	0.3458	610.6
0.5090	0.1010	0.3900	583.3	0.5090	0.2037	0.2873	567.7
0.6100	0.0802	0.3098	489.3	0.6100	0.1618	0.2282	463.5
0.7080	0.0601	0.2319	390.6	0.7080	0.1212	0.1708	379.9
0.8060	0.0399	0.1541	265.6	0.8060	0.0805	0.1135	259.3
0.9040	0.0205	0.0755	141.1	0.9040	0.0398	0.0562	126.1
x_B/x_C = 0.60/0.40				x_B/x_C = 0.80/0.20			
0.1020	0.5442	0.3538	562.6	0.1020	0.7301	0.1679	420.5
0.2040	0.4824	0.3136	663.6	0.2040	0.6472	0.1488	525.1
0.3050	0.3606	0.2738	673.5	0.3050	0.5650	0.1300	542.6
0.4050	0.3606	0.2344	626.6	0.4050	0.4837	0.1113	512.0
0.5050	0.3000	0.1950	554.5	0.5050	0.4024	0.0926	450.9
0.6050	0.2394	0.1556	456.5	0.6050	0.3211	0.0739	366.3
0.7040	0.1794	0.1166	341.9	0.7040	0.2407	0.0553	267.9
0.8030	0.1194	0.0776	223.5	0.8030	0.1602	0.0368	167.0
0.9020	0.0594	0.0386	108.9	0.9020	0.0797	0.0183	71.2

scribed by Keller et al. (1995) and by Bich et al. (1999). The error of the H^E data obtained is estimated to be $< \pm 0.01$ H^E (at least ±1 J·mol^{-1}).

Experimental Results

The new excess molar enthalpies H^E and volumes V^E of the binary mixtures at 298.15 K are listed in Tables 1 and 2. Their dependence on mole fraction is shown in Figures 1−3 together with the literature data if available. H^E is endothermic for all systems; the values of V^E are positive for both the ether + alkane and alkanol + alkane systems, whereas they are negative for the alkanol + ether systems (Kammerer and Lichtenthaler, 1998). Excess molar volumes are slightly positive for the ether + alkane system containing the branched ether (DIPE) compared with the mixture of the linear one (DBE), whereas the H^E values of these systems are only slightly different (Figures 2 and 3). The experimental excess properties of the DIPE + heptane binary sytem agree well with the literature data (Oba et al., 1977; Figure 2). For the system DBE + heptane a comparison with the literature shows that H^E values reported by Benson et al. (1988) and Villamañan et al. (1982a,b) are higher, whereas data by Marongiu et al. (1988) are lower than our results (Figure 3). V^E values reported by Teng and Acree (1992) for this system are somewhat lower than our results. As was emphasized before (Kammerer and Lichtenthaler, 1998), H^E and V^E values of alkanol + ether systems are dominated by the chemical contribution according to the strong hydrogen bonding of the alkanol molecules while the physical contribution is substantially smaller.

The experimental excess molar properties at 298.15 K for the ternary systems 1-propanol + DIPE + heptane (H^E) and 1-butanol + DBE + heptane (H^E and V^E) are listed in Tables 3−5, and their dependence on mole fraction is illustrated in Figures 4−6, respectively. H^E values are positive within the entire composition range. V^E values are mostly positive but negative in the alkanol-rich region.

Modeling and Discussion

The UNIFAC group-contribution method was originally developed and generally accepted for the prediction of vapor−liquid equilibria (VLE). However, poor results were often obtained in the case of the prediction of the activity coefficients at infinite dilution (γ^∞), heats of mixing (H^E), or systems with components very different in size. To overcome these weaknesses, modified forms of the UNIFAC method were proposed by Weidlich and Gmehling (1987) and Larsen et al. (1987). In a comprehensive comparison

