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Isothermal Vapor−Liquid Equilibrium at 333.15 K and Excess Volumes and Molar Refractivity Deviation at 298.15 K for Binary System Dibutyl Ether (DBE) + 2,2,4-Trimethylpentane and for Ternary System DBE + Ethanol + 2,2,4-Trimethylpentane

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Isothermal vapor−liquid equilibrium (VLE) data are reported for the binary system dibutyl ether (DBE) + 2,2,4-trimethylpentane at 333.15 K, as well as for the ternary system DBE + ethanol + 2,2,4-trimethylpentane using headspace gas chromatography. The experimental binary and ternary VLE data are correlated with common activity coefficient models. Excess volumes and deviations in molar refractivity data are also reported for the same binary and ternary systems at 298.15 K. These properties are correlated with the Redlich−Kister equation for binary systems and the Cibulka equation for ternary systems, respectively. The ternary excess volumes and deviations in molar refractivity data are also compared with the estimated values from the binary contribution models of Radojkovič, Tsao−Smith, Kohler, and Rastogi.

Introduction

For several decades, some ether compounds have been highlighted as antiknock additives for gasoline and industrial solvents. However, the phase equilibria and mixture properties of ether compounds such as alkyl and alkyl vinyl ether are still not readily available in the literature, even though they are important solvents and excellent extracting agents for use with aqueous systems. Thus, we have studied the phase equilibria and mixture properties for several ether compounds[1−3] to provide accurate design data. These data could be very useful for the processing of compounds and helpful for the application of group contribution models as a thermodynamic tool.

Dibutyl ether (DBE) is an important solvent and also an excellent extracting agent for aqueous systems owing to its very low water solubility.[4] In the present work, we report the vapor−liquid equilibrium (VLE) data at 333.15 K for the binary system DBE + 2,2,4-trimethylpentane, as well as for the ternary system DBE + ethanol + 2,2,4-trimethylpentane, using headspace gas chromatography (HSGC). Furthermore, densities (ρ) and refractive indices (n_D) at 298.15 K for the same binary and ternary systems at 298.15 K were measured using a digital vibrating tube densimeter and a precision digital refractometer, because these are used for a theoretical understanding of the nature of molecular interaction. These binary VLE data and mixture properties were measured as supplements to complete sub-binary data for the ternary system DBE + ethanol + 2,2,4-trimethylpentane, as we have already reported the VLE data ρ and n_D for binary systems DBE + ethanol and ethanol + 2,2,4-trimethylpentane under the same conditions. The excess molar volumes (V^E) and deviations in molar refractivity (ΔR) were derived from measured densities and refractive indices.

The experimental binary VLE data were correlated with the Margules, van Laar, Wilson, nonrandom two-liquid (NRTL), and universal quiasichemical (UNIQUAC) activity coefficient models, while the ternary VLE data were correlated with the Wilson, NRTL, and UNIQUAC models. In addition, the measured binary V^E and ΔR data were correlated with the Redlich−Kister polynomial,[5] while the ternary data were correlated with the Cibulka equation.[6] Furthermore, the ternary V^E and ΔR data were also compared with the predicted values using the binary contribution models of Radojkovič,[7] Tsao−Smith,[8] Kohler,[9] and Rastogi.[10]

Experimental Section

Materials. Commercial grade DBE ($C_8H_{18}O$, $M = 130.23$ g·mol^{-1}, CAS RN 142-96-1) and 2,2,4-trimethylpentane (C_8H_{18}, $M = 114.23$ g·mol^{-1}, CAS RN 540-84-1) were obtained from Aldrich. Ethanol (C_2H_6O, $M = 46.07$ g·mol^{-1}, CAS RN 64-17-5) was supplied from J. T. Baker Chemical Co. All chemicals were dried using molecular sieves with a pore diameter of 0.4 nm. The purity of the chemicals was examined by gas chromatography and by comparing the densities and refractive indices with the values reported in the literature. The purity of all of the chemicals used was better than 99.9 % in mass fraction as determined by gas chromatographic analysis. The measured densities, refractive indices, and Antoine constants of the chemicals used are summarized in Table 1, along with the literature values.[11−13]

Apparatus and Procedure. The isothermal VLE measurement was carried out using HSGC for the binary and ternary systems. The HSGC consists of a gas chromatograph (HP 6890N) and a headspace sampler (HP19395A), which has an electro-pneumatic sampling system and a precision thermostat, with an accuracy

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Table 1. Densities, Refractive Indices, and Antoine Constants of Used Chemicals

chemicals	ρ/g·cm^{-3} at 298.15 K		n_D at 298.15 K		Antoine constants[a]		
	present	literature	present	literature	*A*	*B*	*C*
DBE	0.76422	0.76410[a]	1.39646	1.3970[c]	6.92880	1398.80	203.600
ethanol	0.78527	0.78517[b]	1.35933	1.35924[b]	8.11220	1592.86	226.184
2,2,4-trimethyl pentane	0.68818	0.68774[b]	1.38898	1.38900[b]	6.96602	1339.49	229.033

[a] Ref 11. [b] Ref 12. [c] Ref 13.

