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Thermodynamic Excess Properties for Ternary Mixtures 1-Butanol + (Butyl Vinyl Ether or Isobutyl Vinyl Ether) + Heptane

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Experimental data are reported at 298.15 K of excess molar volumes V^E and excess molar enthalpies H^E for two ternary mixtures of 1-butanol + (butyl vinyl ether or isobutyl vinyl ether) + heptane. The results are explained in terms of the influence of the *n*-alkane on cross-association between an alkanol and an ether. 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 ERAS model for describing thermodynamic excess properties of ternary mixtures containing an alkanol, an ether, and an alkane.

Introduction

Reliable data on phase behavior and thermodynamic excess properties of multicomponent fluid mixtures are necessary for the proper design of synthesis and separation processes of the chemical substances involved. Experimental determination of all 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. As the excess properties of ternary mixtures reflect differences in molecular size, shape, and interaction of the 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. The ERAS (extended real associated solution) model developed by Heintz[1] has been used successfully for correlating excess properties of mixtures containing molecules which are able to associate. In the present paper experimental results are reported and used to test the applicability of the ERAS model for describing both excess properties (H^E and V^E) of ternary mixtures containing an alkanol, an ether, and an alkane.

Oxygenates such as ethers or alcohols are used as gasoline additives, and therefore, they are of great industrial interest. The thermodynamics of mixtures containing ethers have been extensively investigated, as recently reviewed by Marsh et al.[2] Experimental H^E values of binary and ternary mixtures containing major members of the ether oxygenate family [methyl *tert*-butyl ether (MTBE),[3,4] ethyl *tert*-butyl ether (ETBE),[5] or *tert*-amyl methyl ether (TAME)[6−8]] as well as experimental V^E and excess heat capacities C_p^E of binary, ternary, and quaternary mixtures containing ETBE[9,10] have been published. Kammerer and Lichtenthaler [11] and Rezanova et al.[12,13] have published experimental results of H^E and V^E for binary and ternary mixtures of alkanol + ether (DIPE or DBE) + alkane (heptane) at 298.15 K. In another paper excess thermodynamic properties of binary alkanol or alkane + ether (butyl vinyl ether or isobutyl vinyl ether) have been reported.[14] The ERAS model has been applied for the simultaneous description of thermodynamic properties.

Continuing these investigations in this paper, experimental results of H^E and V^E at 298.15 K are reported for ternary mixtures of 1-butanol + an ether (buyl vinyl ether or isobutyl vinyl ether) + heptane. The two ethers are considered as gasoline additives, heptane is a major component of gasoline, and the alkanol is a basic component in the synthesis of the ethers and therefore is always contained as an impurity. The experimental results are used 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 standard laboratory sources and were used without further purification. The mole fraction purities were >0.995 for 1-butanol (Riedel de Haën), >0.99 for heptane (Merck), >0.98 for butyl vinyl ether (Aldrich), and >0.99 for isobutyl vinyl ether (Aldrich). All substances were carefully dried with molecular sieves and degassed. The densities at 298.15 K of the pure components used in this investigation were 0.80562 g·cm^{-3} (for 1-butanol), 0.77412 g·cm^{-3} (for butyl vinyl ether), 0.76353 g·cm^{-3} (for isobutyl vinyl ether) and 0.67963 g·cm^{-3} (for heptane). These results agree within experimental error with the literature data available.[15,16]

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.[17] The densities of the pure components and the binary

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Table 1. 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)Butyl Vinyl Ether + (x_C)Heptane

x_A	x_B	H^E/J·mol^{-1}	x_A	x_B	H^E/J·mol^{-1}	x_A	x_B	H^E/J·mol^{-1}
$x_B/x_C = 0.2005/0.7995$ (Composition Line L$_1$)								
0.1124	0.1780	710.9	0.5101	0.0983	760.6	0.7644	0.0472	429.5
0.2161	0.1572	829.3	0.6097	0.0783	650.6	0.8046	0.0392	356.9
0.3120	0.1380	861.3	0.7009	0.0600	523.3	0.9162	0.0168	159.4
0.4010	0.1201	839.6						
$x_B/x_C = 0.3988/0.6012$ (Composition Line L$_2$)								
0.0376	0.3838	699.4	0.3067	0.2765	1004.8	0.6037	0.1580	725.6
0.0742	0.3693	843.3	0.3950	0.2413	963.2	0.6956	0.1214	576.0
0.1100	0.3550	901.8	0.4507	0.2191	919.2	0.8007	0.0795	383.7
0.2119	0.3143	994.9	0.5039	0.1979	857.1	0.9143	0.0342	158.6
$x_B/x_C = 0.6007/0.3993$ (Composition Line L$_3$)								
0.0725	0.5572	879.6	0.3888	0.3672	1062.7	0.6447	0.2134	735.4
0.1074	0.5362	957.9	0.4168	0.3504	1037.4	0.6676	0.1997	691.9
0.1416	0.5157	1018.5	0.4442	0.3339	1016.0	0.7122	0.1729	603.4
0.1750	0.4956	1059.6	0.4974	0.3019	950.2	0.7338	0.1599	563.7
0.2076	0.4760	1076.5	0.5232	0.2864	922.8	0.7760	0.1346	479.6
0.2395	0.4569	1097.0	0.5485	0.2712	890.7	0.8166	0.1102	393.8
0.3012	0.4198	1102.5	0.5732	0.2564	849.2	0.8750	0.0751	267.1
0.3310	0.4019	1094.0	0.5975	0.2418	798.8	0.9122	0.0527	183.7
0.3602	0.3844	1078.3	0.6213	0.2275	774.1	0.9482	0.0311	101.6
$x_B/x_C = 0.8013/0.1987$ (Composition Line L$_4$)								
0.1049	0.7173	912.9	0.2956	0.5645	1120.6	0.6386	0.2896	794.5
0.1384	0.6904	991.2	0.3542	0.5175	1114.8	0.7502	0.2002	576.3
0.2033	0.6384	1077.4	0.4377	0.4506	1063.8	0.8526	0.1181	348.4
0.2347	0.6132	1099.3	0.5419	0.3671	948.5	0.9469	0.0425	120.2
$x_A/x_B = 0.7037/0.2963$ (Composition Line M$_2$)								
0.6397	0.2341	751.0	0.4474	0.1884	900.9	0.2868	0.1207	847.3
0.5989	0.2522	799.0	0.4139	0.1743	908.5	0.2063	0.0869	760.0
0.5561	0.2341	841.5	0.3792	0.1597	899.4	0.1417	0.0596	653.3
0.5263	0.2216	862.7	0.3433	0.1445	884.9	0.0730	0.0308	485.2
0.4956	0.2086	888.1	0.3248	0.1367	870.9			

