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Binary and Ternary Vapor−Liquid Equilibrium at 323.15 K and Excess Molar Volumes at 298.15 K for the Mixtures of Propyl Vinyl Ether + 1-Propanol + Toluene

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Isothermal vapor−liquid equilibrium data were determined by static method at 323.15 K for the binary systems {propyl vinyl ether + 1-propanol}, {propyl vinyl ether + toluene}, and {1-propanol + toluene} and also for the ternary system {propyl vinyl ether + 1-propanol + toluene}. The experimental binary and ternary vapor−liquid equilibrium data were correlated with different G^E models such as the Margules, van Laar, Wilson, NRTL, and UNIQUAC equations. In addition, excess molar volume data are reported for the same systems at 298.15 K. The excess molar volume data were correlated with the Redlich−Kister equation for the binary systems and the Cibulka equation for the ternary system, respectively.

Introduction

Lower alkyl vinyl ethers, e.g., methyl vinyl ether, propyl vinyl ether, isopropyl vinyl ether, and hexyl vinyl ether, are copolymerized with maleic anhydride and treated with alkali metal salt sulfite to form a sulfomethylated copolymer. Aqueous solutions of this sulfomethylated copolymer are useful in increasing the viscosity of drive fluids used in the supplemented recovery of petroleum from subterranean formations. Alkyl vinyl ethers are also used increasingly as industrial solvents and chemical intermediates in the chemical or pharmaceutical industry. For the process development of synthesis and separation of these compounds, reliable physical properties and phase equilibrium data are required. However, very few investigations were reported for alkyl vinyl ether compounds, and there are no data for propyl vinyl ether (PVE) systems except our previous reports as far as we know.[1−4]

In the present work, we report vapor−liquid equilibrium (VLE) data at 323.15 K for the binary systems {PVE + 1-propanol}, {PVE + toluene}, and {1-propanol + toluene} and also for the ternary system {PVE + 1-propanol + toluene} by using headspace gas chromatography (HSGC). The experimental binary VLE data were correlated using the Margules, van Laar, Wilson, NRTL, and UNIQUAC models, while the ternary VLE data were correlated with the Wilson, NRTL, and UNIQUAC models. Additionally, densities (ρ) at 298.15 K for the same binary and ternary systems were measured by using a digital vibrating tube density meter. The excess molar volumes (V^E) were calculated from these directly measured pure and mixture densities. Besides, the V^E data were correlated with the Redlich−Kister[10] polynomial for binary data and the Cibulka[12] equation for ternary data, respectively.

Experimental Section

Materials. Commercial grade PVE ($C_5H_{10}O$, M = 86.130 g·mol^{-1}, CAS-RN 764-47-6) and 1-propanol (C_3H_8O, M = 60.096 g·mol^{-1}, CAS-RN 71-23-8) were obtained from Aldrich, and toluene (C_7H_8, M = 92.141 g·mol^{-1}, CAS-RN 108-88-3) was obtained from Junsei Chemical Co. All the 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 with the values reported in the literature.[1,13] All sample purities were more than 99.9 wt %, according to gas chromatographic analysis. The measured

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

	ρ at 298.15 K		GC analysis	Antoine constants[a]		
chemicals	present study	lit. value[a]	(%)	*A*	*B*	*C*
PVE	0.76269	-	99.9	6.68791[b]	1011.39[b]	200.983[b]
1-propanol	0.80061	0.79970	99.9	7.74887	1440.74	198.800
toluene	0.86223	0.86230	99.9	6.95087	1342.31	219.187

[a] Ref 13. [b] Ref 1.