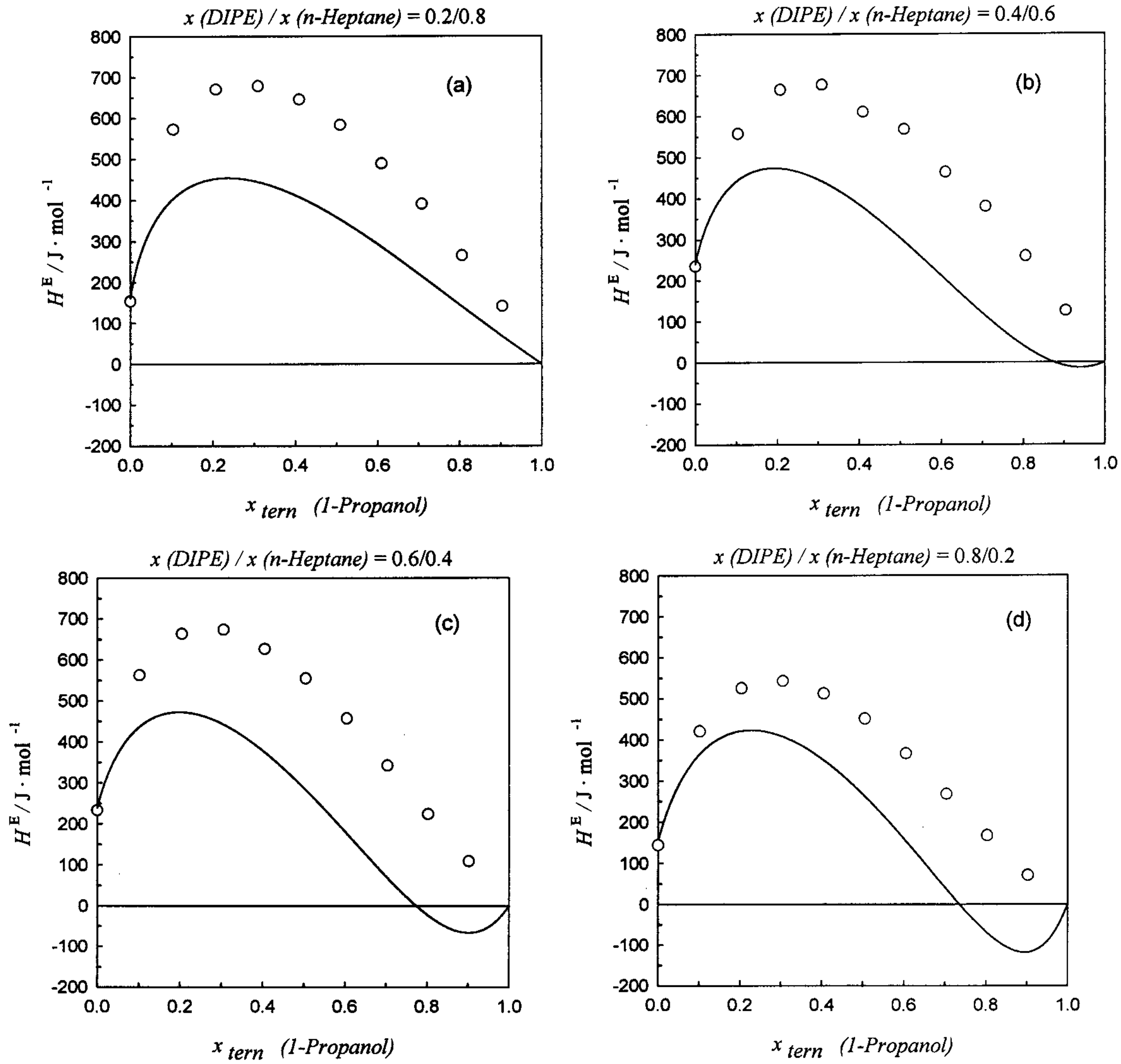

Figure 4. Excess molar enthalpies H^E at 298.15 K for the ternary system 1-propanol + DIPE + heptane: (○) experiment; (—) ERAS model.

Table 4. Experimental Excess Molar Enthalpies H^E at 298.15 K for the Ternary Mixture $x_A = (1 - x_B - x_C)$ 1-Butanol + x_B DBE + x_C Heptane

