

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 (C₁–C₄) Mixtures

Jong-Hyeog Oh and So-Jin Park*

Department of Chemical Engineering, College of Engineering, Chungnam National University, Taejeon, Korea 305-764

Isothermal vapor–liquid equilibria (VLE) were obtained for ethyl *tert*-butyl ether + *n*-alcohol (C₁–C₄) at 333.15 K by headspace gas chromatography, and excess molar volumes were determined from density measurements using a vibrating tube densimeter at 298.15 K. The binary mixtures showed positive deviation from the Raoult's law, and those containing methanol and ethanol have minimum boiling azeotropes. The excess molar volumes of all the binary mixtures were negative. The measured VLE data are well described using a modified UNIFAC equation (Dortmund), and excess molar volumes are correlated with the Redlich–Kister polynomial.

Introduction

Ether mixtures such as methyl *tert*-butyl ether (MTBE), *tert*-amyl methyl ether (TAME), and ethyl *tert*-butyl ether (ETBE; (CH₃)₃COC₂H₅) are used as additives for lead-free and low-leaded gasoline because of their octane-enhancing and pollution-reducing capabilities. To develop calculational models for gasoline reformulation, accurate vapor–liquid equilibrium (VLE) data are needed. Previously the VLE data of the MTBE + alcoh-1-ols and TAME + alcoh-1-ols (C₁–C₄) mixtures at 323.15 K and 333.15 K were determined (Park and Lee, 1995; Oh and Park, 1997). In this work, isothermal VLE were measured by headspace gas chromatography (HSGC) for ETBE + alcoh-1-ols (C₁–C₄) binary mixtures at 333.15 K. Usually, the composition of the liquid phase (x_i) in HSGC method was calculated by an iterative method with G^E model parameters (Weidlich and Gmehling, 1985). However, in our method, x_i was calculated directly from the peak area of the chromatogram and some thermodynamic relations (Oh and Park, 1997). The experimental VLE data were correlated with conventional G^E models and compared with the predicted values by modified UNIFAC (Dortmund) (Weidlich and Gmehling, 1987; Gmehling et al., 1993). Additionally, excess molar volumes (V^E) at 298.15 K were determined from density measurement using a vibrating tube densimeter. The V^E results were correlated with Redlich–Kister polynomial, and the partial excess molar volumes at infinite dilution ($\bar{V}^{E,\infty}$) were calculated by the extrapolation of five parameters of the Redlich–Kister polynomial.

Experimental Section

Materials. Commercial ETBE and alcohols were supplied by TCI and Aldrich Chemical Co. and dried with molecular sieves 3A and 4A (Aldrich) before use. The purity of each chemical was analyzed by GC and digital vibrating densimeter (Anton Paar, DMA 48) with an accuracy of $\pm 1 \times 10^{-4}$ g cm⁻¹. The results of the GC

analysis and measured densities are presented in Table 1 along with the Antoine constants for the calculation of vapor pressure.

Apparatus and Experimental Procedures. (a) **Isothermal VLE.** The HSGC system consists of a conventional GC (Hewlett-Packard, HP5890 series II) and a headspace sampler (HP 19395A), which has an electro-pneumatic sampling system and a precision thermostat. A thermal conductivity detector (TCD) and HP-FFAP (Hewlett-Packard, Polyethylenglycol-TPA modified, 50 m × 0.2 mm × 0.3 μm) capillary column were used for the analysis. Binary samples of ETBE + alcoh-1-ols were prepared directly in a glass vial equilibrium cell, using a digital microbalance (AND Co. HA-202M) with an accuracy of $\pm 1 \times 10^{-5}$ g.

The glass vial with sample mixtures was placed in the thermostat and allowed to equilibrate. More than 2 h were allowed as an equilibration time. Since the volume of the liquid sample (ca. 3 cm³) and the equilibrium cell (ca. 12 cm³) were small, 2 h was sufficient to reach equilibrium. After equilibrium, a constant amount of headspace (vapor phase) was transferred to the sample loop by an electro-pneumatic sampling system. Then the collected equilibrium vapor in the sample loop was automatically transferred to the GC and analyzed.