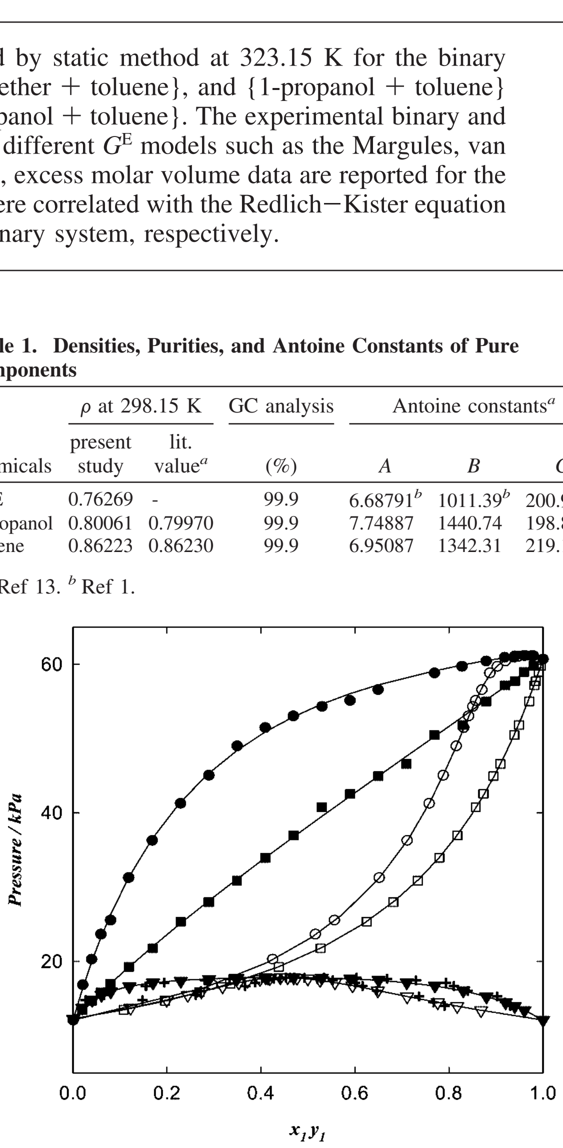

Figure 1. $P-x-y$ for the three binary systems at 323.15 K. Filled symbols, liquid phase; open symbols, vapor phase: ●, {PVE (1) + 1-propanol (2)} from previous work;[8] ■, {PVE (1) + toluene (2)}; ▼, {1-propanol (1) + toluene (2)}; +, {1-propanol (1) + toluene (2)} by Oracz et al.[9] Solid curves were calculated from the NRTL equation.

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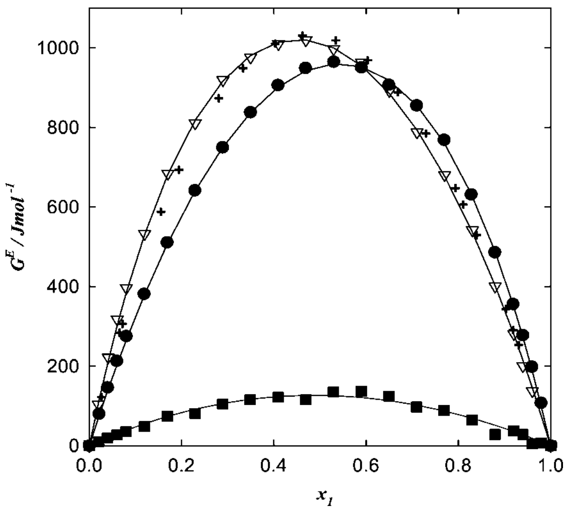

Figure 2. Excess Gibbs free energies for the three binary systems at 323.15 K: ●, {PVE (1) + 1-propanol (2)} from previous work;[8] ■, {PVE (1) + toluene (2)}; □, {1-propanol (1) + toluene (2)}; +, {1-propanol (1) + toluene (2)} by Oracz et al.[9] Solid curves were calculated from the NRTL equation.

