Isothermal Vapor−Liquid Equilibrium at 333.15 K, Density, and Refractive Index at 298.15 K for the Ternary Mixture of Dibutyl Ether + Ethanol + Benzene and Binary Subsystems

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Isothermal vapor−liquid equilibrium (VLE) data at 333.15 K are reported for the binary systems of di-*n*-butyl ether (DBE) + ethanol, ethanol + benzene, DBE + benzene, and the ternary system of DBE + ethanol + benzene by using headspace gas chromatography. The experimental binary VLE data were correlated with common G^E model equations. The ternary VLE data were correlated also with Wilson, NRTL, and UNIQUAC models. Additionally the excess molar volumes (V^E) and deviations in molar refractivity (ΔR) at 298.15 K for the constituent binary and ternary systems of DBE + ethanol + benzene were determined from measured densities and refractive indices. The experimental V^E and ΔR were correlated with Redlich−Kister or Cibulka equation for the binary and ternary systems, respectively. The ternary V^E and ΔR were also compared with the estimated values from the binary contribution models of of Tsao−Smith, Kohler, Rastogi, and Radojkovič.

Introduction

In general, oxygenated ether compounds are neutral and have very low or no solubility in water; however, they are easily dissolved in most organic compounds. Methyl *tert*-butyl ether (MTBE) as an octane booster in reformulated gasoline is providing considerable air quality benefits, while at the same time causing significant contamination of groundwater because of its relatively high solubility in water. It is the one of the important reason that MTBE was faced out in the United States as a gasoline additive. Several petroleum- and non-petroleum-based compounds such as alcohols, other ethers, alkylate, and aromatics may replace MTBE. Unfortunately, none of these alternative fuel additives so far appear to satisfy all the criteria of environmental, public health, supply, and economic concerns. Among other ether compounds, ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), and diisopropyl ether (DIPE) have been used as oxygenates in gasoline. However due to the limited use of ethers, relatively very little scientific or field data are available for ether compounds.

We have studied therefore the phase equilibria and mixture properties systematically for several oxygenated ether compounds because the accurate estimation of such properties are strongly relate to the processing of alternate additives and greatly enhance the application of group contribution method as a thermodynamic tool. We reported previously vapor−liquid equilibria (VLE) and excess properties for various binary and ternary systems involving MTBE, ETBE, or TAME.[1−5]

Di-*n*-butyl ether (DBE) is an important solvent and also an excellent extracting agent for use with aqueous systems owing to its very low water solubility.[6] We report here the isothermal VLE data at 333.15 K for the binary systems of ethanol + di-*n*-butyl ether (DBE), benzene + DBE, and ethanol + benzene and for the ternary system of DBE + ethanol + benzene by using headspace gas chromatography (HSGC). Densities (ρ) and refractive indices (n_D) at 298.15 K for the binary and ternary systems of DBE + ethanol + benzene were also measured by using a digital vibrating tube density meter and a digital refractometer. Then the excess molar volumes (V^E) and deviations in molar refractivity (ΔR) were derived from the measured densities and refractive indices.

The experimental binary VLE data were correlated using common G^E model equations: Margules, van Laar, Wilson, NRTL, and UNIQUAC. While the ternary VLE data were correlated with Wilson, NRTL, and UNIQUAC models. The experimental V^E and ΔR were correlated with the Redlich−Kister polynomial and Cibulka equation for the binary and ternary systems, respectively. Since the ternary mixture properties are still not found in the literature, it is therefore interesting to estimate excess functions of ternary mixtures from binary data.[7,8] Especially for the ternary system, measured V^E and ΔR are therefore compared with the estimated values from the calculation using binary Redlich−Kister parameters.

Experimental Section

Materials. The chemicals used in this investigation were of analytical commercial grade purity. All the chemicals were dried using molecular sieves with a pore diameter of 0.4 nm. The purity of the chemicals was checked by gas chromatography and by comparing the density and refractive index with values reported in the literature.[9−13] The water content of the chemicals, determined by Karl Fischer titration (Metrohm 684 KF-Coulometer), was less than 70 ppm. The densities, refractive indices, and Antoine constants for the vapor pressure of the pure substances are summarized in Table 1.

Apparatus and Procedure. Isothermal VLE measurements have been carried out using HSGC for all the binary and ternary systems. The HSGC consists of a gas chromatograph (HP 6890N) and a headspace sampler (HP19395A), which has an

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Table 1. Purities, Densities, Refractive Indices, and Antoine Constants of Pure Components

	ρ/g·cm^{-3} at 298.15 K		n_D at 298.15 K		Antoine constants[a]		
chemicals	this study	lit. value	this study	lit. value	*A*	*B*	*C*
DBE	0.76422	0.7641[b]	1.39646	1.3970[c]	6.92880	1398.80	203.600
ethanol	0.78527	0.78510[d]	1.35928	1.35922[e]	8.11220	1592.86	226.184
benzene	0.87357	0.87366[f]	1.49764	1.49792[f]	6.87987	1196.76	219.161

[a] Ref 15. [b] Ref 9. [c] Ref 10. [d] Ref 11. [e] Ref 12. [f] Ref 13.