Table 2. 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)Isobutyl Vinyl Ether + (x_C)Heptane

x_A	x_B	H^E/J·mol^{-1}	x_A	x_B	H^E/J·mol^{-1}	x_A	x_B	H^E/J·mol^{-1}
$x_B/x_C = 0.1993/0.8007$ (Composition Line L$_1$)								
0.1126	0.1769	744.4	0.4016	0.1193	809.6	0.7014	0.0595	484.0
0.1482	0.1698	791.3	0.4574	0.1082	768.7	0.7441	0.0510	422.5
0.2165	0.1562	830.7	0.5107	0.0975	721.7	0.8050	0.0389	323.5
0.2493	0.1497	844.4	0.5616	0.0874	670.2	0.8623	0.0274	228.4
0.3125	0.1370	842.9	0.6102	0.0777	609.2	0.9164	0.0167	134.9
$x_B/x_C = 0.3981/0.6019$ (Composition Line L$_2$)								
0.1104	0.3542	912.3	0.4518	0.2182	909.8	0.6966	0.1208	560.9
0.1453	0.3403	953.7	0.5050	0.1970	845.4	0.7398	0.1036	483.7
0.2127	0.3134	997.3	0.5560	0.1768	786.0	0.8014	0.0791	371.0
0.2451	0.3005	1003.7	0.6048	0.1573	709.8	0.8596	0.0559	258.2
0.3077	0.2756	995.6	0.6517	0.1387	632.1	0.9146	0.0340	153.3
0.3961	0.2404	950.1						
$x_B/x_C = 0.5986/0.4014$ (Composition Line L$_3$)								
0.1081	0.5339	971.0	0.4729	0.3155	965.3	0.7136	0.1714	582.5
0.1760	0.4932	1058.9	0.5250	0.2844	898.8	0.7772	0.1334	457.8
0.2408	0.4545	1088.6	0.5750	0.2544	825.0	0.8177	0.1091	374.2
0.3027	0.4174	1087.4	0.6230	0.2257	747.2	0.8567	0.0858	291.6
0.3619	0.3820	1063.1	0.6692	0.1980	665.6	0.9128	0.0522	170.8
0.4186	0.3480	1021.7						
$x_B/x_C = 0.8009/0.1991$ (Composition Line L$_4$)								
0.1058	0.7162	900.7	0.4127	0.4704	1067.3	0.7087	0.2333	656.8
0.2048	0.6369	1062.1	0.4401	0.4484	1035.5	0.8141	0.1489	429.3
0.2976	0.5626	1105.1	0.4932	0.4059	994.7	0.9108	0.0715	220.7
0.3563	0.5156	1097.4	0.5934	0.3257	861.9			
$x_A/x_B = 0.5011/0.4989$ (Composition Line M$_1$)								
0.4522	0.4502	1051.3	0.3214	0.3199	1058.9	0.1948	0.1940	880.9
0.4318	0.4299	1067.4	0.2974	0.2961	1041.7	0.1673	0.1665	811.1
0.4002	0.3983	1082.7	0.2729	0.2716	1008.2	0.1389	0.1383	745.6
0.3784	0.3767	1083.0	0.2476	0.2465	976.3	0.0947	0.0944	614.3
0.3446	0.3431	1074.4	0.2216	0.2206	901.9	0.0485	0.0483	440.6

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:

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

Table 3. 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)Butyl Vinyl Ether + (x_C)Heptane

x_A	x_B	V^E/cm^3·mol^{-1}	x_A	x_B	V^E/cm^3·mol^{-1}	x_A	x_B	V^E/cm^3·mol^{-1}
$x_B/x_C = 0.1999/0.8001$ (Composition Line L$_1$)								
0.0000	0.1999	0.286	0.3989	0.1202	0.301	0.6995	0.0601	0.088
0.1038	0.1792	0.377	0.5029	0.0994	0.226	0.7948	0.0410	0.052
0.1970	0.1606	0.385	0.5968	0.0806	0.168	0.8972	0.0206	0.024
0.2985	0.1403	0.342						
$x_B/x_C = 0.3995/0.6005$ (Composition Line L$_2$)								
0.0000	0.3995	0.419	0.3942	0.2420	0.314	0.6879	0.1247	0.105
0.0978	0.3604	0.460	0.5008	0.1994	0.229	0.7947	0.0820	0.044
0.1970	0.3208	0.434	0.5916	0.1632	0.173	0.8908	0.0436	−0.011
0.2970	0.2809	0.375						
$x_B/x_C = 0.6004/0.3996$ (Composition Line L$_3$)								
0.0000	0.6004	0.421	0.3942	0.3637	0.269	0.7014	0.1792	0.069
0.0997	0.5405	0.415	0.4982	0.3013	0.186	0.7917	0.1251	0.029
0.1934	0.4842	0.386	0.5997	0.2403	0.125	0.8931	0.0642	−0.008
0.3002	0.4201	0.327						
$x_B/x_C = 0.8003/0.1997$ (Composition Line L$_4$)								
0.0000	0.8003	0.289	0.3916	0.4869	0.182	0.6900	0.2481	0.042
0.1010	0.7194	0.289	0.4978	0.4019	0.131	0.7930	0.1657	0.000
0.1929	0.6458	0.268	0.5950	0.3241	0.088	0.8931	0.0855	−0.034
0.2945	0.5645	0.226						
$x_A/x_B = 0.4972/0.5028$ (Composition Line M$_1$)								
0.4972	0.5028	0.002	0.2972	0.3006	0.378	0.1504	0.1521	0.366
0.4405	0.4455	0.143	0.2497	0.2525	0.397	0.1046	0.1058	0.303
0.3932	0.3977	0.246	0.1992	0.2015	0.389	0.0528	0.0534	0.211
0.3475	0.3515	0.318						

Table 4. 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)Isobutyl Vinyl Ether + (x_C)Heptane

x_A	x_B	V^E/cm^3·mol^{-1}	x_A	x_B	V^E/cm^3·mol^{-1}	x_A	x_B	V^E/cm^3·mol^{-1}
$x_B/x_C = 0.1996/0.8004$ (Composition Line L$_1$)								
0.0000	0.1996	0.277	0.3986	0.1200	0.288	0.7296	0.0540	0.032
0.1009	0.1794	0.374	0.4954	0.1007	0.223	0.8007	0.0398	0.017
0.2114	0.1574	0.378	0.5981	0.0802	0.151	0.8975	0.0205	−0.012
0.3013	0.1394	0.336	0.7043	0.0590	0.045			
$x_B/x_C = 0.3950/0.6050$ (Composition Line L$_2$)								
0.0000	0.3950	0.411	0.3973	0.2380	0.289	0.6931	0.1212	0.069
0.1014	0.3549	0.449	0.4981	0.1982	0.212	0.7955	0.0808	0.016
0.1948	0.3180	0.417	0.5914	0.1614	0.136	0.8981	0.0403	−0.007
0.3105	0.2723	0.354						
$x_B/x_C = 0.5985/0.4015$ (Composition Line L$_3$)								
0.0000	0.5985	0.349	0.3947	0.3623	0.212	0.6973	0.1812	−0.018
0.1006	0.5383	0.356	0.4985	0.3002	0.142	0.7960	0.1221	−0.037
0.1976	0.4802	0.319	0.5963	0.2416	0.085.	0.8986	0.0607	−0.058
0.3248	0.4041	0.259						
$x_B/x_C = 0.7994/0.2006$ (Composition Line L$_4$)								
0.0000	0.7994	0.290	0.3932	0.4850	0.120	0.6972	0.2420	−0.024
0.0974	0.7215	0.276	0.4990	0.4004	0.063	0.7934	0.1651	−0.054
0.1945	0.6439	0.236	0.5869	0.3302	0.009	0.8876	0.0899	−0.049
0.2853	0.5713	0.185						
$x_A/x_B = 0.6989/0.3011$ (Composition Line M$_2$)								
0.6989	0.3011	−0.116	0.4270	0.1840	0.286	0.2246	0.0968	0.339
0.6289	0.2710	0.014	0.3549	0.1529	0.321	0.1449	0.0624	0.279
0.5634	0.2428	0.124	0.2830	0.1219	0.340	0.0871	0.0375	0.183
0.4942	0.2129	0.215						

where ρ_i are the densities and M_i the molar masses of the pure components (i = A, B, C), x_i are the mole fractions, and ρ_M is the density of the mixture.

The mixtures were prepared by mass using a *Sartorius R 300 S* balance with a presision of $\pm 10^{-5}$ g. Special attention was paid to avoid errors in the mole fraction due to evaporation by minimizing the vapor space in the flasks and using for the measurements samples recently prepared. In the case of ternary mixtures, the third pure component was added to a binary mixture of known composition. 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.