Table 2. Activity Coefficient Model Parameters and Mean Deviation between the Calculated and the Experimental Vapor-Phase Mole Fraction (Δy_1) for the Binary System DBE (1) + 2,2,4-Trimethylpentane (2) at 333.15 K

P_{cal}/kPa	x_1	y_1	γ_1	γ_2
		DBE (1) + 2,2,4-trimethylpentane (2)		
28.12	0.0208	0.0045	1.09	1.00
27.64	0.0405	0.0094	1.16	1.00
27.13	0.0605	0.0154	1.24	0.99
26.75	0.0808	0.0200	1.19	1.00
25.88	0.1207	0.0308	1.18	1.00
24.93	0.1705	0.0430	1.13	1.01
23.60	0.2299	0.0611	1.12	1.01
22.33	0.2910	0.0802	1.10	1.01
21.16	0.3509	0.0993	1.07	1.03
19.87	0.4106	0.1222	1.06	1.03
18.60	0.4706	0.1474	1.04	1.05
17.31	0.5303	0.1761	1.03	1.06
15.92	0.5907	0.2115	1.02	1.07
14.55	0.6491	0.2529	1.02	1.08
13.05	0.7102	0.3076	1.01	1.09
11.64	0.7708	0.3713	1.01	1.12
10.13	0.8304	0.4579	1.00	1.13
8.80	0.8808	0.5587	1.00	1.14
7.75	0.9199	0.6617	1.00	1.15
7.21	0.9401	0.7273	1.00	1.15
6.68	0.9596	0.8005	1.00	1.15
6.14	0.9795	0.8899	1.00	1.15

model equation	A_{12} (J·mol^{-1})	A_{21} (J·mol^{-1})	α	Δy_1
		DBE (1) + 2,2,4-Trimethylpentane (2)		
Margules	0.77	0.68		0.0010
van Laar	0.77	0.68		0.0011
Wilson	503.61	4.93		0.0011
NRTL	−273.62	789.83	0.3000	0.0011
UNIQUAC	−169.66	273.00		0.0011

Table 3. Calculated G^E Values for Three Sub-binary Systems of the Mixture DBE, Ethanol, and 2,2,4-Trimethylpentane at 333.15 K

x_1	G^E J·mol^{-1}	x_1	G^E J·mol^{-1}	x_1	G^E J·mol^{-1}
		DBE (1) + 2,2,4-Trimethylpentane (2)			
0.0208	4.96	0.3509	118.90	0.8304	57.41
0.0405	16.65	0.4106	114.52	0.8808	43.26
0.0605	9.89	0.4706	122.67	0.9199	31.01
0.0808	38.93	0.5303	119.22	0.9401	23.19
0.1207	55.33	0.5907	109.10	0.9596	15.64
0.1705	80.58	0.6491	110.40	0.9795	7.94
0.2299	93.39	0.7102	88.75		
0.2910	96.36	0.7708	93.19		
		DBE (1) + Ethanol (2)[a]			
0.0198	87.02	0.3504	948.80	0.9396	287.22
0.0399	170.37	0.4104	1008.61	0.9609	193.42
0.0600	248.93	0.4710	1042.77	0.9809	98.09
0.0799	322.18	0.6510	986.85		
0.1204	458.18	0.7722	801.92		
0.1704	603.57	0.8318	658.35		
0.2303	747.80	0.8825	503.60		
0.2905	862.57	0.9218	359.92		
		Ethanol (1) + 2,2,4-Trimethylpentane (2)[b]			
0.0196	142.66	0.4102	1441.53	0.8803	628.87
0.0589	396.82	0.4702	1463.58	0.9198	444.54
0.0791	513.69	0.5303	1449.76	0.9399	341.82
0.1189	717.91	0.5897	1400.74	0.9602	234.47
0.1676	923.11	0.6499	1314.74	0.9799	120.72
0.2292	1129.13	0.7099	1193.80		
0.2904	1280.24	0.7705	1031.41		
0.3486	1379.24	0.8300	832.03		

[a] Calculated using VLE data from ref 1. [b] Calculated using VLE data from ref 18.

of ± 0.1 K. An HP-5 (30 m × 0.32 mm × 0.25 μm) capillary column and a thermal conductivity detector were used for the analysis. The experimental apparatus and the procedure used for the measurements were described in the previous articles.[14,15] Densities were measured by a digital vibrating glass tube densimeter (Anton Paar, model DMA 5000, Graz, Austria). The inaccuracy of the densimeter is reported to be $5 \cdot 10^{-6}$ g·cm^{-3} in the range of 0 to 3. Temperature is controlled within ± 0.01 K in the range from (273.15 to 363.15) K. The operating procedures have been described in detail elsewhere.[14,16] Refractive indices (n_D) were measured by digital precision refractometer (KEM, model RA-520N, Kyoto, Japan). The inaccuracy of this refractometer is reported to be as $\pm 5 \cdot 10^{-5}$ in the range from 1.32 to 1.40 and $\pm 1 \cdot 10^{-4}$ in the range from 1.40 to 1.58. The details of operating procedures have been described elsewhere.[17]

Results and Discussion

Isothermal VLE. In the headspace VLE measuring method, equilibrium pressure is calculated from the experimental vapor phase composition and thermodynamic equations.[14] True liquid mole compositions were calculated from the vapor-phase equilibrium composition and mass balances. Vapor pressures of each pure component at 333.15 K were calculated using the Antoine constants in Table 1. The experimental VLE compositions, calculated equilibrium pressures, and activity coefficients for the binary system DBE + 2,2,4-trimethylpentane at 333.15 K are listed in Table 2.