Table 2. Isothermal VLE for Binary Systems of Ethanol (1) + DBE (2), Benzene (1) + DBE (2), and Ethanol (1) + Benzene (2) at 333.15 K

ethanol (1) + DBE (2)			benzene (1) + DBE (2)			ethanol (1) + benzene (2)		
P_{cal}/kPa	x_1	y_1	P_{cal}/kPa	x_1	y_1	P_{cal}/kPa	x_1	y_1
11.12	0.0191	0.4988	6.52	0.0187	0.1463	55.51	0.0029	0.0632
14.80	0.0391	0.6288	7.48	0.0406	0.2718	55.55	0.0060	0.0639
18.08	0.0604	0.7010	8.33	0.0589	0.3592	56.48	0.0089	0.0833
20.29	0.0782	0.7368	9.31	0.0787	0.4402	63.22	0.0396	0.1982
23.58	0.1175	0.7784	11.24	0.1187	0.5571	65.38	0.0595	0.2361
27.91	0.1682	0.8195	14.74	0.1691	0.6885	67.79	0.0795	0.2763
31.20	0.2278	0.8440	17.30	0.2286	0.7499	70.04	0.1195	0.3140
34.07	0.3490	0.8621	20.17	0.2895	0.8014	71.95	0.1695	0.3401
38.21	0.5290	0.8898	23.09	0.3485	0.8409	73.44	0.2296	0.3725
39.92	0.5896	0.9017	26.38	0.4096	0.8746	73.70	0.2898	0.3808
40.16	0.6496	0.9036	28.44	0.4689	0.8920	74.20	0.3499	0.3906
41.56	0.7095	0.9160	31.08	0.5291	0.9115	74.36	0.4100	0.4115
42.66	0.7697	0.9265	33.90	0.5895	0.9291	74.24	0.4701	0.4308
44.10	0.8296	0.9416	36.70	0.6493	0.9439	73.87	0.5303	0.4522
44.61	0.8796	0.9485	39.23	0.7094	0.9557	73.27	0.5904	0.4677
45.47	0.9201	0.9633	41.91	0.7693	0.9668	72.17	0.6504	0.4903
45.86	0.9400	0.9706	44.69	0.8298	0.9768	70.15	0.7053	0.5360
46.18	0.9601	0.9780	45.95	0.8799	0.9816	68.23	0.7705	0.5762
46.55	0.9802	0.9884	48.13	0.9199	0.9891	65.56	0.8305	0.6154
			48.62	0.9402	0.9908	62.18	0.8804	0.6776
			49.88	0.9603	0.9950	58.95	0.9203	0.7380
			51.13	0.9804	0.9981	56.40	0.9403	0.7891
						54.04	0.9602	0.8401
						51.35	0.9801	0.8927

electro-pneumatic sampling system and a precision thermostat, having an uncertainty of ± 0.1 K. HP-5 (30 m × 0.32 mm × 0.25 μm) capillary column and a thermal conductivity detector were used for the analysis. By HSGC method, only equilibrated vapor phase is automatically analyzed with a help of electro-pneumatic sampling system, while the liquid-phase compositions are calculated with thermodynamic relations and mass balance starting from the feed compositions. The uncertainty of the calculated mole fraction is $\pm 1 \times 10^{-4}$. The procedure is described in detail elsewhere.[1,2]

Densities were measured using a digital vibrating glass tube densimeter(Anton Paar, model DMA 5000, Graz, Austria). The uncertainty of this densimeter is less than 1×10^{-5} g·cm^{-3}. The detail operating procedures have been described elsewhere.[2,14] Refractive indices (n_D) of the pure components and mixture samples were measured with help of digital refractometer (KEM, model RA-520N, Kyoto, Japan). The uncertainty of the refractometer is $\pm 5 \times 10^{-5}$ within range from 1.32 to 1.40 and $\pm 1 \times 10^{-4}$ within range from 1.40 to 1.58. Mixture samples were prepared with the same procedure as the density measurements.

Results and Discussion

Isothermal VLE. To calculate the true liquid mole compositions,[1] the thermophysical data for the SRK equation were adopted from pure component properties stored in the DDB[15] and Reid et al.[16] Vapor pressures of the pure component at 333.15 K were calculated by using the Antoine equation. In the HSGC method, the equilibrium pressure cannot be measured but can be calculated from experimental vapor-phase mole compositions and thermodynamic equations.[2] The experimental VLE compositions and calculated pressures for the binary systems of ethanol (1) + DBE (2), benzene (1) + DBE (2), and ethanol (1) + benzene (2) at 333.15 K are listed in Table 2 and plotted in Figure 1.

There is no azeotrope in the binary VLE for ethanol + DBE and benzene + DBE systems, while a minimum boiling azeotrope was observed in the ethanol + benzene system. The azeotropic point determined by interpolation is $x_1 = 0.412$ and $P = 74.36$ kPa. The measured binary VLE values for ethanol + benzene and benzene + DBE were compared with the

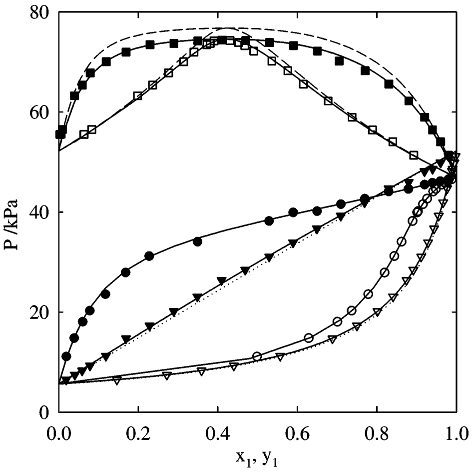

Figure 1. VLE for the three binary systems of DBE, ethanol, and benzene at 333.15 K: Filled symbols, liquid phase; open symbols, vapor phase; ●, ethanol (1) + DBE (2); ■, ethanol (1) + benzene (2); - - -, ethanol (1) + benzene (2) reproduced from UNIQUAC parameter of Udovenko et al.;[17] ▼, benzene (1) + DBE (2); ···, benzene (1) + DBE (2) reproduced with Wilson parameter from Ott et al.[18] Solid curves were calculated from NRTL equation.