Excess molar enthalpies were measured using a modified *Hart Scientific* calorimeter. This quasi-isothermal flow calorimeter and the operating procedure have been described in detail by Malijevská et al.[18] Two *ISCO LC*-2600 syringe pumps deliver continuously liquid components at constant flow rates into a mixing coil where the enthalpy of mixing per second is measured by compensating this heat effect using an automatic control device consisting of a Peltier cooler and a control heater. Endothermic as well as exothermic processes can be investigated by this method. 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

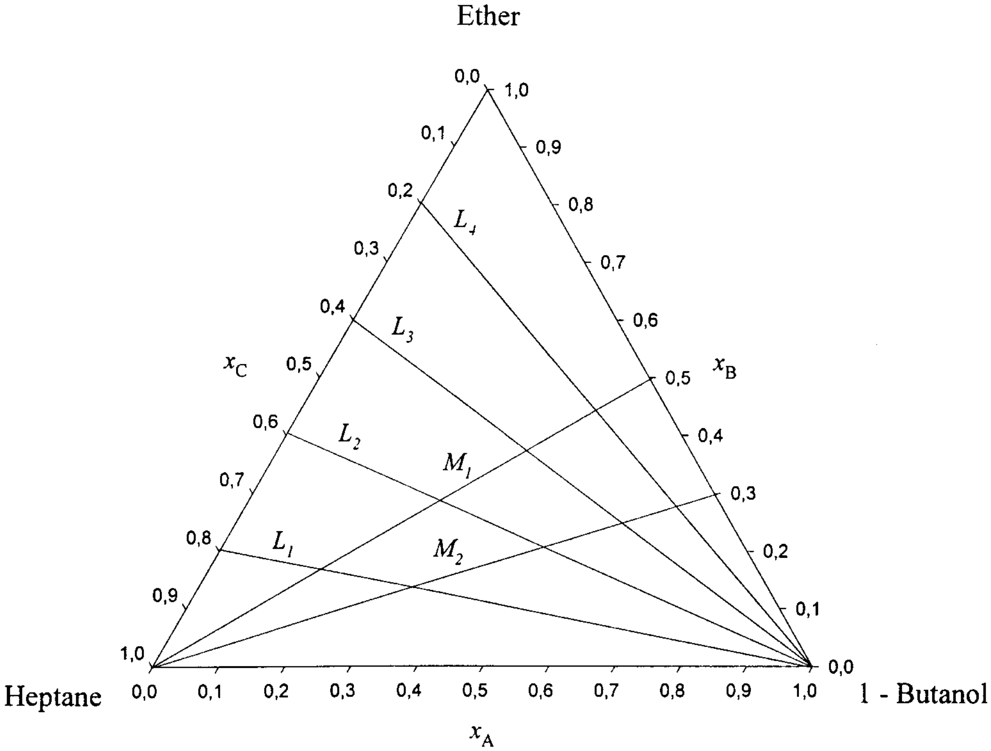

Figure 1. Gibbs triangle indicating the composition lines L_1–L_4, M_1, and M_2, along which excess properties were measured for the ternary systems.