The experimental binary VLE data were correlated with the five common activity coefficient models (Margules, van Laar, Wilson, NRTL, and UNIQUAC). The adjustable binary parameters of the activity coefficient model correlation are also listed in Table 2, along with the mean deviations. The mean deviation of vapor-phase mole fraction (Δy_1) can be expressed as

$$\Delta y_1 = \frac{|\Delta y_{1,\mathrm{exp}} - \Delta y_{1,\mathrm{cal}}|}{N} \qquad (1)$$

where *N* is the number of experimental data points. The binary parameters A_{ij} of the Wilson, NRTL, and UNIQUAC models are

$$A_{ij} = (\lambda_{ij} - \lambda_{ii})/\mathrm{J{\cdot}mol^{-1}} \text{ (Wilson)}$$

$$A_{ij} = (g_{ij} - g_{ii})/\mathrm{J{\cdot}mol^{-1}} \text{ (NRTL)}$$

$$A_{ij} = (u_{ij} - u_{ii})/\mathrm{J{\cdot}mol^{-1}} \text{ (UNIQUAC)}$$

From the activity coefficients, binary excess Gibbs energy can be evaluated using eq 2:

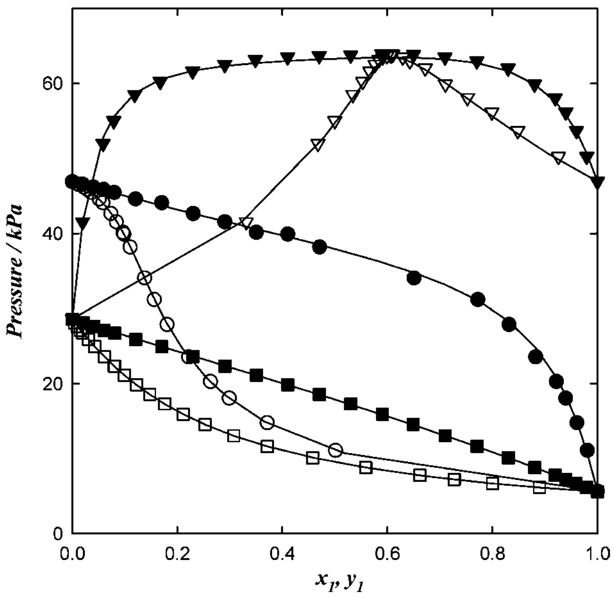

Figure 1. Experimental VLE data: ■, at 333.15 K for the binary system DBE (1) + 2,2,4-trimethylpentane (2) with previous reported VLE data;[1,18] ●, DBE (1) + ethanol (2);[1] and ▼, ethanol (1) + 2,2,4-trimethylpentane (2).[18] Solid curves were calculated from NRTL model parameters.

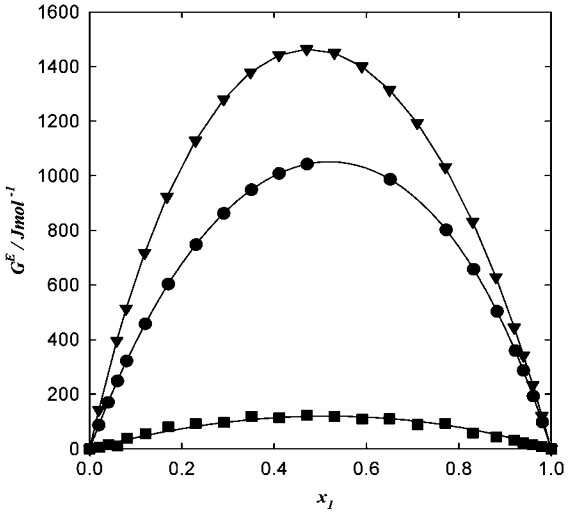

Figure 2. Excess Gibbs free energies for three binary systems at 333.15 K: ●, DBE (1) + ethanol (2) from previous work;[1] ■, DBE (1) + 2,2,4-trimethylpentane (2); ▼, ethanol (1) + 2,2,4-trimethylpentane (2) from previous work.[18] Solid curves were calculated from NRTL model parameters.

$$\frac{G^{\mathrm{E}}}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \tag{2}$$

The calculated excess Gibbs energy G^{E} for three sub-binaries of the DBE + 2,2,4-trimethylpentane + ethanol system are listed in Table 3. The G^{E} values for two binaries of DBE + ethanol and ethanol + 2,2,4-trimethylpentane were calculated from previously reported VLE data.[1,18]

Figure 1 shows the $P-x-y$ diagram for the DBE + 2,2,4-trimethylpentane system at 333.15 K, along with that of binary systems DBE + ethanol and ethanol + 2,2,4-trimethylpentane, as a completion of sub-binaries that were reported in our previous work.[1,18] There is no azeotrope in the DBE + 2,2,4-trimethylpentane system, while a minimum boiling azeotrope was observed in the ethanol + 2,2,4-trimethylpentane system.