Table 3. G^{E} Model Parameters and Mean Deviation between Calculated and Experimental Vapor-Phase Mole Fraction (Δy_1) for the Binary Systems at 333.15 K

model equation	A_{12}/J·mol^{-1}	A_{21}/J·mol^{-1}	α	Δy_1
Ethanol (1) + DBE (2)				
Margules	1.6938	1.4379		0.0080
van Laar	1.7125	1.4392		0.0075
Wilson	1548.8878	−171.2445		0.0039
NRTL	706.6015	918.5882	0.6471	0.0031
UNIQUAC	241.9310	979.7657		0.0084
Benzene (1) + DBE (2)				
Margules	0.1454	0.0377		0.0054
van Laar	0.1344	0.0683		0.0063
Wilson	10.4267	149.1937		0.0062
NRTL	−430.5394	618.2242	0.3000	0.0059
UNIQUAC	203.816	−146.8325		0.0062
Ethanol (1) + Benzene (2)				
Margules	1.9136	1.2650		0.0187
van Laar	2.0237	1.2922		0.0156
Wilson	1452.7392	119.9338		0.0093
NRTL	529.6984	1050.5419	0.5205	0.0094
UNIQUAC	−139.8816	789.2269		0.0132

reproduced data by UNIQUAC and Wilson parameters from the literature[17,18] and showed good agreement as plotted in Figure 1. The experimental binary VLE data were correlated with the five common G^{E} models (Margules, van Laar, Wilson, NRTL, and UNIQUAC).

The adjustable binary parameters of the G^{E} model correlation are listed in Table 3 along with the mean deviations. The mean deviation of vapor-phase mole fraction (Δy_1) means

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

where N is the number of experimental data points. The binary parameters (A_{ij})[16] of the Wilson, NRTL, and UNIQUAC models are as follows:

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

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

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

The isothermal VLE data for the ternary systems of DBE (1) + ethanol (2) + benzene (3) at 333.15 K were measured with the help of HSGC. The experimental VLE compositions and calculated pressures for the ternary system are listed in Table 4 and are plotted in Figure 2. The ternary VLE data were correlated with the Wilson, NRTL, and UNIQUAC models, and the NRTL model provided the best result. Dashed lines in Figure 2 represent the calculated values by the NRTL equation. The G^{E} model parameters and the mean deviation of vapor-phase mole fraction (Δy_{mean}) are given in Table 5. Δy_{mean} can be determined by the following equation:

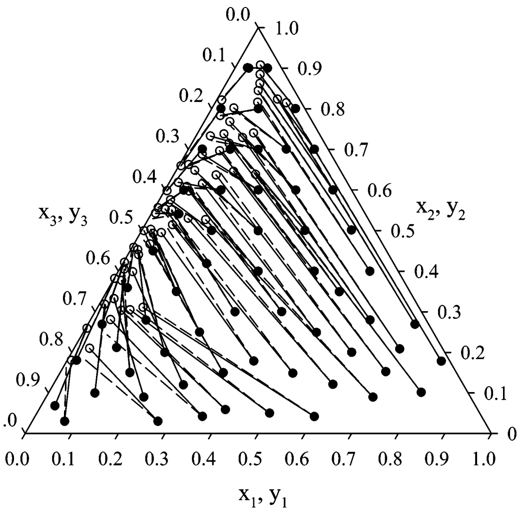

Figure 2. VLE for the ternary system of DBE (1) + ethanol (2) + benzene (3) at 333.15 K; ●, liquid phase; ○, vapor phase. Dashed lines were calculated from NRTL equation.

$$\Delta y_{\mathrm{mean}} = \frac{\Delta y_1 + \Delta y_2 + \Delta y_3}{3} \tag{2}$$

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

$$V^{\mathrm{E}} = \frac{\sum_i x_i M_i}{\rho_m} - \sum_i \left(\frac{x_i M_i}{\rho_i}\right) \tag{3}$$