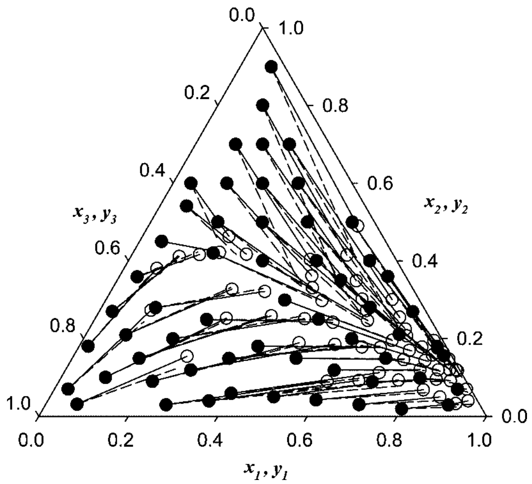

Figure 3. VLE for the ternary system {PVE (1) + 1-propanol (2) + toluene (3)} at 323.15 K: ●, liquid phase; ○, vapor phase. Dashed lines were calculated from the NRTL equation.

densities of the samples are summarized in Table 1 with Antoine constants of the pure substances.

Apparatus and Procedure. Isothermal VLE measurement were carried out by the headspace gas chromatograph method (HSGC), one of the static methods. 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, having an accuracy of ± 0.1 K. A capillary column (30 m × 0.32 mm × 0.25 μm) with an HP-5 (5 %-Diphenyl-95 %-Dimethylsiloxane) stationary phase and a thermal conductivity detector was used for the analysis. In this work, the vapor phase compositions were directly measured; however, the liquid phase compositions were calculated from thermodynamic relations and the mass balance. The uncertainty of the calculated mole fraction is about $\pm 1 \cdot 10^{-4}$. The procedure is described in detail elsewhere.[5,6] Densities were measured by a digital vibrating glass tube density meter (Anton Paar, model DMA 5000, Graz, Austria). The uncertainty of this density meter is less than $\pm 5 \cdot 10^{-6}$ g·cm^{-3} in the ranges from (0 to 3) g·cm^{-3}. The measuring procedure can be found elsewhere.[6,7]

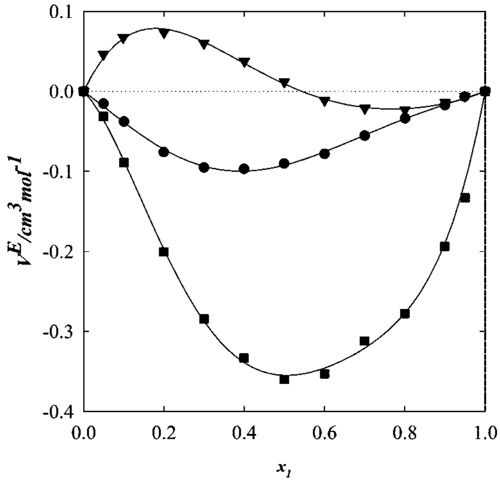

Figure 4. V^E (cm^3·mol^{-1}) for three binary systems at 298.15 K: ●, {PVE (1) + 1-propanol (2)} from previous work;[8] ■, {PVE (1) + toluene (2)}; ▼, {1-propanol (1) + toluene (2)} from previous work.[11] The solid lines represent the Redlich−Kister-type fittings with the parameters indicated in Table 8.

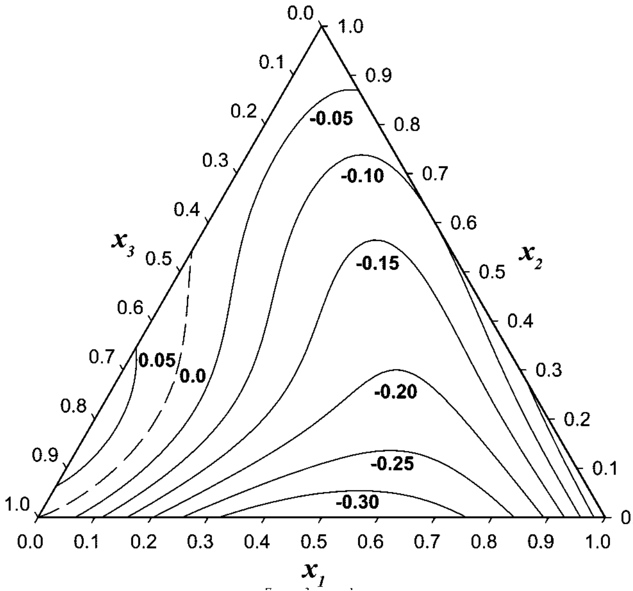

Figure 5. Isoclines of constant V^E (cm^3·mol^{-1}) for the ternary system {PVE (1) + 1-propanol (2) + toluene (3)} at 298.15 K.