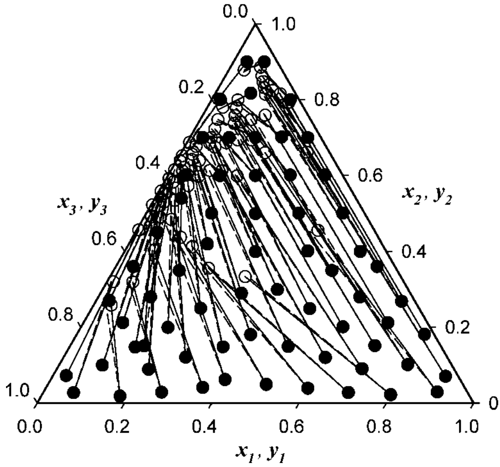

Figure 3. VLE for the ternary system DBE (1) + ethanol (2) + 2,2,4-trimethylpentane (3) at 333.15 K; ●, liquid phase; ○, vapor phase. Dashed lines were calculated from NRTL equation.

Figure 2 shows excess Gibbs energy for the three constituent binaries of the mixture DBE + ethanol + 2,2,4-trimethylpentane. These show positive deviations from the ideal. The composition dependence is approximately symmetrical in shape, as is usually the case.

The isothermal VLE data for the ternary system DBE + ethanol + 2,2,4-trimethylpentane at 333.15 K are plotted in Figure 3 and listed in Table 4. The ternary VLE data were correlated with the Wilson, NRTL, and UNIQUAC models. The NRTL model provided slightly better results. The dashed lines in Figure 3 represent the values calculated using the NRTL equation. The G^{E} model parameters and the mean deviation of the vapor-phase mole fraction (Δy_{mean}) are given in Table 5. Δy_{mean} can be determined from eq 3.

$$\Delta y_{\mathrm{mean}} = \frac{\Delta y_1 + \Delta y_2 + \Delta y_3}{3} \tag{3}$$

Excess Molar Volumes and Deviations in Molar Refractivity. The excess molar volumes (V^{E}) for the multicomponent mixtures are calculated from the measured densities of pure substances and mixtures from eq 4.

$$V^{\mathrm{E}} = \frac{\sum_{\mathrm{i}} x_{\mathrm{i}} M_{\mathrm{i}}}{\rho_{\mathrm{m}}} - \sum_{\mathrm{i}} \left(\frac{x_{\mathrm{i}} M_{\mathrm{i}}}{\rho_{\mathrm{i}}}\right) \tag{4}$$

where x_{i}, M_{i}, ρ_{i}, and ρ_{m} are the mole fraction, molar mass, and density for a given pure component i and mixture, respectively.

Deviations in molar refractivity (ΔR) were calculated from the molar refractivity (R_{m}) of each pure component and mixture, derived from measured densities and refractive indices with the following equations.[19,20]

$$\Delta R/\mathrm{cm^3 \cdot mol^{-1}} = R_{\mathrm{m}} - \sum_{\mathrm{i}} \phi_{\mathrm{i}} R_{\mathrm{i}} \tag{5}$$

$$R_{\mathrm{m}} = \left(\frac{n_{\mathrm{D}}^2 - 1}{n_{\mathrm{D}}^2 + 1}\right)\left(\frac{\sum_{\mathrm{i}} x_{\mathrm{i}} M_{\mathrm{i}}}{\rho_{\mathrm{m}}}\right) \tag{6}$$

$$R_{\mathrm{i}} = \left(\frac{n_{\mathrm{D,i}}^2 - 1}{n_{\mathrm{D,i}}^2 + 1}\right)\left(\frac{M_{\mathrm{i}}}{\rho_{\mathrm{i}}}\right) \tag{7}$$

and

Table 4. Isothermal VLE for the Ternary System DBE (1) + Ethanol (2) + 2,2,4-Trimethylpentane (3) at 333.15 K