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

P_{cal}/kPa	x_1	x_2	y_1	y_2	P_{cal}/kPa	x_1	x_2	y_1	y_2	P_{cal}/kPa	x_1	x_2	y_1	y_2
39.36	0.4003	0.0589	0.0549	0.3034	40.35	0.2699	0.0300	0.0333	0.2100	50.62	0.4491	0.5013	0.0775	0.8448
33.96	0.4994	0.0499	0.0725	0.3049	47.85	0.1738	0.0541	0.0203	0.1651	52.65	0.3601	0.6001	0.0723	0.8622
28.53	0.5995	0.0417	0.0974	0.3109	49.62	0.3502	0.1498	0.0345	0.4669	53.55	0.2700	0.7003	0.0614	0.8848
22.18	0.7022	0.0284	0.1439	0.2833	50.37	0.2797	0.1198	0.0314	0.3987	53.17	0.1798	0.8003	0.0507	0.9077
16.53	0.8011	0.0187	0.2224	0.2581	50.51	0.2097	0.0898	0.0244	0.3323	52.68	0.4201	0.3998	0.0690	0.6966
49.10	0.4012	0.1784	0.0448	0.4949	48.29	0.0697	0.0299	0.0091	0.1801	54.94	0.3501	0.5003	0.0573	0.7383
43.32	0.4998	0.1487	0.0589	0.5143	56.43	0.3005	0.2997	0.0391	0.5511	56.08	0.2806	0.5997	0.0548	0.7685
36.94	0.5996	0.1209	0.0844	0.5303	57.20	0.2492	0.2499	0.0286	0.4930	56.12	0.2097	0.7007	0.0466	0.8020
29.62	0.7011	0.0896	0.1237	0.5271	57.38	0.1999	0.1997	0.0229	0.4406	52.02	0.0700	0.9000	0.0265	0.9010
13.68	0.9019	0.0284	0.3989	0.3208	56.94	0.1496	0.1500	0.0186	0.3770	57.28	0.2999	0.3998	0.0427	0.6083
52.74	0.4002	0.3000	0.0530	0.5973	55.41	0.0998	0.0997	0.0112	0.3187	58.68	0.2501	0.4995	0.0396	0.6484
47.52	0.5003	0.2489	0.0728	0.6154	61.10	0.1799	0.4186	0.0239	0.5530	59.07	0.2001	0.6001	0.0357	0.6882
41.42	0.6002	0.2000	0.0912	0.6370	61.61	0.1496	0.3497	0.0183	0.5028	58.43	0.1500	0.6997	0.0311	0.7328
34.52	0.6973	0.1525	0.1243	0.6457	61.62	0.1195	0.2793	0.0152	0.4531	56.47	0.1000	0.8000	0.0270	0.7834
26.10	0.7988	0.1013	0.1750	0.6386	61.06	0.0904	0.2117	0.0100	0.4049	61.77	0.1498	0.5002	0.0240	0.5757
49.13	0.4993	0.3492	0.0799	0.7149	55.25	0.0296	0.0683	0.0032	0.2593	61.61	0.1200	0.6000	0.0192	0.6187
43.71	0.5998	0.2796	0.1016	0.7292	63.86	0.0594	0.5409	0.0084	0.5426	60.44	0.0900	0.6999	0.0195	0.6627
37.01	0.6993	0.2083	0.1197	0.7404	64.41	0.0497	0.4497	0.0053	0.4997	53.66	0.0298	0.9001	0.0111	0.8214
18.48	0.8990	0.0690	0.2522	0.6662	64.43	0.0397	0.3593	0.0037	0.4586	63.83	0.0403	0.5995	0.0071	0.5562
38.54	0.7015	0.2690	0.1292	0.8239	63.93	0.0305	0.2693	0.0025	0.4216	62.34	0.0298	0.7007	0.0056	0.5979
30.63	0.8035	0.1782	0.1527	0.8147	62.60	0.0202	0.1803	0.0014	0.3818	59.46	0.0199	0.8003	0.0045	0.6597
38.67	0.3594	0.0421	0.0430	0.2806	47.36	0.5395	0.3996	0.0908	0.8162					

Table 5. G^E Model Parameters and Mean Deviation between the Calculated and Experimental Vapor-Phase Mole Fraction (Δy_{mean}) for the Ternary System DBE (1) + Ethanol (2) + Benzene (3) at 333.15 K

model equation	A_{ij}/J·mol^{-1}	A_{ji}/J·mol^{-1}	α	Δy_{mean}
Wilson				
1 + 2	3084.9461	1091.4941		0.0112
2 + 3	1375.6764	171.4691		
1 + 3	280.2404	−13.6916		
NRTL				
1 + 2	852.2870	4883.0529	0.4699	0.0096
2 + 3	861.9412	954.8272	0.6555	
1 + 3	1253.5011	−1025.2997	0.1000	
UNIQUAC				
1 + 2	268.2425	101.5573		0.0156
2 + 3	−158.5513	728.9906		
1 + 3	−283.7420	296.9739		

where x_i, M_i, ρ_i, and ρ_m are the mole fraction, molar mass, pure component density, and mixture density, respectively.

Deviations in molar refractivity (ΔR) were calculated from molar refractivities (R_m) of each pure components and mixture, derived from measured densities and refractive indices:[19,20]

$$\Delta R/\text{cm}^3\cdot\text{mol}^{-1} = R_m - \sum_i \phi_i R_i \tag{4}$$

$$R_m = \left(\frac{{n_D}^2 - 1}{{n_D}^2 + 1}\right)\left(\frac{\sum_i x_i M_i}{\rho_m}\right) \tag{5}$$

$$R_i = \left(\frac{{n_{D,i}}^2 - 1}{{n_{D,i}}^2 + 1}\right)\left(\frac{M_i}{\rho_i}\right) \tag{6}$$

and

$$\phi_i = \frac{x_i V_i}{\sum_j x_j V_j} \tag{7}$$

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

The binary V^E and ΔR data were correlated with the four-parameter Redlich−Kister polynomial:[21]

$$V^E_{12} \text{ or } \Delta R/\text{cm}^3\cdot\text{mol}^{-1} = x_1 x_2 \sum_{i=1}^{n} A_i (x_1 - x_2)^{i-1} \tag{8}$$

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

$$\sigma_{st}/\text{cm}^3\cdot\text{mol}^{-1} = \left[\frac{\sum_i ((V^E \text{ or } \Delta R)_{cal} - (V^E \text{ or } \Delta R)_{exp})_i^2}{(N - n)}\right]^{1/2} \tag{9}$$

where N is the number of experimental data points and n is the number of fitted parameters.

The experimental densities, excess molar volumes (V^E), refractive indices, and deviations in molar refractivity (ΔR) for the binary systems of DBE (1) + ethanol (2) and DBE (1) + benzene (2) at 298.15 K aere listed in Table 6. Measured V^E and ΔR are plotted in Figures 3 and 4, respectively. The binary V^E and ΔR for ethanol (1) + benzene (2) were taken from our previous work[22] and are also presented in the figures for comparison.