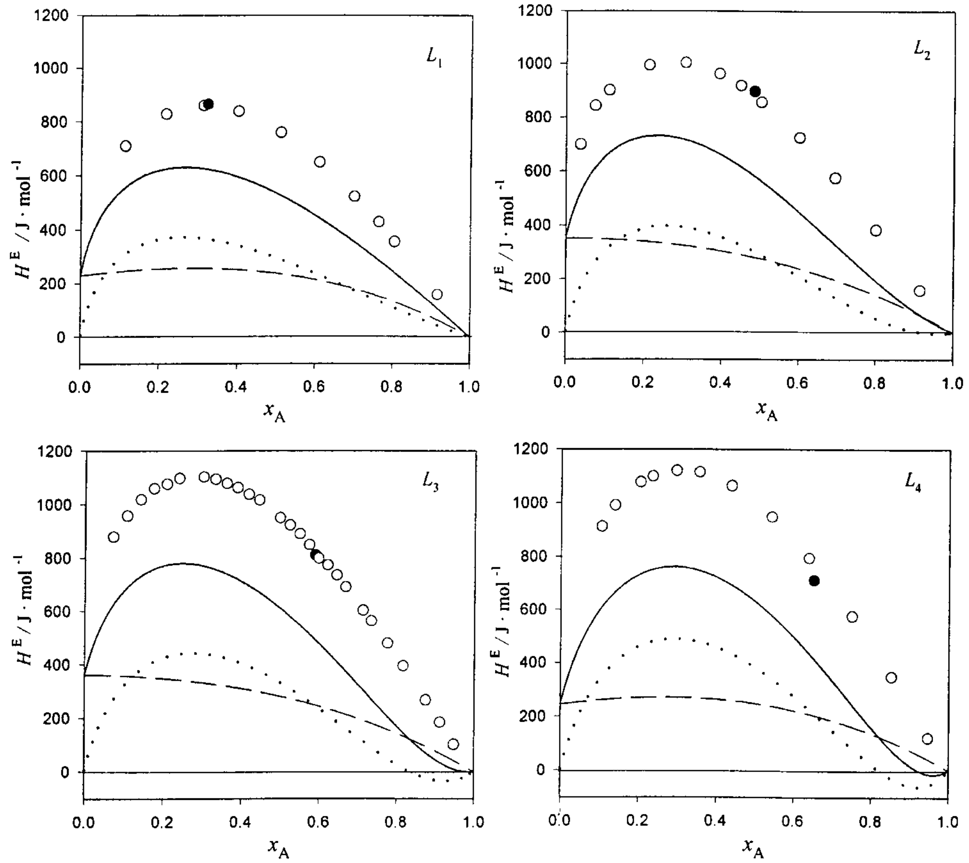

Figure 2. Excess molar enthalpies H^E at 298.15 K for the ternary system 1-butanol (A) + butyl vinyl ether (B) + heptane (C). Experiment: (○) obtained by adding 1-butanol to mixtures with fixed composition ratios of $x_B/x_C = 0.2005/0.7995$ (L_1), $x_B/x_C = 0.3988/0.6012$ (L_2), $x_B/x_C = 0.6007/0.3993$ (L_3), $x_B/x_C = 0.8013/0.1987$ (L_4); (●) measured by mixing heptane with a mixture of fixed composition ratio of $x_A/x_B = 0.7037/0.2963$ along line M_2 of the Gibbs triangle; (—) ERAS model; (- - -) physical contribution; (···) chemical contribution.

effect is measured directly. The molar excess enthalpy H^E_{term} of the ternary mixture, obtained by mixing pure component A with a binary system ether (B) + heptane (C), is determined according to the following relation:

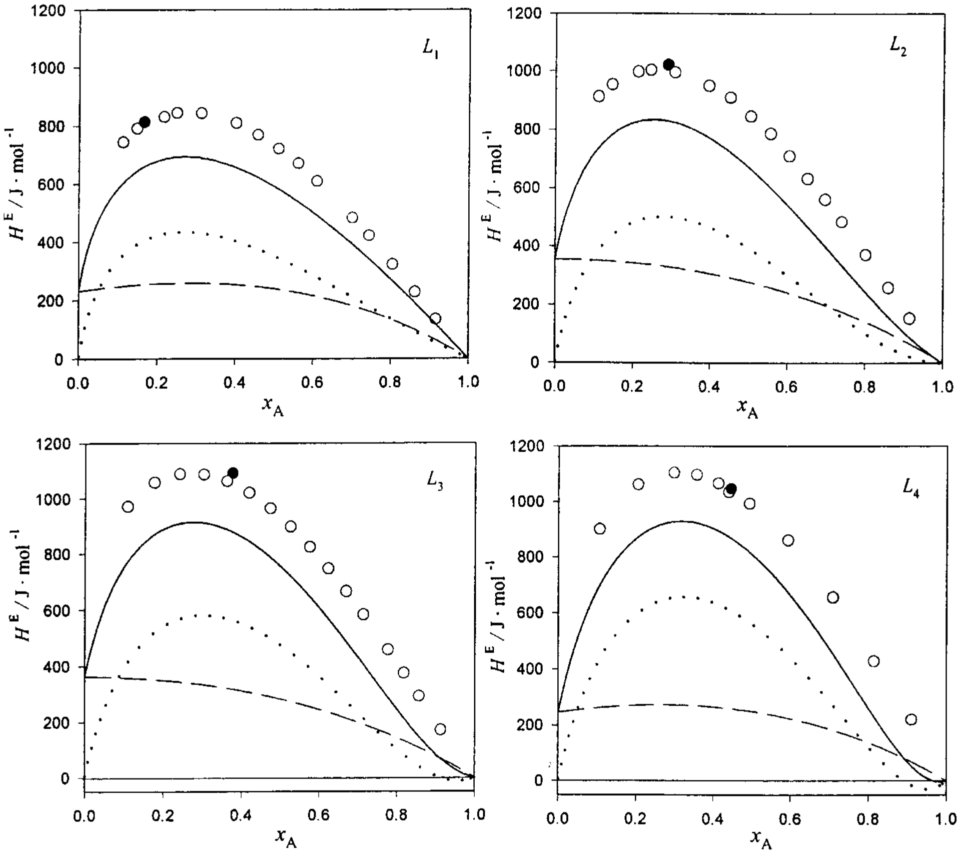

Figure 3. Excess molar enthalpies H^E at 298.15 K for the ternary system 1-butanol (A) + isobutyl vinyl ether (B) + heptane (C). Experiment: (○) obtained by adding 1-butanol to mixtures with fixed composition ratios of $x_B/x_C = 0.1993/0.8007$ (L_1), $x_B/x_C = 0.3981/0.6019$ (L_2), $x_B/x_C = 0.5986/0.4014$ (L_3), $x_B/x_C = 0.8009/0.1991$ (L_4); (●) measured by mixing heptane with a mixture of fixed composition ratio of $x_A/x_B = 0.5011/0.4989$ along line M_1 of the Gibbs triangle; (—) ERAS model; (- - -) physical contribution; (···) chemical contribution.

$$H^E_{\text{tern}} = \frac{\dot{Q} + (\dot{n}_B + \dot{n}_C)H^E_{BC}}{\dot{n}_A + \dot{n}_B + \dot{n}_C} \tag{2}$$

where $\dot{Q}$ is the measured heat effect upon mixing, $\dot{n}_i$ are the molar fluxes of components i (i = A, B, C) and H^E_{BC} is the molar excess enthalpy of the binary mixture ether (B) + heptane (C) delivered by one of the syrings pumps. The accuracy of the H^E data obtained is estimated to be $\pm 0.015H^E$ but at least ±1 J·mol^{-1}. The mole fraction x is accurate to the third decimal place.