P_{cal} kPa	x_1	x_2	y_1	y_2	r_1	r_2
58.80	0.0605	0.5395	0.0098	0.6373	1.30	1.38
58.34	0.0507	0.4500	0.0075	0.6150	1.13	1.60
57.63	0.0403	0.3601	0.0065	0.5918	1.02	1.97
56.72	0.0303	0.2707	0.0050	0.5583	0.97	2.59
50.61	0.1703	0.1510	0.0034	0.5220	0.92	3.66
55.64	0.1805	0.4195	0.0342	0.6416	1.15	1.64
55.45	0.1506	0.3497	0.0274	0.6116	1.04	1.91
55.10	0.1198	0.2803	0.0210	0.5823	0.98	2.35
54.52	0.0905	0.2121	0.0153	0.5533	0.95	3.04
49.47	0.0307	0.0722	0.0050	0.4559	0.98	6.34
50.00	0.3231	0.2900	0.0521	0.6391	1.03	2.06
51.29	0.2498	0.2500	0.0428	0.6023	0.97	2.38
51.42	0.1997	0.1998	0.0346	0.5666	0.93	2.92
51.05	0.1508	0.1477	0.0258	0.5298	0.93	3.78
49.94	0.0997	0.0999	0.0169	0.4907	0.94	5.04
44.54	0.3516	0.1483	0.0598	0.5727	0.91	3.20
45.47	0.2796	0.1211	0.0478	0.5342	0.90	3.82
45.32	0.2109	0.0890	0.0368	0.4895	0.92	4.77
39.18	0.0699	0.0271	0.0144	0.3199	0.99	8.07
32.99	0.3592	0.0411	0.0669	0.4037	0.89	5.43
33.09	0.2712	0.0285	0.0594	0.3192	0.91	6.40
32.89	0.1806	0.0185	0.0404	0.2586	0.95	7.54
59.30	0.0400	0.6000	0.0084	0.6383	1.44	1.27
59.36	0.0297	0.7001	0.0065	0.6518	1.84	1.15
58.58	0.0200	0.8000	0.0057	0.6870	2.64	1.07
56.99	0.1495	0.4999	0.0276	0.6558	1.30	1.45
58.04	0.1196	0.5991	0.0257	0.6768	1.57	1.29
58.47	0.0902	0.7000	0.0222	0.6991	2.03	1.18
55.36	0.0303	0.8999	0.0140	0.8017	5.09	1.06
52.32	0.3005	0.3993	0.0532	0.6850	1.20	1.66
54.55	0.2506	0.4991	0.0492	0.6995	1.41	1.46
56.20	0.2002	0.5993	0.0459	0.7223	1.73	1.32
57.15	0.1500	0.7003	0.0407	0.7472	2.25	1.23
57.11	0.0808	0.8172	0.0357	0.7798	3.36	1.13
48.29	0.4195	0.4011	0.0832	0.7369	1.31	1.67
51.31	0.3490	0.5002	0.0747	0.7577	1.56	1.50
53.64	0.2794	0.6008	0.0678	0.7772	1.93	1.38
55.20	0.2094	0.7012	0.0606	0.7988	2.50	1.29
53.60	0.0705	0.8995	0.0351	0.8780	5.87	1.12
42.85	0.5399	0.4001	0.1160	0.8140	1.47	1.74
46.68	0.4497	0.5003	0.1052	0.8312	1.75	1.58
49.89	0.3589	0.6008	0.0937	0.8473	2.16	1.46
52.22	0.2703	0.6995	0.0836	0.8628	2.78	1.36
53.33	0.1800	0.7998	0.0690	0.8854	3.89	1.27
35.13	0.3994	0.0622	0.0658	0.4834	0.88	4.64
29.30	0.5006	0.0491	0.1101	0.4369	0.87	4.59
23.94	0.6005	0.0388	0.1495	0.4123	0.87	4.52
18.66	0.6991	0.0278	0.2147	0.3556	0.88	4.53
14.54	0.7989	0.0218	0.3099	0.3337	0.90	4.48
44.36	0.3989	0.1806	0.0713	0.5970	0.93	2.75
39.08	0.5002	0.1495	0.0888	0.6130	0.93	2.91
33.28	0.6000	0.1203	0.1169	0.6126	0.92	3.11
26.93	0.6990	0.0904	0.1590	0.5985	0.93	3.38
12.89	0.9017	0.0293	0.4155	0.4551	0.96	4.24
47.67	0.4007	0.2993	0.0703	0.6743	1.07	1.97
42.93	0.5001	0.2491	0.0896	0.6861	1.05	2.17
37.48	0.5999	0.2011	0.1131	0.6937	1.02	2.40
31.30	0.6977	0.1515	0.1456	0.6930	1.00	2.73
24.13	0.7981	0.1011	0.1926	0.6599	0.99	3.19
44.61	0.5002	0.3497	0.0967	0.7404	1.26	1.81
39.47	0.5991	0.2798	0.1164	0.7472	1.18	2.04
33.68	0.6974	0.2121	0.1429	0.7588	1.11	2.35
17.99	0.9004	0.0704	0.2876	0.6612	1.02	3.58
39.94	0.5982	0.3605	0.1276	0.8240	1.41	1.85
34.49	0.7008	0.2683	0.1493	0.8149	1.26	2.14
28.43	0.7967	0.1815	0.1804	0.7925	1.14	2.57

Table 5. Activity Coefficient Model Parameters and Mean Deviation between the Calculated and the Experimental Vapor-Phase Mole Fraction (Δy_{mean}) for the Ternary System DBE (1) + Ethanol (2) + 2,2,4-Trimethylpentane (3) at 333.15 K

model equation	A_{ij} J·mol^{-1}	A_{ji} J·mol^{-1}	α	Δ*y*
Wilson				
1 + 2	−1388.42	6018.81		
2 + 3	8597.89	−74.85		0.0096
1 + 3	−48.89	−124.53		
NRTL				
1 + 2	3097.48	5931.28	0.7088	
2 + 3	1630.98	5174.81	0.3000	0.0094
1 + 3	2862.72	−1953.38	0.3000	
UNIQUAC				
1 + 2	4102.07	−1198.55		
2 + 3	−1200.79	5347.86		0.0122
1 + 3	−71.59	33.12		

$$\phi_i = \frac{x_i V_i}{\sum_j x_j V_j} \tag{8}$$

where ϕ_i, n_D, $n_{D,i}$, and V_i are the volume fractions of each pure component in the mixture, the refractive index of the mixture, and the refractive index and molar volume of a given pure component i, respectively.