The equilibrium liquid-phase compositions were calculated from the measured vapor-phase composition and other thermophysical properties by using some of thermodynamic equations. Calculation procedures has been detailed in a previous paper (Oh and Park, 1997)

(b) **Excess Molar Volumes.** Densities of the pure components and each binary mixtures were determined by an Anton Paar digital vibrating glass tube densimeter (DMA 48) at 298.15 K with an accuracy of 1×10^{-4} g cm⁻³. Bidistilled water ($\rho_{298.15K} = 0.997\ 047$ g cm⁻³) and dry air were used for the calibration of the densimeter and the determination of apparatus constant.

Results and Discussion

Isothermal VLE. To calculate the liquid-phase composition of equilibrium, the SRK equation of state was used.

* To whom correspondence should be addressed. E-mail: sjpark@hanbat.chungnam.ac.kr.

Table 1. Purities, Measured Densities, $\rho/\text{g cm}^{-3}$, at 298.15 K, and Antoine Constants of Pure Components^e

components	GC H analysis (wt %)	density, $\rho/\text{g cm}^{-3}$		Antoine constants ^d		
		present study	lit. value	A	B	C
ETBE	99.8	0.7350	0.735 28 ^a	6.095 24	1213.284	-49.453
methanol	99.8	0.7864	0.786 37 ^b	7.205 87	1581.271	-33.424
ethanol	99.9	0.7850	0.785 00 ^b	7.237 10	1592.864	-46.996
1-propanol	99.8	0.7995	0.799 60 ^b	7.503 85	1788.080	-45.712
1-butanol	99.9	0.8056	0.805 80 ^c	6.962 90	1558.190	-76.269

^a Data from Domanska (1996). ^b Data from Riddick et al. (1986). ^c Data from Venkataramana et al. (1995). ^d Data from Gmehling et al. (1977) except ETBE (Stephenson and Malanowski, 1987). ^e $\log P/\text{kPa} = A - B/(C + TK)$.

Table 2. Isothermal Vapor-Liquid Equilibria of ETBE + *n*-Alcohol (C₁-C₄) at 333.15 K