Results and Discussion

Isothermal VLE. In the HSGC measuring method, the equilibrium pressure and liquid phase compositions are calculated from the experimental vapor phase compositions, mass balance, and thermodynamic equations.[5] The measured VLE compositions, pressures, and excess Gibbs free energies (G^E) for the binary systems {PVE (1) + toluene (2)} and {1-propanol (1) + toluene (2)} at 323.15 K are listed and plotted in Table 2 and Figures 1 and 2, respectively, while the binary VLE for the {PVE (1) + 1-propanol (2)} were taken from our previous work[8] and also represented in Figures 1 and 2 and for completion of sub-binary systems of the {PVE + 1-propanol + toluene} mixture.

As shown in the Figure 1, the binary systems {PVE + 1-propanol} and {PVE + toluene} are zeotropic systems, while a minimum boiling azeotrope was observed in the {1-propanol + toluene} system. The azeotropic point was determined by interpolation: $x_1^{az} = 0.450$ and $P^{az} = 17.86$ kPa. The measured VLE for {1-propanol + toluene} was compared with the

Table 2. Isothermal VLE Data for Binary Systems {PVE (1) + Toluene (2)} and {1-Propanol (1) + Toluene (2)} at 323.15 K

P_{cal}/kPa	x_1	y_1	γ_1	γ_2	G^E/J·mol^{-1}
		PVE (1) + Toluene (2)			
13.49	0.0201	0.1079	1.20	1.00	9.85
14.67	0.0395	0.1959	1.20	1.00	19.35
15.83	0.0598	0.2698	1.18	1.00	26.59
16.99	0.0793	0.3341	1.18	1.00	35.26
19.28	0.1195	0.4377	1.16	1.00	47.65
21.77	0.1694	0.5272	1.12	1.01	73.78
25.35	0.2293	0.6251	1.14	1.00	80.72
27.97	0.2890	0.6813	1.09	1.02	104.74
30.89	0.3489	0.7340	1.07	1.03	115.13
33.93	0.4090	0.7795	1.07	1.03	121.28
36.96	0.4693	0.8178	1.06	1.03	115.61
40.77	0.5292	0.8570	1.09	1.01	135.11
42.56	0.5896	0.8733	1.04	1.07	136.73
44.95	0.6495	0.8944	1.02	1.10	124.31
46.58	0.7096	0.9090	0.98	1.19	97.20
50.48	0.7688	0.9390	1.02	1.08	88.71
51.82	0.8296	0.9488	0.98	1.27	64.39
55.01	0.8793	0.9707	1.00	1.09	27.95
57.16	0.9195	0.9817	1.01	1.06	37.18
57.70	0.9401	0.9848	1.00	1.19	27.99
58.98	0.9601	0.9914	1.00	1.04	4.20
59.79	0.9797	0.9953	1.00	1.13	6.67
		1-Propanol (1) + Toluene (2)			
13.75	0.0196	0.1226	7.12	1.00	103.36
14.82	0.0409	0.1996	5.97	1.01	221.98
15.50	0.0606	0.2443	5.16	1.02	317.14
15.94	0.0804	0.2731	4.47	1.03	396.48
16.64	0.1199	0.3183	3.65	1.05	532.44
17.14	0.1703	0.3526	2.93	1.09	683.96
17.38	0.2294	0.3718	2.33	1.15	810.68
17.62	0.2898	0.3978	2.00	1.22	919.10
17.75	0.3496	0.4189	1.76	1.29	975.94
17.84	0.4100	0.4414	1.59	1.37	1009.84
17.85	0.4696	0.4566	1.43	1.49	1019.52
17.80	0.5295	0.4766	1.32	1.61	996.95
17.68	0.5902	0.4998	1.24	1.76	963.50
17.48	0.6503	0.5257	1.17	1.93	892.07
17.17	0.7102	0.5575	1.11	2.13	787.84
16.75	0.7702	0.5947	1.07	2.40	680.52
16.07	0.8304	0.6485	1.04	2.71	541.77
15.27	0.8798	0.7111	1.02	2.99	400.51
14.47	0.9203	0.7762	1.01	3.31	280.90
13.99	0.9400	0.8175	1.00	3.46	200.09
13.42	0.9604	0.8684	1.00	3.64	137.46