x_A	x_B	x_C	H^E/J·mol^{-1}	x_A	x_B	x_C	H^E/J·mol^{-1}
$x_B/x_C = 0.16/0.84$				$x_B/x_C = 0.34/0.66$			
0.0908	0.1495	0.7597	461.2	0.0908	0.3078	0.5942	514.4
0.1834	0.1342	0.6820	561.2	0.1967	0.2742	0.5291	656.9
0.2784	0.1187	0.6029	616.9	0.2955	0.2404	0.4641	719.4
0.3740	0.1030	0.5230	630.6	0.3938	0.2069	0.3993	721.8
0.4727	0.0867	0.4406	600.6	0.4935	0.1729	0.3336	674.0
0.5739	0.0701	0.3560	543.2	0.5943	0.1385	0.2672	596.5
0.6769	0.0539	0.2692	450.4	0.6949	0.1041	0.2010	482.4
0.7816	0.0359	0.1825	326.4	0.7955	0.0698	0.1347	338.3
0.8900	0.0181	0.0919	174.7	0.8980	0.0343	0.0672	173.7
$x_B/x_C = 0.56/0.44$				$x_B/x_C = 0.73/0.27$			
0.0960	0.5050	0.3990	580.0	0.0981	0.6583	0.2436	612.5
0.1932	0.4507	0.3561	747.5	0.1969	0.5862	0.2169	821.5
0.2909	0.3961	0.3130	819.1	0.2957	0.5141	0.1902	907.4
0.3885	0.3416	0.2699	826.1	0.3941	0.4423	0.1636	925.9
0.4880	0.2860	0.2260	775.0	0.4939	0.3694	0.1367	887.6
0.5889	0.2297	0.1814	681.6	0.5946	0.2959	0.1095	762.5
0.6902	0.1731	0.1367	542.4	0.6952	0.2225	0.0823	615.2
0.7919	0.1163	0.0918	377.1	0.7958	0.1491	0.0551	447.0
0.8959	0.0582	0.0459	180.3	0.8981	0.0744	0.0275	220.4

Table 5. Experimental Excess Molar Volumes V^E at 298.15 K for the Ternary Mixture $x_A = (1 - x_B - x_C)$ 1-Butanol + x_B DBE + x_C Heptane

x_A	x_B	x_C	V^E/ cm^3·mol^{-1}	x_A	x_B	x_C	V^E/ cm^3·mol^{-1}
$x_B/x_C = 0.22/0.78$				$x_B/x_C = 0.41/0.59$			
0.1012	0.1975	0.7013	0.1364	0.1056	0.3666	0.5278	0.1314
0.2048	0.1748	0.6204	0.1573	0.2203	0.3195	0.4602	0.1204
0.2985	0.1542	0.5473	0.1375	0.3127	0.2817	0.4056	0.0918
0.4017	0.1315	0.4668	0.1065	0.4111	0.2414	0.3475	0.0639
0.5021	0.1094	0.3885	0.0810	0.5268	0.1939	0.2793	0.0352
0.6035	0.0871	0.3094	0.0381	0.5608	0.1800	0.2592	0.0180
0.7123	0.0632	0.2245	0.0134	0.7014	0.1224	0.1762	−0.0018
0.8041	0.0431	0.1528	0.0062	0.8160	0.0754	0.1086	−0.0039
0.9256	0.0164	0.0580	−0.0095	0.9057	0.0386	0.0557	−0.0113
$x_B/x_C = 0.64/0.36$				$x_B/x_C = 0.76/0.24$			
0.1068	0.5726	0.3206	0.0476	0.1257	0.6649	0.2094	0.0128
0.2113	0.5056	0.2831	−0.0194	0.2182	0.5945	0.1873	−0.0425
0.3026	0.4471	0.2503	−0.0475	0.3198	0.5173	0.1629	−0.0852
0.3927	0.3893	0.2108	−0.0688	0.4021	0.4547	0.1432	−0.1086
0.5127	0.3124	0.1749	−0.1062	0.5346	0.3539	0.1115	−0.1501
0.6239	0.2411	0.1350	−0.1101	0.6495	0.2665	0.0840	−0.1634
0.7014	0.1914	0.1072	−0.1109	0.6982	0.2295	0.0723	−0.1516
0.8035	0.1260	0.0705	−0.1011	0.7921	0.1581	0.0498	−0.1282
0.9151	0.0544	0.0305	−0.0499	0.8577	0.1082	0.0341	−0.0956

by Gmehling et al. (1990, 1993), the great advantages of the modified forms of the UNIFAC method have been demonstrated. In the present paper the modified UNIFAC model is used to correlate H^E values using the group parameters proposed by Gmehling et al. (1993). This method, however, does not allow the prediction of excess properties based on volumetric properties such as the excess volume V^E. A successful attempt toward this direction was made by introducing the so-called ERAS model