<i>P</i> /kPa (calcd)	<i>x</i> ₁ (calcd)	<i>y</i> ₁	γ ₁	γ ₂	<i>P</i> /kPa (calcd)	<i>x</i> ₁ (calcd)	<i>y</i> ₁	γ ₁	γ ₂
ETBE (1) + Methanol (2)									
88.13	0.0148	0.0547	4.8676	1.0008	109.53	0.5739	0.4640	1.3223	1.6307
91.07	0.0298	0.0973	4.4455	1.0028	108.26	0.6386	0.4863	1.2309	1.8214
93.68	0.0456	0.1343	4.1148	1.0058	106.30	0.7099	0.5120	1.1447	2.1165
95.70	0.0598	0.1624	3.8786	1.0091	102.54	0.7751	0.5551	1.0965	2.4007
97.41	0.0741	0.1860	3.6523	1.0135	98.77	0.8431	0.5938	1.0386	3.0277
99.09	0.0891	0.2094	3.4771	1.0179	88.53	0.9119	0.7005	1.0154	3.5637
104.70	0.1596	0.2894	2.8359	1.0477	86.48	0.9234	0.7243	1.0127	3.6846
107.75	0.2297	0.3398	2.3793	1.0931	83.30	0.9396	0.7624	1.0092	3.8770
109.22	0.2935	0.3725	2.0699	1.1480	79.77	0.9566	0.8073	1.0051	4.1967
110.34	0.3618	0.4100	1.8670	1.2073	76.30	0.9704	0.8544	1.0031	4.4367
110.54	0.4286	0.4258	1.6398	1.3146	72.67	0.9842	0.9082	1.0013	4.9814
110.29	0.4999	0.4437	1.4615	1.4521					
ETBE (1) + Ethanol (2)									
49.41	0.0151	0.0647	3.1652	1.0003	78.82	0.5702	0.6279	1.2959	1.4546
53.71	0.0445	0.1636	2.9447	1.0024	79.08	0.6340	0.6491	1.2088	1.6164
55.75	0.0587	0.2058	2.9167	1.0029	79.01	0.7051	0.6799	1.1374	1.8284
57.55	0.0743	0.2408	2.7853	1.0062	78.46	0.7738	0.7139	1.0808	2.1156
59.28	0.0904	0.2732	2.6755	1.0098	77.10	0.8431	0.7595	1.0371	2.5193
66.06	0.1576	0.3877	2.4266	1.0235	73.50	0.9238	0.8499	1.0096	3.0883
70.95	0.2250	0.4613	2.1721	1.0512	72.77	0.9353	0.8673	1.0075	3.1790
73.32	0.2933	0.4980	1.8587	1.1103	71.28	0.9557	0.9020	1.0045	3.3601
75.15	0.3610	0.5312	1.6511	1.1755	70.15	0.9702	0.9278	1.0017	3.6215
76.86	0.4294	0.5673	1.5160	1.2427	68.62	0.9859	0.9627	1.0005	3.8586
78.10	0.5035	0.6002	1.3902	1.3406					
ETBE (1) + 1-Propanol (2)									
21.76	0.0153	0.1307	2.7708	1.0007	59.49	0.5656	0.8063	1.2654	1.3806
23.78	0.0292	0.2145	2.6039	1.0020	60.94	0.6367	0.8239	1.1776	1.5382
25.82	0.0443	0.2868	2.4960	1.0036	62.57	0.7005	0.8458	1.1280	1.6776
27.96	0.0602	0.3515	2.4372	1.0049	63.90	0.7732	0.8677	1.0706	1.9411
29.46	0.0746	0.3914	2.3090	1.0089	65.24	0.8408	0.8968	1.0390	2.2032
31.32	0.0898	0.4363	2.2712	1.0103	66.16	0.9087	0.9296	1.0106	2.6568
38.63	0.1569	0.5717	2.1020	1.0219	66.40	0.9250	0.9410	1.0085	2.7184
44.19	0.2255	0.6476	1.8947	1.0473	66.54	0.9385	0.9494	1.0051	2.8483
48.91	0.2930	0.7011	1.7474	1.0768	66.72	0.9558	0.9625	1.0032	2.9438
53.52	0.3606	0.7461	1.6533	1.1067	66.82	0.9678	0.9719	1.0019	3.0433
55.11	0.4284	0.7611	1.4619	1.1996	66.93	0.9848	0.9859	1.0004	3.2275
57.25	0.4975	0.7831	1.3455	1.2873					
ETBE (1) + 1-Butanol (2)									
10.30	0.0146	0.2447	2.5852	1.0002	53.94	0.5696	0.9111	1.2882	1.4126
17.11	0.0593	0.5652	2.4340	1.0024	55.90	0.6367	0.9199	1.2059	1.5623
19.42	0.0744	0.6230	2.4289	1.0024	57.42	0.7042	0.9275	1.1292	1.7834
21.71	0.0899	0.6682	2.4102	1.0031	60.34	0.7729	0.9429	1.0990	1.9236
30.04	0.1573	0.7752	2.2115	1.0156	62.09	0.8427	0.9527	1.0481	2.3647
36.90	0.2249	0.8282	2.0284	1.0366	63.57	0.9086	0.9653	1.0083	3.0578
41.59	0.2928	0.8554	1.8144	1.0780	64.21	0.9235	0.9713	1.0082	3.0594
45.28	0.3599	0.8738	1.6412	1.1311	65.35	0.9547	0.9820	1.0036	3.2888
49.77	0.4289	0.8936	1.5483	1.1747	65.92	0.9702	0.9879	1.0022	3.4025
52.11	0.4989	0.9032	1.4085	1.2758	66.45	0.9851	0.9936	1.0006	3.6437