Experimental Results

The performance of the equipment (the densitometer and the calorimeter) was checked by measuring V^E and H^E over the entire composition range for the test binary mixture (1-butanol + heptane). The experimental V^E and H^E data agree within experimental error with literature results reported by Treszczanowicz et al.[19] and Oswald et al.,[20] respectively.

The experimental excess molar properties at 298.15 K for the ternary systems 1-butanol + butyl vinyl ether + heptane and 1-butanol + isobutyl vinyl ether + heptane are listed in Tables 1−4, in which the data are arranged in accordance with the six "composition lines" indicated in the Gibbs triangle shown in Figure 1. Lines L_1−L_4 represent the cases when pure 1-butanol is mixed with a binary of ether (B) + heptane (C) of various fixed composition ratios x_B/x_C. In oder to check the consistency of the experimental results, measurements were also carried out by mixing pure heptane with the binary 1-butanol + ether (lines M_1 and M_2). The dependence of the excess properties of the ternary mixtures on mole fraction measured along lines L_1−L_4 is shown in Figures 2−5 (open symbols) together with the results of the model calculations discussed later. Also shown are the experimental values from lines M_1 and M_2 (black symbols) at the crossing points with lines L_1−L_4. The results clearly demonstrate the good consistency of the data, since the black symbols fit very well within the open symbols (within experimental error). The H^E values (Tables 1 and 2; Figures 2 and 3) are positive in the entire composition range. The maximum value of H^E appears at low alkanol mole fractions, because in that region, upon mixing, energy is consumed for breaking alkanol associates which is not compensated by the formation of cross-associates. The maximum value increases for both ternary systems with increasing mole fraction of the ether in the binary ($x_B \simeq 0.2 < 0.4 < 0.6 < 0.8$) mixed with the third component (861 J·mol^{-1} < 1005 J·mol^{-1} < 1103 J·mol^{-1} < 1121 J·mol^{-1} and 844 J·mol^{-1} < 1004 J·mol^{-1} < 1089 J·mol^{-1} < 1105 J·mol^{-1} for the mixtures containing butyl vinyl ether and isobutyl vinyl ether, respectively). This is due to the fact that with increasing mole fraction of the ether a relatively larger amount of alkanol associates is broken which is still not compensated by the also more pronounced formation of cross-associates. V^E values (Tables 2 and 3; Figures 4 and 5) are mostly positive but slightly negative in the alkanol-rich region. For both ternary systems V^E values corresponding to low mole fractions of the ether ($x_B \simeq 0.2, 0.4$) have a maximum at low alkanol mole fractions. With increasing mole fraction of the ether ($x_B \simeq 0.6, 0.8$) the maximum disappears. This indicates that the formation of cross-associates between ether and alkanol