reported data[9] as shown in Figure 1. The literature data of Oracz et al.[9] for the system {1-propanol + toluene} were measured at 313.15 K. So we convert these data to the data at 323.15 K using binary NRTL model parameters for comparison. Both sets of data agreed relatively well within $\Delta y_1 = 0.0112$. The experimental binary VLE data were correlated with 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 the vapor-phase mole fraction (Δy_1) was calculated from eq 1.

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

where N is the number of experimental data points. The binary interaction parameters (A_{ij}) in the activity coefficient (γ) expression for the Wilson,[14] NRTL,[15] and UNIQUAC[16] models are

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

The excess Gibbs energy could then be evaluated using eq 2

$$\frac{G^E}{RT} = x_i \ln \gamma_i + x_j \ln \gamma_j \tag{2}$$

Figure 2 show the excess Gibbs energy for the three systems investigated, from which it is concluded that positive deviations from ideality are present and almost symmetric as usual.

The ternary VLE data of {PVE (1) + 1-propanol (2) + toluene (3)} at 323.15 K are listed in Table 4 and illustrated in Figure 3. The ternary VLE data were correlated with the Wilson, NRTL, and UNIQUAC models. The NRTL model gave slightly better correlation results with ca. 1.10 % of mean deviation of the vapor phase mole fraction. The G^E model parameters and the mean deviation of the vapor-phase mole fraction (Δy_{mean}) are given in Table 5. Δy_{mean} is determined by

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

Dashed lines in Figure 3 represent the fitted values from the NRTL model. Additionally, we compared the calculated ternary VLE data with calculated ternary data from the best-correlated binary parameters of sub-binary systems. The mean deviation of comparing result was $\Delta y = 0.0226$.

Excess Molar Volumes. The excess molar volumes (V^E) for binary mixtures were calculated from the measured densities by using eq 4.

Table 3. G^E Model Parameters and Mean Deviation between the Calculated and Experimental Vapor-Phase Mole Fraction (Δy_1) for the Binary Systems at 323.15 K

model equation	A_{12} / (J·mol^{-1})	A_{21} / (J·mol^{-1})	α	Δy_1
	PVE (1) + 1-Propanol (2)[a]			
Margules	5.094	6.904	−	0.0077
van Laar	5.143	7.145	−	0.0073
Wilson	329.836	1191.377	−	0.0059
NRTL	3823.447	2004.198	0.610	0.0052
UNIQUAC	4040.840	−1948.501	−	0.0058
	PVE (1) + Toluene (2)			
Margules	0.828	0.745	−	0.0028
van Laar	0.829	0.748	−	0.0028
Wilson	396.480	136.006	−	0.0028
NRTL	−179.292	715.247	0.305	0.0028
UNIQUAC	219.605	−1543.679	−	0.0028
	1-Propanol (1) + Toluene (2)			
Margules	7.425	5.347	−	0.0115
van Laar	7.728	5.409	−	0.0092
Wilson	5325.574	589.328	−	0.0031
NRTL	2164.962	4326.876	0.596	0.0020
UNIQUAC	−634.250	2587.098	−	0.0077

[a] Parameters taken from ref 8.