The thermophysical data for using of the SRK EOS were adapted from Steinhagen and Sandler (1994) and Reid et al., (1987). The measured isothermal VLE data at 333.15 K for ETBE + alcohol-1-ols (C₁-C₄) binary mixtures are listed in Table 2. By using the HSGC method, the equilibrium total pressure was not measured but calculated from the experimental data of the vapor phase and thermodynamic equations. This method has been discussed previously (Oh and Park, 1997). The *x*-*y*-*P* data for the ETBE + alcohol-1-ols (C₁-C₄) system at 333.15 K

are plotted in Figure 1. ETBE + methanol and ETBE + ethanol mixtures have a minimum boiling azeotropes. All the results were correlated very well with the common G^E models, and these results are given in Table 3. The nonrandomness parameter of NRTL equation, α , was fixed to 0.3 if it was not fitted in the region from 0.1 to 0.8 as recommended by Renon and Prausnitz (1968). The solid lines in the figures are those calculated by the best correlated equation. The predicted VLE data with the modified UNIFAC (Dortmund) equation were also

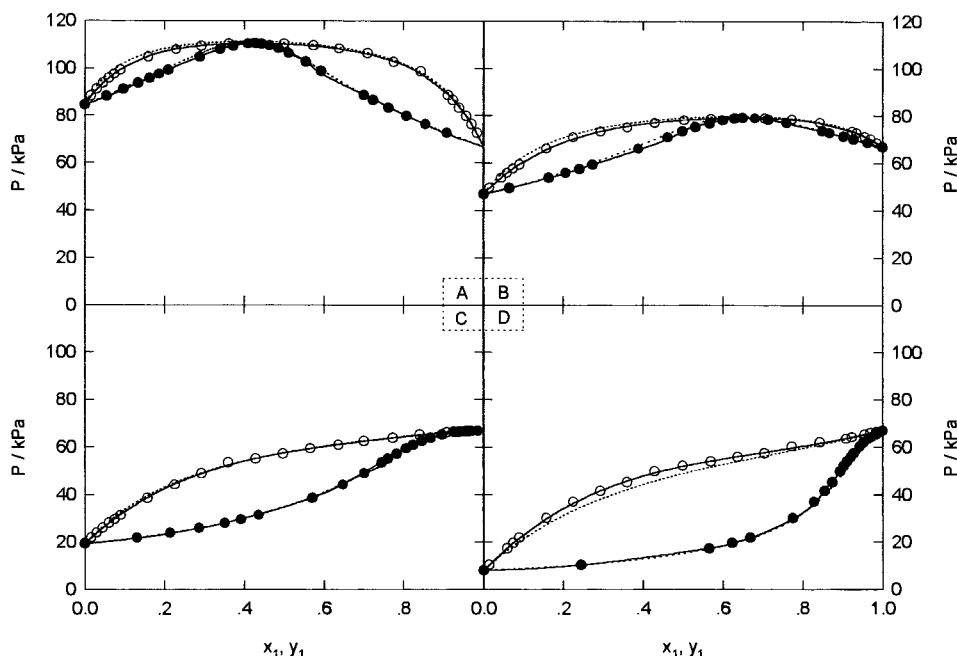


Figure 1. Pressure–composition diagrams of (A) ETBE (1) + methanol (2), (B) ETBE (1) + ethanol (2), (C) ETBE (1) + 1-propanol (2), and (D) ETBE (1) + 1-butanol (2); \circ x_1 and \bullet y_1 at 333.15 K; — g^E model equation and - - - modified UNIFAC (Dortmund) equation.