Table 6. Densities, Excess Molar Volumes, Refractive Indices, and Deviations in Molar Refractivity for the Binary Systems of DBE (1) + Ethanol (2) and DBE (1) + Benzene (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) + Ethanol (2)				
0.0502	0.78269	−0.0178	1.36430	−3.0988
0.0997	0.78050	−0.0313	1.36848	−5.3719
0.1995	0.77702	−0.0613	1.37548	−8.2256
0.3000	0.77428	−0.0810	1.38028	−9.5142
0.4000	0.77209	−0.0936	1.38429	−9.6922
0.5003	0.77031	−0.1046	1.38771	−9.0881
0.6022	0.76881	−0.1129	1.39046	−7.9052
0.7013	0.76753	−0.1102	1.39237	−6.3605
0.8005	0.76635	−0.0901	1.39414	−4.4731
0.9014	0.76528	−0.0624	1.39550	−2.3096
0.9489	0.76479	−0.0403	1.39608	−1.2103
DBE (1) + Benzene (2)				
0.0502	0.86310	0.0497	1.48717	−0.8699
0.0999	0.85373	0.0851	1.47826	−1.5540
0.1999	0.83731	0.1258	1.46325	−2.5077
0.2999	0.82335	0.1489	1.45049	−3.0406
0.4000	0.81131	0.1606	1.43935	−3.2459
0.4994	0.80095	0.1565	1.42978	−3.1758
0.6002	0.79170	0.1477	1.42142	−2.8612
0.6985	0.78371	0.1308	1.41407	−2.3807
0.8005	0.77638	0.0972	1.40759	−1.6935
0.9014	0.76991	0.0526	1.40163	−0.8992
0.9506	0.76702	0.0228	1.39897	−0.4668

The V^E of DBE + ethanol at 298.15 K show negative deviations from ideal behavior over the whole composition range, while those of DBE + benzene show positive deviations. There is stronger interaction between each polar substance for the DBE + ethanol mixture, but no interaction was observed for DBE + benzene. The binary V^E data were correlated with the Redlich−Kister polynomial, and the calculated values are in good agreement as shown in Figure 3 with solid curves. The binary V^E were compared with the reported data in the literature.[23,24] ΔR of DBE + ethanol and DBE + benzene show negative values, and the interaction between DBE and ethanol led to larger deviations in molar refractivity. The binary ΔR were correlated well with the Redlich−Kister polynomial, as shown in Figure 4.

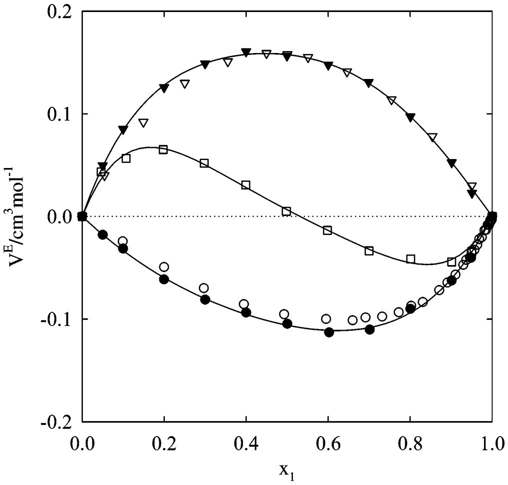

Figure 3. V^E (cm^3·mol^{-1}) for the three binary systems of DBE, ethanol, and benzene at 298.15 K; ●, DBE (1) + ethanol (2); ○, DBE (1) + ethanol (2) by Tanaka et al.;[23] □, ethanol (1) + benzene (2) from previous work;[22] ▼, DBE (1) + benzene (2); ▽, DBE (1) + benzene (2) by George et al.[23] Solid curves were calculated from the Redlich−Kister polynomial.