$$V^{\mathrm{E}} = \frac{\sum_i x_i M_i}{\rho_{\mathrm{m}}} - \sum_i \left(\frac{x_i M_i}{\rho_i}\right) \tag{4}$$

where x_i, M_i, and ρ_i are the mole fraction, molar mass, and density of pure component *i*, respectively. ρ_{m} means mixture density. The binary V^{E} data were correlated with a four-parameter Redlich−Kister polynomial, eq 5.[10]

$$V^{\mathrm{E}}_{12}/\mathrm{cm^3{\cdot}mol^{-1}} = x_1 x_2 \sum_{i=1}^{n} A_i (x_1 - x_2)^{i-1} \tag{5}$$

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

$$\sigma_{\mathrm{st}}/\mathrm{cm^3{\cdot}mol^{-1}} = \left[\frac{\sum_i ((V^{\mathrm{E}})_{\mathrm{cal}} - (V^{\mathrm{E}})_{\mathrm{exp}})_i^2}{(N-n)}\right]^{1/2} \tag{6}$$

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

Table 4. Isothermal VLE Data for the Ternary System {PVE (1) + 1-Propanol (1) + Toluene (3)} at 323.15 K

P_{cal}/kPa	x_1	x_2	y_1	y_2	γ_1	γ_2
23.68	0.0597	0.5413	0.2549	0.4174	1.52	1.50
22.54	0.0493	0.4503	0.1929	0.4219	1.38	1.75
21.57	0.0404	0.3590	0.1510	0.4164	1.27	2.10
20.45	0.0297	0.2697	0.1082	0.4115	1.18	2.58
19.09	0.0200	0.1804	0.0738	0.3809	1.11	3.33
30.57	0.1795	0.4205	0.4834	0.2979	1.32	1.79
25.46	0.1212	0.2796	0.3444	0.3213	1.16	2.47
23.00	0.0898	0.2095	0.2680	0.3273	1.11	3.00
17.24	0.0305	0.0702	0.1142	0.2730	1.05	4.93
31.72	0.2506	0.2490	0.5360	0.2421	1.11	2.61
28.30	0.2002	0.1993	0.4682	0.2514	1.08	3.03
24.93	0.1497	0.1494	0.3902	0.2587	1.05	3.59
21.40	0.0992	0.1001	0.2928	0.2524	1.04	4.32
34.27	0.3502	0.1489	0.6326	0.1783	1.02	3.47
30.21	0.2801	0.1192	0.5690	0.1852	1.01	3.89
26.12	0.2091	0.0899	0.4870	0.1890	1.01	4.40
17.44	0.0699	0.0310	0.2541	0.1546	1.03	5.80
30.77	0.3603	0.0396	0.6689	0.0922	0.97	5.27
26.31	0.2696	0.0297	0.5990	0.0901	0.98	5.60
22.43	0.0399	0.6000	0.1931	0.4633	1.63	1.39
29.76	0.1499	0.5003	0.4460	0.3308	1.46	1.57
28.87	0.1202	0.6000	0.4293	0.3615	1.66	1.36
27.40	0.0896	0.7001	0.4047	0.4036	1.92	1.21
37.79	0.3000	0.4003	0.6114	0.2466	1.30	1.82
36.98	0.2497	0.4999	0.5957	0.2724	1.48	1.53
35.64	0.2001	0.5995	0.5714	0.3015	1.70	1.34
33.42	0.1499	0.7004	0.5348	0.3490	1.99	1.20
29.81	0.1000	0.8005	0.4810	0.4150	2.39	1.10
45.88	0.4203	0.4004	0.7186	0.2070	1.33	1.78
44.85	0.3503	0.5002	0.7068	0.2244	1.52	1.51
42.97	0.2798	0.6000	0.6786	0.2552	1.76	1.32
39.90	0.2101	0.6999	0.6391	0.3007	2.08	1.19
26.42	0.0698	0.8996	0.4677	0.4898	3.05	1.03
54.83	0.5391	0.4005	0.8031	0.1754	1.38	1.76
53.56	0.4506	0.4996	0.7852	0.1949	1.58	1.49
33.45	0.4004	0.0591	0.7044	0.1126	0.97	4.81
37.50	0.4999	0.0500	0.7569	0.0932	0.96	4.91
41.69	0.5985	0.0422	0.8252	0.0680	0.96	4.99
45.97	0.7005	0.0301	0.8711	0.0498	0.96	5.17
50.49	0.8010	0.0191	0.9151	0.0328	0.97	5.34
37.51	0.3994	0.1803	0.6744	0.1772	1.04	3.11
41.50	0.5001	0.1494	0.7423	0.1456	1.02	3.38
45.38	0.6005	0.1190	0.7917	0.1200	1.00	3.70
49.21	0.7006	0.0889	0.8401	0.0955	0.99	4.08
56.81	0.9004	0.0289	0.9389	0.0397	0.99	5.05
40.97	0.4000	0.2991	0.6917	0.1955	1.16	2.23
45.04	0.5001	0.2498	0.7428	0.1696	1.11	2.50
48.70	0.5993	0.1996	0.7910	0.1438	1.07	2.85
52.21	0.7006	0.1492	0.8328	0.1194	1.04	3.30
55.44	0.8021	0.0986	0.8736	0.0918	1.02	3.89
49.18	0.4996	0.3505	0.7665	0.1784	1.26	1.96
52.51	0.6000	0.2806	0.8009	0.1575	1.18	2.28
55.32	0.6995	0.2110	0.8576	0.1202	1.11	2.73
59.64	0.9006	0.0695	0.9204	0.0701	1.02	4.29
57.06	0.5995	0.3602	0.8202	0.1649	1.32	1.90
58.83	0.7007	0.2694	0.8426	0.1472	1.19	2.33
60.14	0.8009	0.1791	0.8767	0.1173	1.10	2.97
60.40	0.8263	0.1560	0.8717	0.1200	1.08	3.19