Table 3. g^E Model Parameters and Mean Deviation between the Calculated and Experimental Vapor-Phase Mole Fraction (Δy_1)^a for ETBE + n -Alcohol (C_1 – C_4) at 333.15 K^b

model equation	A_{12}	A_{21}	α	Δy_1
ETBE + Methanol				
Margules	1.5006	1.5337		0.0045
van Laar	1.5010	1.5335		0.0045
Wilson	-755.5911	6197.5285		0.0034
NRTL	2863.3321	2734.7363	0.5223	0.0035
UNIQUAC	4537.7458	-616.8873		0.0045
mod. UNIFAC				0.0076
ETBE + Ethanol				
Margules	1.1715	1.3414		0.0029
van Laar	1.1745	1.3481		0.0028
Wilson	-719.9908	5025.0177		0.0028
NRTL	2635.7111	1300.4364	0.3000	0.0027
UNIQUAC	3249.0782	-878.3344		0.0030
mod. UNIFAC				0.0093
ETBE + 1-Propanol				
Margules	0.9878	1.2088		0.0026
van Laar	0.9964	2.2190		0.0026
Wilson	-522.0048	4219.0312		0.0031
NRTL	2689.0383	764.5971	0.3000	0.0027
UNIQUAC	2508.1054	883.9982		0.0026
mod. UNIFAC				0.0063
ETBE + 1-Butanol				
Margules	0.9846	1.3517		0.0017
van Laar	1.0072	1.3772		0.0022
Wilson	-134.6465	4263.7254		0.0030
NRTL	3403.6233	447.3207	0.3000	0.0023
UNIQUAC	2290.2241	-853.8597		0.0021
mod. UNIFAC				0.0100

^a $\Delta y_1 = |y_{1,\text{exp.}} - y_{1,\text{calcd}}|/n$, n = number of data. ^b Units for parameters of equations of Wilson, NRTL, and UNIQUAC are J mol^{-1} .

plotted as dashed lines in each of diagrams. The calculated and predicted vapor-phase mole fractions were compared with the experimental data. The deviations between experimental and predicted values by the modified UNIFAC (Dortmund) method were less than 0.1%. These comparisons are listed in Table 4 with the fitted G^E model parameters. Parameters (A_{ij}) for the Wilson,

NRTL, and UNIQUAC equations are

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

$$\text{NRTL: } A_{ij} = (g_{ij} - g_{jj}) \text{ J mol}^{-1}$$

$$\text{UNIQUAC: } A_{ij} = (u_{ij} - u_{jj}) \text{ J mol}^{-1}$$

The equilibrium liquid- and vapor-phase compositions are shown in Figure 2. As the carbon number of alcohol increases, the azeotropic points move to the alcohol-rich region and the deviations from Raoult's law decrease.

Excess Molar Volumes. The excess molar volume for the binary mixture, V^E , can be calculated by eq 1 from the experimental densities of the mixture and the pure component. M_i and ρ_i are the mole fraction, molecular weight, and the density of pure component i , respectively, and ρ_m is the density of the binary mixture.

$$V^E = \left[\frac{x_1 M_1 + x_2 M_2}{\rho_m} \right] - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \quad (1)$$

The Redlich–Kister polynomial was used to describe the composition dependence of the experimental V^E data.

$$V^E = x_1 x_2 \sum_{i=1}^5 A_i (x_1 - x_2)^{i-1} \quad (2)$$

where A_i are adjustable parameters. The standard deviation of the fits δ_{st} is defined as

$$\delta_{\text{st}} = \left[\frac{\sum_i (V_{\text{cal}}^E - V_{\text{exp}}^E)^2}{(N - n)} \right]^{1/2} \quad (3)$$

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

The partial molar excess volumes at infinite dilution were calculated with only adjustable parameters of the Redlich–Kister polynomial. In this experiment, five ad-