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

x_1	x_2	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	n_D	ΔR/cm^3·mol^{-1}	x_1	x_2	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	n_D	ΔR/cm^3·mol^{-1}
0.4002	0.0587	0.80811	0.1104	1.43470	−3.9226	0.0999	0.0994	0.84741	0.1003	1.47000	−2.2174
0.4991	0.0499	0.79848	0.0891	1.42615	−3.7923	0.1802	0.4193	0.81291	−0.0065	1.42489	−5.6994
0.5990	0.0408	0.78995	0.0660	1.41858	−3.4114	0.1501	0.3492	0.82252	0.0313	1.43628	−4.7491
0.7048	0.0257	0.78226	0.0449	1.41212	−2.6912	0.1199	0.2787	0.83226	0.0690	1.44803	−3.7861
0.8004	0.0190	0.77561	0.0474	1.40634	−1.9710	0.0901	0.2101	0.84210	0.0775	1.46034	−2.8189
0.4004	0.1804	0.80112	0.0333	1.42443	−5.3111	0.0301	0.0687	0.86251	0.0752	1.48585	−0.8716
0.4998	0.1492	0.79295	0.0160	1.41811	−5.0219	0.0602	0.5400	0.82315	−0.0058	1.42623	−3.6606
0.6015	0.1181	0.78565	0.0030	1.41282	−4.3934	0.0497	0.4502	0.83234	0.0228	1.43873	−3.1365
0.7004	0.0887	0.77923	0.0210	1.40786	−3.5746	0.0405	0.3591	0.84090	0.0555	1.45188	−2.5446
0.9009	0.0289	0.76854	0.0298	1.39981	−1.3199	0.0301	0.2697	0.84923	0.0790	1.46398	−1.9299
0.3998	0.2994	0.79368	−0.0107	1.41384	−6.6188	0.0203	0.1800	0.85723	0.0902	1.47571	−1.2945
0.4997	0.2489	0.78699	−0.0248	1.41024	−6.1893	0.5394	0.4005	0.77377	−0.0910	1.39389	−8.0138
0.6009	0.1973	0.78107	−0.0121	1.40649	−5.4240	0.4497	0.4995	0.77508	−0.1105	1.39083	−8.9644
0.7013	0.1483	0.77594	−0.0092	1.40344	−4.3756	0.3604	0.5997	0.77636	−0.1067	1.38718	−9.3791
0.7988	0.1017	0.77160	−0.0219	1.40087	−3.1425	0.2706	0.6986	0.77792	−0.0842	1.38265	−9.0748
0.5006	0.3497	0.78055	−0.0658	1.40094	−7.4149	0.1803	0.7997	0.77971	−0.0576	1.37674	−7.7710
0.6000	0.2801	0.77627	−0.0539	1.39992	−6.4782	0.4205	0.4001	0.78485	−0.0575	1.40274	−7.7751
0.6998	0.2095	0.77279	−0.0663	1.39908	−5.2020	0.3506	0.4997	0.78506	−0.0690	1.39866	−8.3648
0.5996	0.3597	0.77160	−0.1212	1.39344	−7.4794	0.2794	0.5994	0.78542	−0.0755	1.39379	−8.4759
0.7003	0.2689	0.76943	−0.1094	1.39471	−5.9773	0.0698	0.8995	0.78558	−0.0326	1.37114	−4.1628
0.8009	0.1795	0.76738	−0.0732	1.39542	−4.2027	0.2993	0.3997	0.79826	−0.0199	1.41371	−7.0016
0.3600	0.0406	0.81356	0.1419	1.44030	−3.6503	0.2500	0.5005	0.79701	−0.0425	1.40790	−7.3135
0.2700	0.0293	0.82546	0.1457	1.45156	−3.2142	0.1993	0.6012	0.79563	−0.0527	1.40125	−7.2099
0.1799	0.0200	0.83903	0.1245	1.46448	−2.5137	0.1507	0.6994	0.79390	−0.0591	1.39380	−6.6234
0.3498	0.1510	0.80859	0.0544	1.43201	−4.8415	0.0996	0.8003	0.79183	−0.0552	1.38448	−5.3546
0.2796	0.1208	0.81897	0.0899	1.44253	−4.1876	0.1487	0.5010	0.81138	−0.0212	1.41928	−5.6478
0.2098	0.0904	0.83038	0.1086	1.45400	−3.4033	0.1203	0.5997	0.80767	−0.0372	1.41080	−5.4585
0.0699	0.0289	0.85725	0.0849	1.48147	−1.3135	0.0898	0.7000	0.80360	−0.0502	1.40065	−4.8913
0.3001	0.3003	0.80509	0.0050	1.42330	−6.0977	0.0300	0.9000	0.79275	−0.0405	1.37543	−2.3052
0.2505	0.2486	0.81485	0.0399	1.43397	−5.2001	0.0402	0.5997	0.82179	−0.0177	1.42116	−3.1469
0.1997	0.2000	0.82504	0.0750	1.44513	−4.2667	0.0299	0.6999	0.81452	−0.0379	1.40817	−2.7897
0.1501	0.1484	0.83590	0.0961	1.45687	−3.2849	0.0202	0.7999	0.80613	−0.0463	1.39369	−2.2006

The V^E and ΔR for the ternary systems of DBE + ethanol + benzene were derived from measured densities and refractive indices at 298.15 K. The densities, V^E, refractive indices, and ΔR for the ternary system of DBE + ethanol + benzene at 298.15 K are listed in Table 7. The ternary V^E and ΔR were correlated with the Cibulka equation (eq 8)[25] as a modification of the Radojkovič equation (eq 9):[26]

$$V^E_{123} = V^E_{12*} + V^E_{23*} + V^E_{13*} + x_1x_2x_3(A_1 + A_2x_1 + A_3x_2) \quad (10)$$

$$V^E_{123} = V^E_{12*} + V^E_{23*} + V^E_{13*} \quad (11)$$

where V^E_{12*}, V^E_{23*}, and V^E_{13*} represent the excess molar volumes and x_1, x_2, and x_3 are the ternary mole fractions.

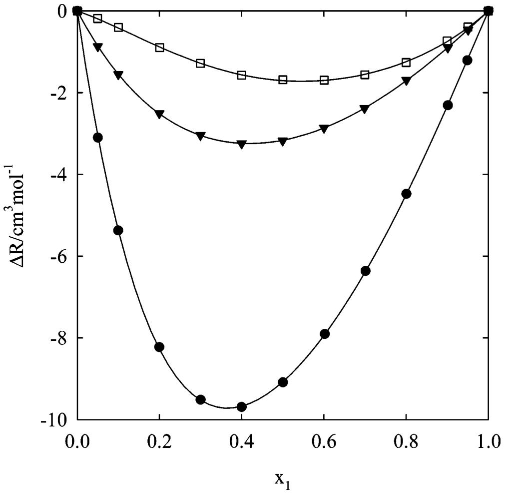

Figure 4. ΔR (cm^3·mol^{-1}) for the three binary systems of DBE, ethanol, and benzene at 298.15 K; ●, DBE (1) + ethanol (2); □, ethanol (1) + benzene (2) from previous work;[22] ▼, DBE (1) + benzene (2). Solid curves were calculated from the Redlich−Kister polynomial.

The correlated values are in good agreement with the experimental data with standard deviations of 0.0109 and 0.0168 for the ternary V^E and ΔR of DBE + ethanol + benzene. The correlation results are presented in Figures 5 and 6 for the ternary V^E and ΔR, respectively. The solid lines in the figures represent the constant V^E and ΔR of the ternary systems calculated by the Cibulka equation. The adjusted parameters of the Redlich−Kister and Cibulka equations are given in Table 8 along with standard deviations between calculated and experimental data.

Additionally, the ternary V^E and ΔR were calculated using four conventional prediction models of Tsao−Smith,[27] Kohler,[28] Rastogi,[29] and Radojkovič[26] and compared with experimental results. The standard deviations in estimation with each model are given in Table 9. The Radojkovič model provided the best results with the standard deviations of (0.0282 and 0.2358) cm^3·mol^{-1} for ternary V^E and ΔR.