The binary V^E and ΔR data were correlated with the Redlich−Kister polynomial.[5]

$$V_{12}^E \quad \text{or} \quad \Delta R/\text{cm}^3\text{·mol}^{-1} = x_1 x_2 \sum_{i=1}^{n} A_i (x_1 - x_2)^{i-1} \tag{9}$$

The standard deviation of the fits, σ_{st}, is defined as

Table 6. Densities, Excess Molar Volumes, Refractive Indices, and Deviations in Molar Refractivity for the Binary System DBE (1) + 2,2,4-Trimethylpentane (2) at 298.15 K

x_1	ρ g·cm^{-3}	V^E cm^3·mol^{-1}	n_D	ΔR cm^3·mol^{-1}
DBE (1) + 2,2,4-Trimethylpentane (2)				
0.0497	0.69210	−0.0124	1.38937	−0.0056
0.1000	0.69609	−0.0303	1.38978	−0.0109
0.1996	0.70390	−0.0521	1.39059	−0.0162
0.3000	0.71173	−0.0730	1.39139	−0.0214
0.4001	0.71945	−0.0851	1.39217	−0.0242
0.5005	0.72717	−0.1014	1.39296	−0.0258
0.6003	0.73481	−0.1156	1.39376	−0.0238
0.7000	0.74231	−0.1108	1.39449	−0.0217
0.8000	0.74975	−0.0940	1.39521	−0.0155
0.9000	0.75711	−0.0705	1.39589	−0.0100
0.9500	0.76070	−0.0423	1.39621	−0.0037

$$\sigma_{st}/\text{cm}^3\text{·mol}^{-1} = \left[\frac{\sum_i ((V^E \text{ or } \Delta R)_{cal} - (V^E \text{ or } \Delta R)_{exp})_i^2}{(N - n)} \right]^{1/2} \tag{10}$$

where *N* is the number of experimental data points and *n* is the number of fitted parameters. In this work, we used four parameters.

The experimental densities, excess molar volumes (V^E), refractive indices, and deviations in molar refractivity (ΔR) for the binary system DBE + 2,2,4-trimethylpentane at 298.15 K are listed in Table 6. The measured V^E and ΔR are plotted together in Figure 4. The V^E data show negative deviations from ideal behavior over the whole composition range. These V^E data correlated well with the Redlich−Kister polynomial, as shown

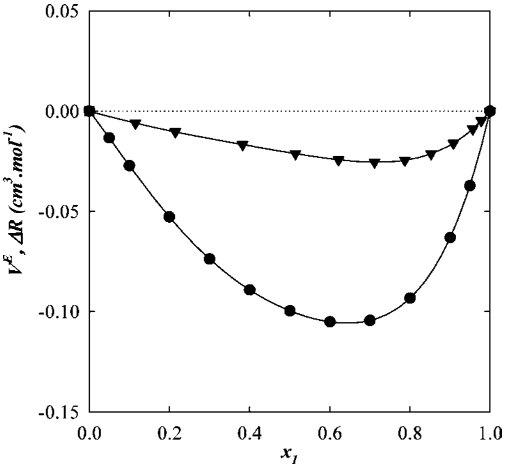

Figure 4. Experimental ●, V^E; ▼, ΔR; for the binary system DBE (1) + 2,2,4-trimethylpentane (2) at 298.15 K. Solid curves were calculated from Redlich−Kister polynomial.

in Figure 4. The solid line represents calculated values using correlated parameters. In the same way, the ΔR data show negative values and also correlated well with the Redlich−Kister polynomial, as shown in Figure 4. The correlated Redlich−Kister parameters for binary V^E and ΔR data are listed in Table 8, together with the Cibulka parameters for ternary systems, as well as their standard deviations.

The V^E and ΔR for the ternary system DBE + ethanol + 2,2,4-trimethylpentane were derived from measured densities and refractive indices at 298.15 K. The densities, V^E, refractive indices, and ΔR for this ternary system at 298.15 K are listed in Table 7. The ternary V^E and ΔR were correlated with the Cibulka equation (eqs 11a, 11b)[6] as a modification of the Radojkovič equation (eqs 12a, 12b).[7]

$$V^E_{123} = V^E_{12} + V^E_{23} + V^E_{13} + x_1x_2x_3(A_1 + A_2x_1 + A_3x_2) \tag{11a}$$

$$\Delta R_{123} = \Delta R_{12} + \Delta R_{23} + \Delta R_{13} + x_1x_2x_3(A_1 + A_2x_1 + A_3x_2) \tag{11b}$$

$$V^E_{123} = V^E_{12*} + V^E_{23*} + V^E_{13*} \tag{12a}$$

$$\Delta R_{123} = \Delta R_{12*} + \Delta R_{23*} + \Delta R_{13*} \tag{12b}$$

where V^E_{12}, V^E_{23}, V^E_{13}, ΔR_{12}, ΔR_{23}, and ΔR_{13} represent the excess molar volumes and refractive indices of each binary mixture, respectively, and x_1, x_2, and x_3 are mole fractions of components 1, 2, and 3, respectively.

The correlated Cibulka parameters for ternary V^E and ΔR data are listed in Table 8 along with the standard deviation between the calculated and the experimental data. The correlated values are in good agreement with the experimental data with standard deviations of 0.0140 and 0.0152 for the ternary V^E and ΔR, respectively. The correlation results using the Cibulka equation are represented as isochors in Figures 5 and 6 for the ternary V^E and ΔR, respectively.

In addition, the ternary V^E and ΔR were calculated using different estimation models of Radojkovič, Tsao−Smith, Kohler, and Rastogi and compared with experimental results. For this calculation, the previously reported Redlich−Kister parameters in Table 8 were used.[1,21] The estimated standard deviations for each model are given in Table 9. The Radojkovič model provided the best results with the standard deviations of 0.0273 $cm^3 \cdot mol^{-1}$ and 0.5962 $cm^3 \cdot mol^{-1}$ for ternary V^E and ΔR, respectively.