Table 4. Excess Molar Volume Data of ETBE + Alcoh-1-ols (C₁–C₄) at 298.15 K

x_1	$\rho/\text{g cm}^{-3}$	$V^E/\text{cm}^3 \text{mol}^{-1}$	x_1	$\rho/\text{g cm}^{-3}$	$V^E/\text{cm}^3 \text{mol}^{-1}$	x_1	$\rho/\text{g cm}^{-3}$	$V^E/\text{cm}^3 \text{mol}^{-1}$
ETBE + Methanol								
0.0151	0.7853	-0.0685	0.2937	0.7645	-0.7441	0.8404	0.7415	-0.6288
0.0304	0.7839	-0.1272	0.3497	0.7615	-0.8189	0.9088	0.7390	-0.4445
0.0470	0.7826	-0.1987	0.4290	0.7574	-0.8672	0.9251	0.7384	-0.3930
0.0601	0.7817	-0.2594	0.4995	0.7543	-0.9035	0.9383	0.7379	-0.3468
0.0752	0.7802	-0.2963	0.5700	0.7515	-0.9220	0.9556	0.7372	-0.2753
0.0897	0.7790	-0.3429	0.6384	0.7488	-0.8922	0.9726	0.7366	-0.2178
0.1580	0.7737	-0.5269	0.7066	0.7463	-0.8420	0.9866	0.7359	-0.1303
0.2261	0.7686	-0.6361	0.7673	0.7442	-0.7785			
ETBE + Ethanol								
0.0174	0.7838	-0.0620	0.2936	0.7658	-0.6021	0.8396	0.7418	-0.5219
0.0316	0.7829	-0.1161	0.3623	0.7622	-0.6781	0.9126	0.7390	-0.3676
0.0461	0.7820	-0.1702	0.4288	0.7590	-0.7636	0.9243	0.7385	-0.3293
0.0599	0.7809	-0.1994	0.4975	0.7557	-0.7509	0.9388	0.7379	-0.2835
0.0744	0.7797	-0.2238	0.5697	0.7526	-0.7648	0.9525	0.7373	-0.2329
0.0901	0.7787	-0.2708	0.6386	0.7497	-0.7423	0.9687	0.7366	-0.1719
0.1577	0.7740	-0.4024	0.7058	0.7648	-0.6673	0.9867	0.7358	-0.0971
0.2261	0.7696	-0.5041	0.7734	0.7442	-0.6001			
ETBE + 1-Propanol								
0.0149	0.7986	-0.0539	0.2935	0.7779	-0.7559	0.9063	0.7407	-0.4078
0.0313	0.7974	-0.1211	0.3617	0.7732	-0.8340	0.9242	0.7396	-0.3355
0.0459	0.7965	-0.1957	0.4995	0.7642	-0.9020	0.9345	0.7391	-0.3162
0.0597	0.7955	-0.2496	0.5686	0.7601	-0.9172	0.9540	0.7380	-0.2498
0.0762	0.7945	-0.3305	0.6372	0.7561	-0.8970	0.9696	0.7370	-0.1713
0.0906	0.7935	-0.3859	0.7047	0.7521	-0.8202	0.9855	0.7361	-0.1102
0.1582	0.7878	-0.5107	0.7713	0.7483	-0.7230			
0.2274	0.7828	-0.6701	0.8284	0.7451	-0.6146			
ETBE + 1-Butanol								
0.0153	0.8048	-0.0944	0.2940	0.7844	-0.8129	0.8398	0.7468	-0.6680
0.0310	0.8036	-0.1459	0.3620	0.7795	-0.9006	0.9019	0.7426	-0.5004
0.0453	0.8026	-0.2012	0.4330	0.7745	-0.9675	0.9260	0.7409	-0.4131
0.0602	0.8015	-0.2505	0.4998	0.7699	-1.0057	0.9399	0.7399	-0.3564
0.0750	0.8004	-0.2981	0.5698	0.7651	-1.0103	0.9516	0.7390	-0.2963
0.0957	0.7989	-0.3651	0.6389	0.7605	-0.9962	0.9713	0.7375	-0.1957
0.1584	0.7943	-0.5389	0.7057	0.7561	-0.9517	0.9845	0.7365	-0.1264
0.2260	0.7894	-0.6994	0.7746	0.7515	-0.8567			