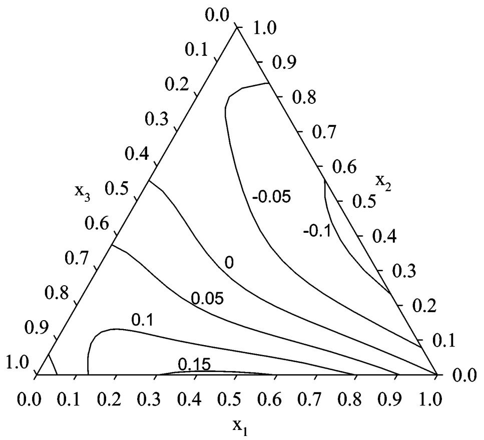

Figure 5. Lines of constant V^E (cm^3·mol^{-1}) for the ternary system of DBE (1) + ethanol (2) + benzene (3) at 298.15 K.

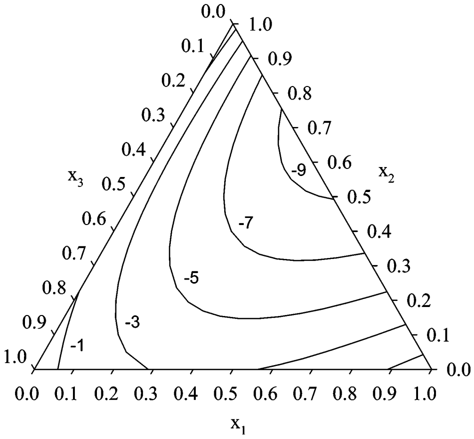

Figure 6. Lines of constant ΔR ($\mathrm{cm^3 \cdot mol^{-1}}$) for the ternary system of DBE (1) + ethanol (2) + benzene (3) at 298.15 K.

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

	systems	A_1	A_2	A_3	A_4	σ_{st}
V^E	(1) + (2)	−0.4237	−0.1603	−0.1562	−0.0505	0.0022
	(2) + (3)[a]	0.0629	−0.5394	0.1493	−0.3524	0.0044
	(1) + (3)	0.6307	−0.0855	0.2061	−0.2022	0.0015
	(1) + (2) + (3)	−1.8842	−0.8617	2.5851		0.0109
ΔR	(1) + (2)	−36.2900	17.8057	−10.0735	5.1896	0.0268
	(2) + (3)[a]	−6.8282	−1.3777	0.5351	−1.4161	0.0175
	(1) + (3)	−12.6608	3.8817	−1.5186	0.9177	0.0095
	(1) + (2) + (3)	−17.3979	17.9093	−3.3441		0.0168

[a] Parameters taken from ref 22.

Table 9. Standard Deviations[a] for the Estimation Results of V^E and ΔR for the Ternary System of DBE + Ethanol + Benzene at 298.15 K

	model eq			
property	Tsao−Smith	Kohler	Rastogi	Radojkovič
V^E	0.0837	0.0524	0.0624	0.0281
ΔR	1.2977	0.4779	1.4336	0.2358

[a] Calculated using eq 9.

Conclusions

Isothermal VLE data at 333.15 K and V^E and ΔR at 298.15 K were experimentally determined for the binary and ternary systems of DBE, ethanol, and benzene. The binary VLE of ethanol + benzene show a minimum boiling azeotrope. The binary VLE data were correlated very well with common G^E model equations. The ternary data were correlated with the Wilson, NRTL, and UNIQUAC models, and the NRTL model provided the best results. The binary V^E data of DBE + ethanol show negative deviations from ideal behavior, while those of DBE + benzene show positive values. The binary ΔR of both binaries show negative values. These binary data correlated well with the Redlich−Kister equation, while the Cibulka equation was applied reliably for the ternary data correlation. Besides, the ternary data were also compared with the predicted values using the binary contribution models of Tsao−Smith, Kohler, Rastogi, and Radojkovič. The Radojkovič model gave the best estimation results.

Literature Cited

(1) Oh, J. H.; Park, S. J. Isothermal vapor−liquid equilibria of 2-methoxy-2-methylbutane (TABE) + *n*-alcohol (C_1−C_4) mixtures at 323.15 and 333.15 K. *J. Chem. Eng. Data* **1997**, *42*, 517−522.

(2) Oh, J. H.; Park, S. J. Isothermal vapor−liquid equilibria at 333.15 K and excess molar volumes at 298.15 K of ethyl *tert*-butyl ether (ETBE) + Alcoh-1-ol (C_1−C_4) Mixtures. *J. Chem. Eng. Data* **1998**, *43*, 1009−1013.

(3) Park, S. J.; Han, K. J.; Gmehling, J. Vapor−liquid equilibria and excess properties for methyl *tert*-butyl ether (MTBE) containing binary systems. *Fluid Phase Equilib.* **2002**, *200*, 399−409.

(4) Oh, J. H.; Han, K. J.; Won, D. B.; Park, S. J. Vapor−liquid equilibria for the ternary systems of methyl *tert*-butyl ether + methanol + benzene and methyl *tert*-butyl ether + methanol + toluene and constituent binary systems at 313.15 K. *Fluid Phase Equilib.* **2003**, *209*, 215−228.

(5) Han, K. J.; Oh, J. H.; Park, S. J. Densities and viscosities for the ternary systems of methyl *tert*-butyl ether (MTBE) + methanol + benzene and methyl *tert*-butyl ether + methanol + toluene and their sub-binary systems at 298.15 K. *J. Chem. Eng. Data* **2006**, *51*, 1339−1343.

(6) Wypych, G. *Handbook of Solvents*; ChemTec Publishing: Toronto, 2001.

(7) Domínguez, M.; Pardo, J.; López, M. C.; Royo, F. M.; Urieta, J. S. Viscosities of the ternary mixture (1-butanol + *n*-hexane + 1-butylamine) at the temperatures 298.15 and 313.15 K. *Fluid Phase Equilib.* **1996**, *124*, 147−159.