Table 7. Densities, Excess Molar Volumes, Refractive Indices, and Deviations in Molar Refractivity for the Ternary System DBE (1) + Ethanol (2) + 2,2,4-Trimethylpentane (3) at 298.15 K

x_1	x_2	ρ $g \cdot cm^{-3}$	V^E $cm^3 \cdot mol^{-1}$	n_D	ΔR $cm^3 \cdot mol^{-1}$
0.0601	0.5400	0.72178	0.2985	1.38021	−8.7409
0.0504	0.4509	0.71354	0.3284	1.38238	−7.9437
0.0405	0.3612	0.70654	0.3438	1.38387	−6.8221
0.0308	0.2708	0.70062	0.3373	1.38536	−5.3976
0.0200	0.1797	0.69553	0.2928	1.38692	−3.7182
0.1799	0.4200	0.72579	0.2018	1.38539	−7.7026
0.1509	0.3496	0.71748	0.2275	1.38599	−6.7233
0.1202	0.2811	0.71001	0.2578	1.38634	−5.6315
0.0904	0.2123	0.70346	0.2646	1.38696	−4.3920
0.0302	0.0740	0.69259	0.1654	1.38873	−1.5562
0.3006	0.2992	0.72901	0.1089	1.38889	−6.0126
0.2501	0.2506	0.72066	0.1594	1.38857	−5.1537
0.2006	0.1991	0.71302	0.1667	1.38832	−4.2035
0.1505	0.1505	0.70598	0.1830	1.38836	−3.2290
0.0997	0.0993	0.69938	0.1624	1.38869	−2.1447
0.3493	0.1512	0.72343	0.0753	1.39015	−3.3318
0.2791	0.1205	0.71563	0.0961	1.38969	−2.6825
0.2108	0.0889	0.70829	0.1026	1.38947	−1.9893
0.0702	0.0315	0.69458	0.0672	1.38931	−0.6827
0.3608	0.0388	0.71819	−0.0104	1.39136	−0.9130
0.2691	0.0322	0.71059	0.0002	1.39078	−0.7443
0.1810	0.0187	0.70300	0.0151	1.39021	−0.4294
0.0398	0.6000	0.72460	0.3144	1.37800	−8.9781
0.0299	0.6996	0.73394	0.2816	1.37389	−8.8454
0.0198	0.8006	0.74624	0.2180	1.36917	−7.6744
0.1498	0.4996	0.72925	0.1982	1.38294	−8.5572
0.1203	0.6004	0.73555	0.1943	1.37913	−9.1702
0.0898	0.7007	0.74325	0.1795	1.37419	−9.0626
0.0299	0.9003	0.76668	0.0776	1.36524	−5.0868
0.3001	0.4009	0.73730	0.0905	1.38776	−7.5525
0.2499	0.4999	0.74119	0.0976	1.38469	−8.6908
0.2006	0.5992	0.74609	0.0972	1.38043	−9.3387
0.1497	0.7001	0.75217	0.0949	1.37521	−9.2440
0.1001	0.7999	0.76012	0.0744	1.37002	−8.0463
0.4201	0.4006	0.75001	0.0076	1.38935	−7.6674
0.3501	0.4996	0.75288	0.0139	1.38625	−8.8252
0.2799	0.6001	0.75655	0.0196	1.38185	−9.4904
0.2099	0.7001	0.76099	0.0327	1.37696	−9.3680
0.0702	0.8996	0.77436	0.0288	1.36646	−5.3059
0.5395	0.3999	0.76248	−0.0675	1.38991	−7.8530
0.4490	0.5007	0.76446	−0.0575	1.38744	−8.9896
0.3604	0.5997	0.76689	−0.0496	1.38362	−9.6146
0.2703	0.6996	0.76980	−0.0383	1.37907	−9.4742
0.1798	0.8000	0.77353	−0.0254	1.37366	−8.2332
0.4001	0.0588	0.72240	−0.0073	1.39156	−1.3618
0.4996	0.0510	0.72987	−0.0267	1.39242	−1.1988
0.5997	0.0399	0.73709	−0.0536	1.39321	−0.9681
0.7009	0.0293	0.74429	−0.0810	1.39421	−0.7174
0.8004	0.0197	0.75119	−0.0858	1.39508	−0.4868
0.3987	0.1821	0.72981	0.0477	1.39027	−3.9852
0.5008	0.1495	0.73642	0.0016	1.39174	−3.3346
0.6974	0.0933	0.74847	−0.0294	1.39373	−2.1705
0.8978	0.0303	0.75916	−0.0327	1.39572	−0.7254
0.4000	0.2993	0.73862	0.0631	1.38981	−6.0972
0.5004	0.2503	0.74403	0.0214	1.39104	−5.3099
0.7007	0.1495	0.75330	−0.0457	1.39357	−3.3861
0.7974	0.1028	0.75731	−0.0489	1.39465	−2.3845
0.5000	0.3503	0.75310	−0.0062	1.38992	−7.0605
0.5985	0.2811	0.75602	−0.0478	1.39196	−5.9269
0.7063	0.2030	0.75844	−0.0541	1.39292	−4.5361
0.8976	0.0707	0.76248	−0.0386	1.39556	−1.6688
0.5996	0.3601	0.76413	−0.0680	1.39112	−7.2897
0.7004	0.2690	0.76422	−0.0703	1.39260	−5.8034
0.8018	0.1786	0.76438	−0.0675	1.39418	−4.0421