Table 5. Fitted Redlich–Kister Parameters and Standard Deviations (δ_{st}) of the Excess Molar Volume at 298.15 K

systems	A_1	A_2	A_3	A_4	A_5	$\delta_{st}/\text{cm}^3 \text{mol}^{-1}$
ETBE + methanol	-3.6487	-0.4491	-0.6184	-0.5822	-1.8682	0.0161
ETBE + ethanol	-3.0578	-0.3292	0.3575	-0.6561	-2.4737	0.0083
ETBE + 1-propanol	-3.6656	-0.3489	-0.5344	0.0131	-1.3293	0.0160
ETBE + 1-butanol	-4.0378	-0.6925	-0.7818	-0.3418	-1.1481	0.0130

adjustable parameters of the Redlich–Kister polynomial were used.

$$\bar{V}_1^{E,\infty} = \lim_{x_1 \rightarrow 0} \bar{V}_1^E = A_1 - A_2 + A_3 - A_4 + A_5 \quad (4)$$

$$\bar{V}_2^{E,\infty} = \lim_{x_2 \rightarrow 0} \bar{V}_2^E = A_1 + A_2 + A_3 + A_4 + A_5 \quad (5)$$

Table 4 and Figure 3 give the measured densities and excess volumes for ETBE + alcoh-1-ol (C₁–C₄). For all systems, V^E was negative. The ETBE + 1-butanol system was most negative, and the ETBE + ethanol mixture was the least negative. Negative deviations are attributed to hydrogen-bonding formation between the ETBE and the alcoh-1-ols. Standard deviations between experimental data and calculated values by the Redlich–Kister polynomial were less than 2% of V^E . The adjustable parameters and standard deviations are listed in Table 5.

Partial molar excess volumes of the components are defined as the volume variation on addition of a small amount of component i (Pettenati et al. 1990). Partial excess molar volumes at infinite dilution were calculated from eqs 4 and 5 with five Redlich–Kister parameters and are listed in Table 6.

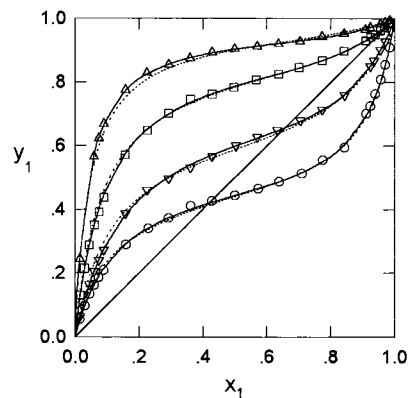


Figure 2. Comparison of VLE data between ETBE (1) + alcoh-1-ol (2) at 333.15 K: (○) methanol; (▽) ethanol; (□) 1-propanol; (△) 1-butanol; (—) g^E model equation and (---) modified UNIFAC (Dortmund) equation.

Conclusion

VLE data of the ETBE + alcoh-1-ols (C₁–C₄) showed positive deviations from Raoult's law. ETBE + methanol and ETBE + ethanol have minimum boiling azeotropes. Experimental data were compared with values calculated

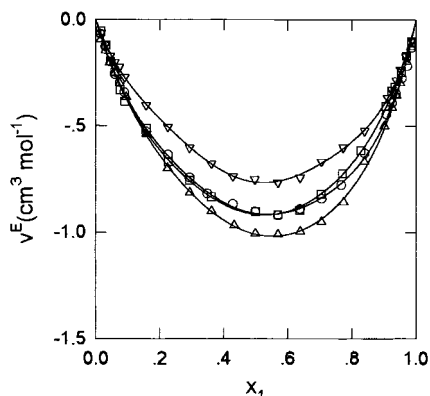


Figure 3. Excess molar volumes of ETBE (1) + alcohol-1-ol (2) binary systems at 298.15 K: Symbols are the same as shown in Figure 2; (—) Redlich–Kister polynomial.