(8) Martinez, S.; Garriga, R.; Perez, P.; Gracia, M. Densities and viscosities of binary mixtures of butanone with butanol isomers at several temperatures. *Fluid Phase Equilib.* **2000**, *168*, 267−279.

(9) Riddick, J. A.; Bunger, W. B. *Organic Solvents*; Techniques of Chemistry, Vol. II; Wiley-Interscience: New York, 1970.

(10) Lladosa, E.; Montón, J. B.; Burguet, M. C.; Muñoz, R. Isobaric vapor−liquid equilibria for the binary systems 1-propyl alcohol + dipropyl ether and 1-butyl alcohol + dibutyl ether at 20 and 101.3 kPa. *Fluid Phase Equilib.* **2006**, *247*, 47−53.

(11) Sastry, N. V.; Raj, M. M. Densities, speeds of sound, viscosities, dielectric constants, and refractive indices for 1-heptanol + hexane and + heptane at 303.15 and 313.15 K. *J. Chem. Eng. Data* **1996**, *41*, 612−618.

(12) Canosa, J.; Rodríguez, A.; Tojo, J. Densities, refractive indices and speeds of sound of the ternary mixtures (dimethyl carbonate + methanol + ethanol) and (dimethyl carbonate + methanol + 1-propanol) at T = 298.15 K. *J. Chem. Thermodyn.* **2003**, *35*, 2021−2031.

(13) Das, A.; Frenkel, M.; Gadalla, N. M.; Marsh, K.; Wilhoit, R. C. *TRC Thermodynamic Tables*; Thermodynamic Research Center, The Texas A&M University: College Station, TX, 1994.

(14) Park, S. J.; Kim, H. H.; Han, K. J.; Won, D. B.; Lee, S. B.; Choi, M. J. Isothermal vapor−liquid equilibria and excess molar volumes for 2-methyl pyrazine (2MP) containing binary mixtures. *Fluid Phase Equilib.* **2001**, *180*, 361−373.

(15) *Dortmund Data Bank Software Package* (DDBSP), version 1998.

(16) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.

(17) Udovenko, V. V.; Fatkulina, L. G. Vapor pressure of three-component systems. I. The system ethyl alcohol-1,2-dichloroethane-benzene. *Zh. Fiz. Khim.* **1952**, *26*, 719−730.

(18) Ott, J. B.; Marsh, K. N.; Richards, A. E. Excess enthalpies, excess Gibbs free energies, and excess volumes for (di-*n*-butyl ether + benzene) and excess Gibbs free energies and excess volumes for (di-*n*-butyl ether + tetrachloromethane) at 298.15 and 308.15 K. *J. Chem. Thermodyn.* **1981**, *13*, 447−455.

(19) Aminabhavi, T. M.; Golalakrishina, B. Density, viscosity, refractive index, and speed of sound in aqueous mixtures of *N*,*N*-dimethylformamide, dimethyl sulfoxide, *N*,*N*-dimethylformamide, acetonitrile, ethylene glycol, diethylene glycol, 1,4-dioxane, tetrahydrofuran, 2-methoxyethanol, and 2-ethoxyethanol at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 856−861.

(20) Al-Dujaili, A. H.; Yassen, A. A.; Awwad, A. M. Refractive indices, densities, and excess properties of 4-(2-hydroxyethyl)morpholine + water at (298.15, 308.15, and 318.15) K. *J. Chem. Eng. Data* **2000**, *45*, 647−649.

(21) Redlich, O.; Kister, A. T. Algebraic representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

(22) Han, K. J.; Oh, J. H.; Park, S. J. Densities and refractive indices for the ternary system ethyl *tert*-butyl ether (ETBE) + ethanol + benzene and the binary subsystems at 298.15 K. *J. Ind. Eng. Chem.* **2007**, *13*, in press.

(23) Tanaka, R.; Toyama, S. Excess molar volumes and excess molar heat capacities for binary mixtures of ethanol with chlorocyclohexane, 1-nitropropane, dibutyl ether, and ethyl acetate at the temperature of 298.15 K. *J. Chem. Eng. Data* **1996**, *41*, 1455−1458.

(24) George, J.; Sastry, N. V. Measurements of densities, viscosities, speeds of sound and relative permittivities and excess molar volumes, excess isentropic compressibilities and deviations in relative permittivities and molar polarizations for dibutyl ether + benzene, + toluene and + *p*-xylene at different temperatures. *J. Chem. Thermodyn.* **2003**, *35*, 1837−1853.

(25) Cibulka, I. Estimation of excess volume and density of ternary liquid mixtures of nonelectrolytes from binary data. *Collect. Czech. Chem. Commun*. **1982**, *47*, 1414−1419.

(26) Radojkovič, N.; Tasič, A.; Grozdanič, B.; Malič, M. Excess volumes of acetone + benzene, acetone + cyclohexane, and acetone + benzene + cyclohexane at 298.15 K. *J. Chem. Thermodyn.* **1977**, *9*, 349−356.

(27) Tsao, C. C.; Smith, J. M. Heat of mixing of liquids. *Chem. Eng. Prog. Symp. Ser*. **1953**, *No. 49*, 107−117.

(28) Kohler, F. Estimation of the thermodynamic data for a ternary system from the corresponding binary systems. *Monatsh. Chem.* **1960**, *91*, 738−740.

(29) Rastogi, R. P.; Nath, J.; Das, S. S. Thermodynamic properties of ternary mixtures. 2. The excess volumes of mixing of ternary mixtures of cyclohexane, aromatics, and halomethanes. *J. Chem. Eng. Data* **1977**, *22*, 249−252.

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