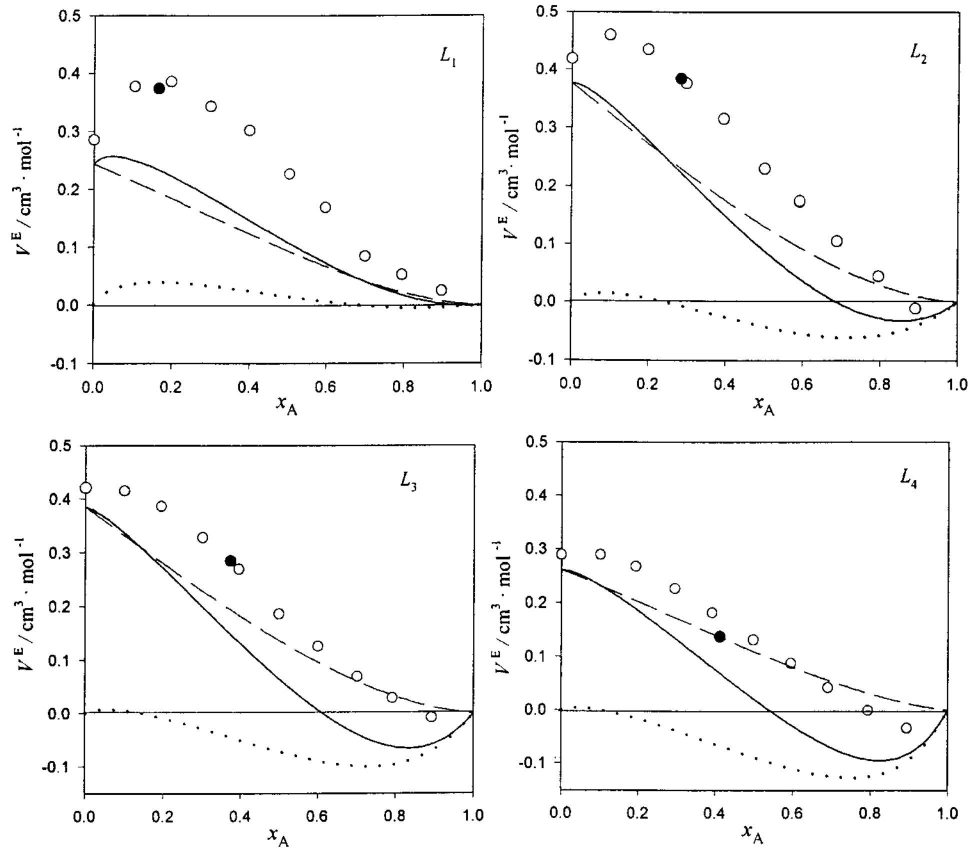

Figure 4. Excess molar volumes V^E at 298.15 K for the ternary system 1-butanol (A) + butyl vinyl ether (B) + heptane (C). Experiment: (○) obtained by adding 1-butanol to mixtures with fixed composition ratios of x_B/x_C = 0.1999/0.8001 (L_1), x_B/x_C = 0.3995/0.6005 (L_2), x_B/x_C = 0.6004/0.3996 (L_3), x_B/x_C = 0.8003/0.1997 (L_4); (●) measured by mixing heptane with a mixture of fixed composition ratio of x_A/x_B = 0.4972/0.5028 along line M_1 of the Gibbs triangle; (—) ERAS model; (- - -) physical contribution; (···) chemical contribution.

molecules is more pronounced in mixtures with higher mole fractions of the ether.

Modeling and Discussion

The ERAS model[1] separates thermodynamic excess properties of fluid mixtures into two distinct contributions, a chemical contribution due to hydrogen bonding and a physical contribution arising from the free-volume differences due to the differences in the van der Waals interactions between like and unlike molecules. As emphasized by Prausnitz et al.,[21] the distinction between the chemical and physical contributions to the excess properties leads to an arbitrary and, perhaps, artificial approach based on a simplified picture of solution properties. The designation of molecular interactions as either chemical or physical is merely a convenience which probably cannot be justified by a sophisticated modern theory of intermolecular forces. Nevertheless, a joint chemical and physical description of equilibrium properties of mixtures provides a reasonable and useful treatment for nonideal solutions. This clearly holds for the ERAS model, which has been rather successfully used for describing simultaneously H^E, V^E, and G^E of binary[22] as well as multicomponent mixtures.[7,23-25] In these papers the relevant equations are given, which also have been used in the model calculations presented here.

By means of the ERAS model, the constituting binary mixtures of the ternary systems investigated can be divided into two groups. The first group are the systems 1-butanol (A) + heptane (C) and ether (B) (butyl vinyl ether, isobutyl vinyl ether) + heptane (C), which do not exhibit cross-association. Therefore, the only adjustable parameters in the model calculations of H^E and V^E for these systems are the Flory interaction parameters X_{AC} and X_{BC}, respectively. The second group are the systems 1-butanol (A) + ether (B) with cross-association due to hydrogen bonding between the alkanol and ether molecules which has to be taken into account.[14] 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).

Binary 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 binary parameters used in the model calculations are listed in Table 5. The physical contributions of the binary alkanol + ether mixtures were described with X_{AB} = 9.0 J·cm^{-3}, which is different from the value reported by Rezanova and Lichtenthaler.[14] Discussing the physical and chemical contributions separately revealed that the ERAS model predicts only, with $X_{AB} > 8.0$ J·cm^{-3}, positive values for the physical contribution to the excess volume, which is in agreement with the Flory theory.[26] The excess properties of the two binary systems 1-butanol + heptane and butyl vinyl ether + heptane were described with X_{AC} = 8.1 J·cm^{-3} and X_{BC} = 13.3 J·cm^{-3}, respectively, which give an almost quantitative description of H^E but not of V^E, as already discussed by Rezanova and Lichtenthaler.[14]

Comparison of the experimental data and the results of the ERAS model calculations using only model parameters which have been adjusted to the constituting binary systems shown in Figures 2−5 indicates that the composition dependence of H^E and V^E of the ternary systems can only be described qualitatively. This fact confirms the