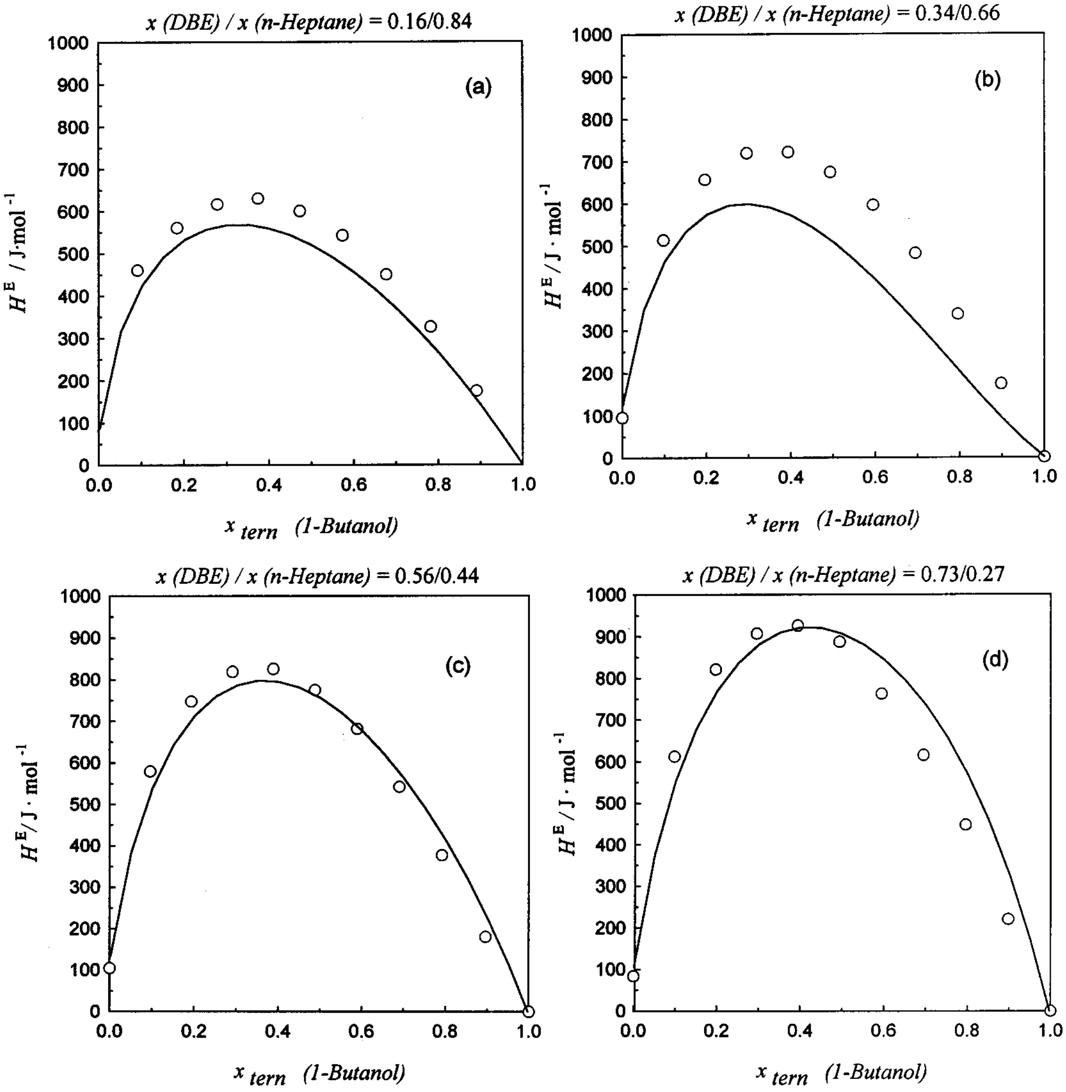

Figure 5. Excess molar enthalpies H^E at 298.15 K for the ternary system 1-butanol + DBE + heptane: (○) experiment; (—) ERAS model.

(Heintz, 1985), which is particularly useful when strongly associating components are involved. The ERAS model combines the linear chain association model with Flory's equation of state (Flory et al., 1964). It is rather successful in describing H^E, V^E, and G^E simultaneously for binary (Funke et al., 1989) as well as for multicomponent systems (Keller et al., 1995; Bich et al., 1999). In these papers, the relevant model equations are given.