Table 6. Calculated Partial Excess Molar Volumes at Infinite Dilution at 298.15 K

systems	$\bar{V}_1^{E,\infty}$ cm ³ mol ⁻¹	$\bar{V}_2^{E,\infty}$ /cm ³ mol ⁻¹
ETBE + methanol	-5.1040	-7.1666
ETBE + ethanol	-4.1887	-6.1593
ETBE + 1-propanol	-5.1934	-5.8650
ETBE + 1-butanol	-4.9334	-7.0021

by G^E models and predicted values by modified UNIFAC (Dortmund). Their deviations of vapor-phase mole fraction were less than 1%. Increasing the carbon number of the n -alcohol causes the azeotropic point to move to the alcohol-rich region, and deviations from Raoult's law decreased.

Excess molar volumes (V^E) were determined from densities using a vibrating tube densimeter at 298.15 K. In all the binaries, V^E was negative. Partial excess molar volumes at infinite dilution were determined from the five adjustable parameters of the Redlich–Kister polynomial.

Literature Cited

- Domanska, U. The Excess Molar Volumes of (Hydrocarbon + Branched Chain Ether) Systems at 298.15 and 308.15 K, and the Application of PFE theory. *Fluid Phase Equilib.* **1996**, *130*, 207–222.
- Gmehling, J.; Onken, U.; Arlt, W. *Vapor–Liquid Equilibrium Data Collection*; DECHEMA: Frankfurt, 1977.
- Gmehling, J.; Li, J.; Schiller, M. A Modified UNIFAC Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties. *Ind. Eng. Chem. Res.* **1993**, *32*, 178–193.
- Oh, J. H.; Park, S. J. Isothermal Vapor–Liquid Equilibria of 2-Methoxy-2-methylbutane (TAME) + n -Alcohol (C_1 – C_4) Mixtures at 323.15 and 333.15 K. *J. Chem. Eng. Data* **1997**, *42*, 517–522.
- Park, S. J.; Lee, T. J. Vapor–Liquid Equilibria and Excess Molar Properties of MTBE + Methanol and + Ethanol Mixtures. *Korean J. Chem. Eng.* **1995**, *12*, 110–114.
- Pettenati, C.; Alessi, P.; Fermeglia, M.; Kikic, I. Excess Volumes of Binary Mixtures Containing Morpholine. *Thermochim. Acta* **1990**, *162*, 203–212.
- Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases & Liquids*, 4th ed.; McGraw-Hill: New York, 1987.
- Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135–144.
- Riddick, J. A.; Bunger, W.; Sakano, T. *Organic Solvents Physical Properties and Methods of Purification*, 4th ed.; John Wiley & Sons: New York, 1986.
- Steinhagen, V.; Sandler, S. I. Vapor–Liquid Equilibria of Binary Mixtures with Ethyl *tert*-Butyl Ether. *J. Chem. Eng. Data* **1994**, *39*, 588–590.
- Stephenson, R. M.; Malanowski, S. *Handbook of the Thermodynamics of Organic Compounds*; Elsevier Science Publishing Co., Inc.: New York, 1987.
- Venkataramana, K. R.; Kantipudi, R.; Tummala, D.; Abburi, K. Volume of Mixing, Speed of Sound, and Viscosity of Methyl Cellosolve with Aliphatic Alcohols at 308.15 K. *J. Chem. Eng. Data* **1995**, *40*, 124–127.
- Weidlich, U.; Gmehling, J. Extension of UNIFAC by Headspace Gas Chromatography. *J. Chem. Eng. Data* **1985**, *30*, 95–101.
- Weidlich, U.; Gmehling, J. A Modified UNIFAC Model. 1. Prediction of VLE, h^E , and γ^E . *Ind. Eng. Chem. Res.* **1987**, *26*, 1372–1381.

Received for review April 22, 1998. Accepted August 12, 1998. The authors thank "National Special Project Corporation, Chungnam National University" and "Green Environment Co. Ltd." for financial support.

JE980089C