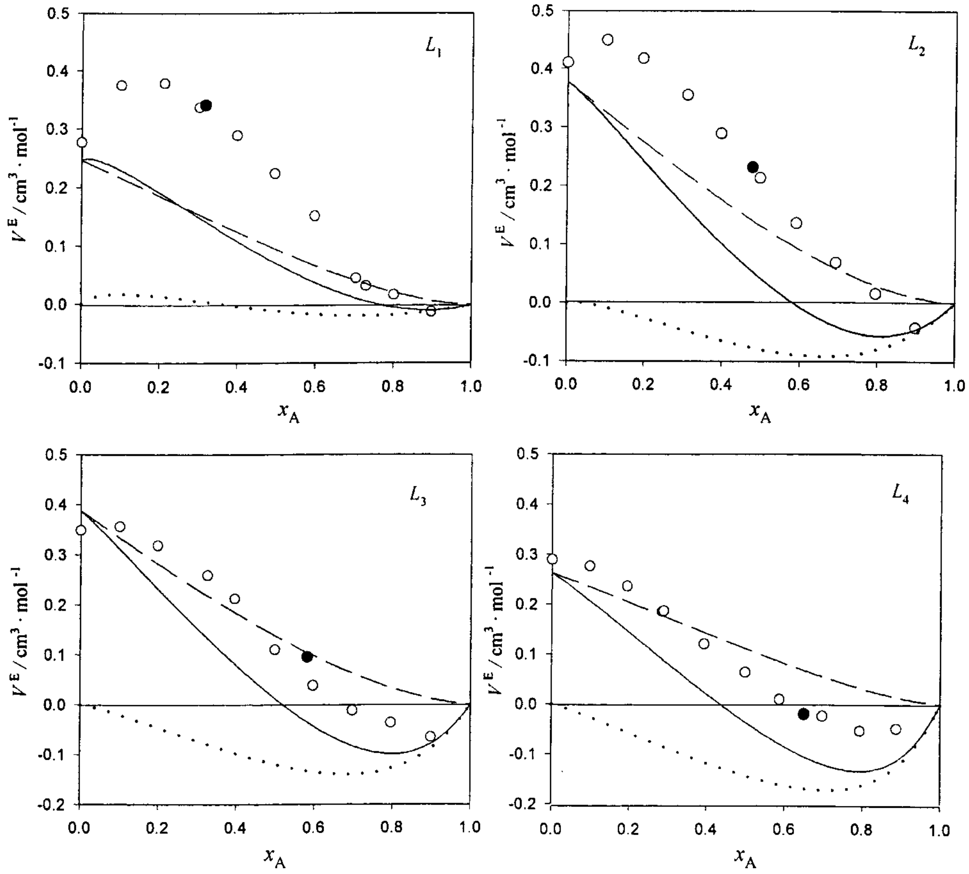

Figure 5. Excess molar volumes V^E at 298.15 K for the ternary system 1-butanol (A) + isobutyl vinyl ether (B) + heptane (C). Experiment: (○) obtained by adding 1-butanol to mixtures with fixed composition ratios of x_B/x_C = 0.1996/0.8004 (L_1), x_B/x_C = 0.3950/0.6050 (L_2), x_B/x_C = 0.5985/0.4015 (L_3), x_B/x_C = 0.7994/0.2006 (L_4); (●) measured by mixing heptane with a mixture of fixed composition ratio of x_A/x_B = 0.6989/0.3011 along line M_2 of the Gibbs triangle; (—) ERAS model; (- - -) physical contribution; (···) chemical contribution.

Table 5. Parameters at 298.15 K Used in ERAS Model Calculations

pure component	V_{mol}(298 K) cm^3·mol^{-1}	K_{AB}(298 K)	P^* J·cm^{-3}	V^* cm^3·mol^{-1}	T^* K	s nm^{-1}
1-butanol[a]	92.08	175	425.4	75.1	5588	14.21
butyl vinyl ether	129.49	0	434.3	99.8	4659	14.21
isobutyl vinyl ether	131.28	0	434.3	101.2	4659	14.23
heptane	147.51	0	431.7	113.7	4664	14.21

binary system	Δh^*_{AB} kJ·mol^{-1}	Δv^*_{AB} cm^3·mol	K_{AB}(298 K)	X_{AB} J·cm^{-3}
1-butanol + butyl vinyl ether	−18.3	−5.3	33.3	9
1-butanol + isobutyl vinyl ether	−17.3	−5.6	39.9	9
butyl vinyl ether + heptane				13.6[b]
isobutyl vinyl ether + heptane				13.3[b]
1-butanol + heptane				8.1

[a] For 1-butanol the self-association parameters are assumed to be: $\Delta h^*_A = -25.1$ kJ·mol^{-1} and $\Delta v^*_{AB} = -5.6$ cm^3·mol^{-1}. [b] Parameters were recalculated; therefore, they are different from those reported by Rezanova and Lichtenthaler.[14]

influence of the third component on the specific interactions in ternary mixtures in comparison to those in binary mixtures. The nonpolar component (heptane) serves mainly as an inert diluting solvent. In Figures 2−5 are also shown separately the physical and chemical contributions to the excess properties. It is evident that the physical contribution is always positive and that its composition dependence is a monotonic function of alkanol mole fraction. The composition dependence of the chemical contribution is positive for low mole fractions of the ether and shows a maximum at low alkanol mole fractions. With increasing mole fractions of the ether, the maximum decreases, and at high alkanol mole fractions, the chemical contribution becomes more and more negative, which is due to the more and more dominating formation of cross-associates. It is obvious that the overall shape of the experimental H^E curve is mainly determined by the chemical contribution. The physical contribution dominates the excess properties only at low alkanol mole fractions, where the effects due to breaking hydrogen bonds between the akanol molecules are compensated by the effects due the formation of cross-associates.

Conclusion

Excess molar enthalpies and excess molar volumes at 298.15 K have been reported for two ternary systems containing 1-butanol, an ether (butyl vinyl ether or isobutyl vinyl ether), and heptane.

For the constituting 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 only a qualitative description of H^E and V^E for the ternary mixtures with the set of system-specific model parameters adjusted only to data of the binary mixtures. The predicted values of the excess properties of the ternary mixtures are in general too low, clearly indicating that ternary model parameters are necessary in order to achieve a quantitative description.

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