As already mentioned above, the ERAS model combines the association effects coming from hydrogen bonding with free-volume effects arising from differences of the van der Waals interaction between like and unlike molecules in the mixture. Thus, the mixtures investigated can be divided into two groups by means of the ERAS model. The representatives of the first group are the systems alkanol + alkane (alkanol (A) = 1-propanol or 1-butanol; alkane (C) = heptane) and ether (B) + alkane (C) (ether = DIPE or DBE), which do not exhibit cross association. Therefore, the only adjustable parameters in model calculations of H^E and V^E for these systems are the Flory interaction parameters X_{AC} and X_{BC}, respectively. For the systems alkanol + ether (alkanol (A) = 1-propanol or 1-butanol; ether (B) = DIPE or DBE), cross-association, i.e., hydrogen bonding between the alkanol and the ether, has to be taken into account (Kammerer and Lichtenthaler, 1998). The adjustable parameters of these binary systems are X_{AB}, K_{AB} (the association constant), Δh^*_{AB} (the association energy per mole of hydrogen bonds), and Δv^*_{AB} (the "reaction" volume per mole of hydrogen bonds). The parameters were fitted simultaneously to experimental H^E and V^E data using least-squares analysis. The properties and parameters of the pure substances and the adjusted parameters for the binary mixtures are listed in Table 6.

As shown in Figures 1−3, the ERAS model represents the dependence of H^E on mole fraction for binary systems in good agreement with experimental values, but V^E is not described well in all cases. It is evident that in all cases the H^E curves calculated with the ERAS model agree significantly better with the experimental data than those calculated with the modified UNIFAC method. The description with UNIFAC is not satisfactory. Also the description of V^E for the binary mixtures 1-propanol + heptane and DBE + heptane with the ERAS model is not good. It was shown by Keller et al. (1995) that for the mixture 1-propanol + heptane experimental V^E can be described quantitatively using a different value for the reaction volume Δv^*_{AB} of pure 1-propanol. Nevertheless, in the present paper the pure-component parameters suggested by Renon and Prausnitz (1967) were used to be consistent with results published in previous papers cited