Table 8. Fitted Parameters for the Redlich−Kister Equation, Cibulka Equation, and Standard Deviations for V^E and ΔR of DBE (1) + Ethanol (2) + 2,2,4-Trimethylpentane (3) at 298.15 K

	system	A_1	A_2	A_3	A_4	σ_{st}
V^E	(1) + (2)[a]	−0.4237	−0.1603	−0.1562	−0.0505	0.0022
	(2) + (3)[b]	1.5472	−0.2547	0.6632	−0.0991	0.0065
	(1) + (3)	−0.4405	−0.1504	−0.2099	−0.0487	0.0040
	(1) + (2) + (3)	2.2243	1.7309	−6.1264		0.0140
ΔR	(1) + (2)[a]	−36.2900	17.8057	−10.0735	5.1896	0.0268
	(2) + (3)[b]	−33.3886	−16.1668	−8.5427	−5.7627	0.0219
	(1) + (3)	−0.1179	−0.0111	−0.0167	0.0675	0.0009
	(1) + (2) + (3)	14.1279	0.9665	52.2099		0.0152

[a] Parameters taken from ref 1. [b] Parameters taken from ref 21.

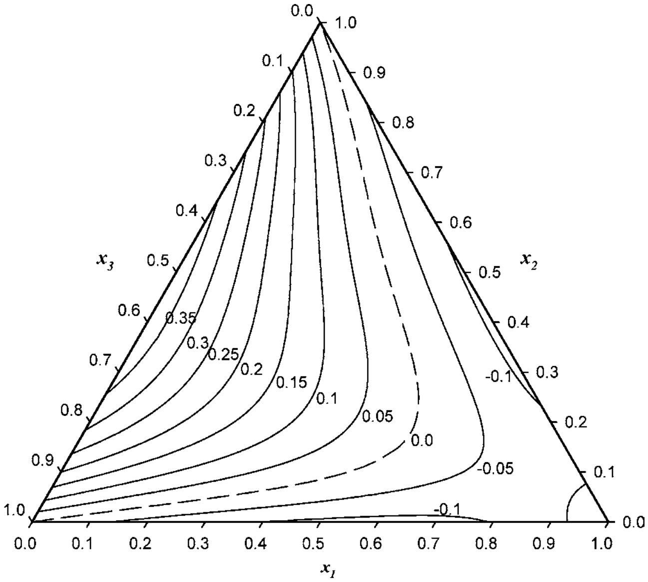

Figure 5. Constant lines of V^E ($cm^3 \cdot mol^{-1}$) for the ternary system DBE (1) + ethanol (2) + 2,2,4-trimethylpentane (3) at 298.15 K.

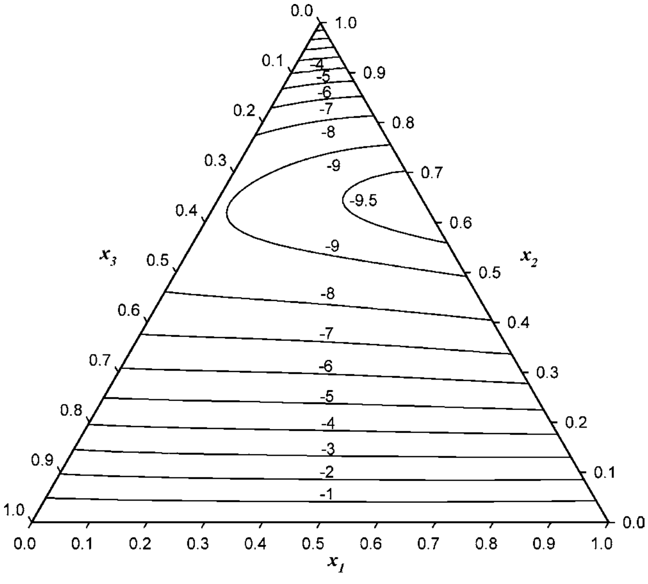

Figure 6. Constant lines of ΔR ($cm^3 \cdot mol^{-1}$) for the ternary system DBE (1) + ethanol (2) + 2,2,4-trimethylpentane (3) at 298.15 K.

Table 9. Standard Deviations[a] for the Estimation Results of V^E and ΔR for the Ternary System DBE (1) + Ethanol (2) + 2,2,4-Trimethylpentane (3) at 298.15 K

	model eq			
property	Radojkovič	Tsao−Smith	Kohler	Rastogi
V^E	0.0273	0.1322	0.0275	0.0388
ΔR	0.5962	1.7754	1.7881	1.2879

[a] Calculated using eq 10.

Conclusion

Isothermal VLE data at 333.15 K, as well as excess molar volumes (V^E) and changes of refractive index (ΔR) at 298.15 K, were determined experimentally for the binary system DBE + 2,2,4-trimethylpentane and the ternary system DBE + ethanol + 2,2,4-trimethylpentane. The binary VLE data have no azeotropes and correlated well with common G^E model equations. The ternary data correlated with the Wilson, NRTL, and UNIQUAC models, and the NRTL model provided the best correlation result. The experimental V^E and ΔR data for the same binary system show negative deviations from ideal behavior and correlated well with the Redlich−Kister equation, while the Cibulka equation was applied reliably for the ternary V^E and ΔR data of the same ternary system. In addition, the ternary V^E and ΔR data were also compared with the predicted values using the binary contribution models of Radojkovič, Tsao−Smith, Kohler, and Rastogi. The Radojkovič model gave the best estimation results.

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