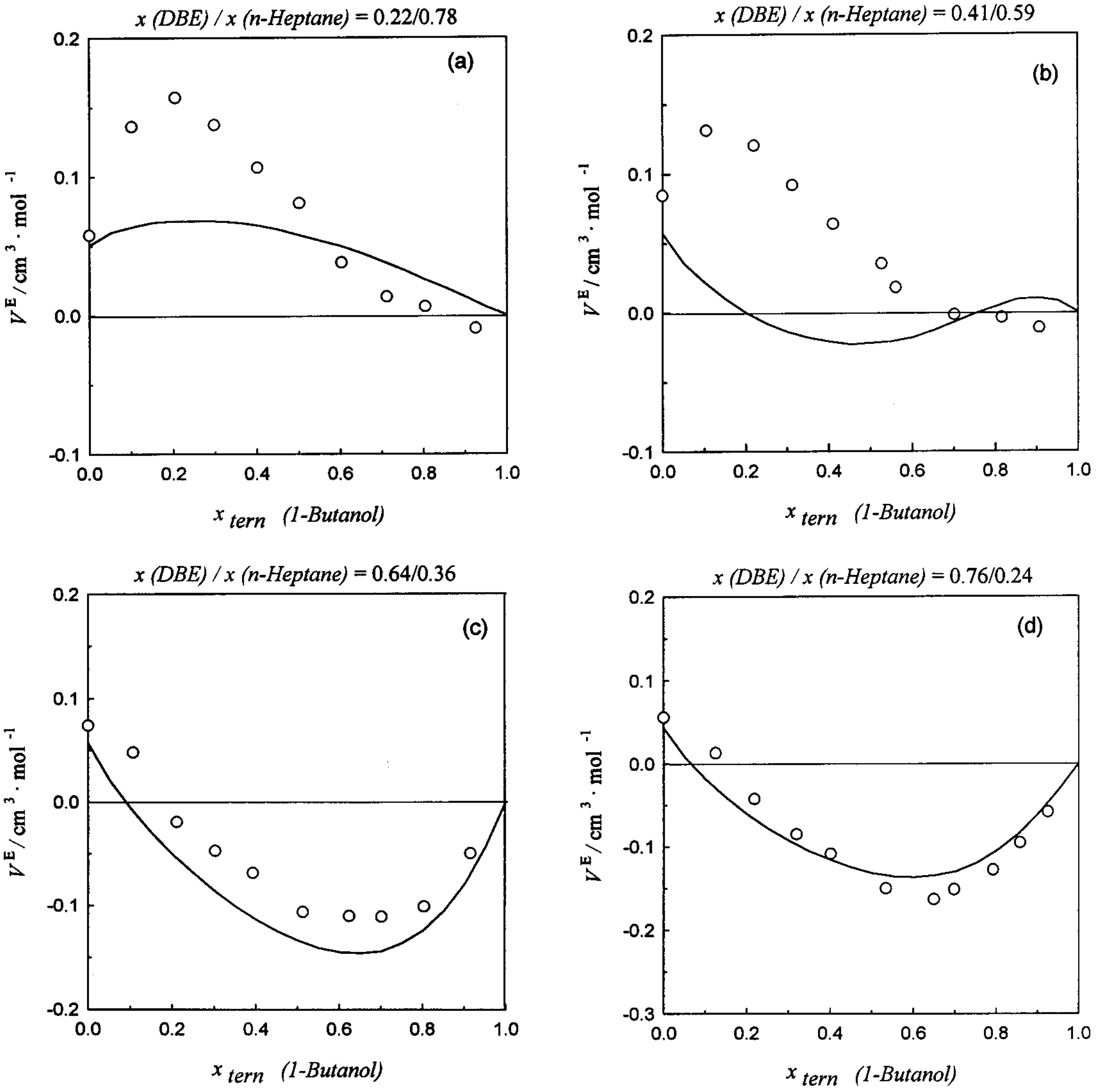

Figure 6. Excess molar volumes V^E at 298.15 K for the ternary system 1-butanol + DBE + heptane: (O) experiment; (—) ERAS model.

Table 6. Parameters at 298.15 K Used in ERAS Model Calculations

pure component	V_{mol}/cm^3·mol^{-1}	K_A	P^*/J·cm^{-3}	V^*/cm^3·mol^{-1}	T^*/K	s/nm^{-1}
1-propanol[a]	75.17	197	412.5	61.1	5493	14.90
1-butanol[a]	92.08	175	425.4	75.1	5588	14.21
DIPE	142.51	0	439.1	109.7	4641	14.20
DBE	170.78	0	455.3	133.7	4883	14.23
heptane	147.42	0	432.2	113.7	4663	13.97

binary system	Δh^*_{AB}/kJ·mol^{-1}	Δv^*_{AB}/cm^3·mol^{-1}	K_{AB}	X_{AB}/J·cm^3
1-propanol + DIPE	−22.0	−10.0	39.9	3
1-butanol + DBE	−18.5	−6.4	37.4	3
DIPE + heptane				8.3
DBE + heptane				3.8
1-propanol + heptane				4.0
1-butanol + heptane				9.0

[a] For both alkanols the self-association parameters are assumed to be the same: $\Delta h^*_A = -25.1$ k J·mol^{-1} and $\Delta v^*_A = -5.6$ cm^3·mol^{-1}.

above. In any way the main advantage of ERAS remains that this model in many cases allows one to describe various excess properties (H^E, V^E, and G^E) with appropriate accuracy for the binary systems.

The ERAS model has not been applied widely for predicting ternary excess properties (e.g., Keller et al. (1995)). Experimental results of H^E and ERAS model calculations presented by Bich et al. (1999) for the ternary system 1-propanol + MTBE + *i*-octane show that the general characteristics of the ternary system can be described correctly. The same holds for the ternary systems investigated in the present paper. As shown in Figures 4−6, the ERAS model gives a qualitative description of ternary H^E curves, and also the general characteristics of ternary V^E curves can be predicted using only binary parameters. The modified UNIFAC model has not been used for a correlation of the ternary data of H^E because an already worse description of binary H^E data has been obtained compared to the results achieved with the ERAS model.

Conclusion

Data of excess molar enthalpies and excess molar volumes at 298.15 K have been reported for ternary and some of the constituent binary systems containing an alkanol (1-propanol or 1-butanol), an ether (DIPE or DBE), and heptane. The modified UNIFAC model is able to describe H^E of binary mixtures qualitatively, but as a rigid lattice model it cannot correlate V^E at all.

For binary systems the ERAS model represents H^E in good agreement with experimental values, but for V^E the agreement is not always good. The model gives a reasonably good prediction of H^E but only a qualitative description of V^E of the ternary mixtures.

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