The experimental densities and V^{E} for the binary system {PVE (1) + toluene} at 298.15 K are listed in Table 6 and plotted in Figure 4, and the binary V^{E} for the {PVE (1) + 1-propanol (2)} and {1-propanol (1) + toluene (2)} were taken from our previous work[8,11] and also represented in Figure 4 also for completion of sub-binary systems of the {PVE + 1-propanol + toluene} mixture. As shown in the figure, measured V^{E} values of {PVE (1) + 1-propanol (2)} and {PVE (1) + toluene (2)} at 298.15 K show negative deviations from ideal behavior over the whole composition range of PVE. The system {1-propanol + toluene} at 298.15 K shows negative deviation in the 1-propanol-rich region resulting from the strong polarity of 1-propanol, while it shows positive deviation in the toluene-rich region because of the nonpolar hydrocarbon. The negative deviation may be caused from the self-association by hydrogen bonding, which is a phenomenon of great relevance in the behavior of mixtures containing alcohols, and positive deviation may be caused from hydrogen bond rupture or dispersive interaction forces between two unlike molecules. The binary V^{E} data were correlated with the Redlich−Kister polynomial. The calculated V^{E} values, the solid curves, in Figure 4 using Redlich−Kister parameters, are in good agreement with experimental values. The mean deviations of V^{E} between experimental and calculated data are (0.0028, 0.0058, and 0.0033) $\mathrm{g{\cdot}cm^{-3}}$ for each system of {PVE + 1-propanol}, {PVE + toluene}, and {1-propanol + toluene}, respectively. The V^{E} data for the ternary system {PVE + 1-propanol + toluene} were also derived from measured densities at 298.15 K. The experimental densities and V^{E}data for the ternary system at 298.15 K are listed in Table 7. The ternary V^{E} data are correlated with the Cibulka equation.[12]

$$V^{\mathrm{E}}_{123} = V^{\mathrm{E}}_{12*} + V^{\mathrm{E}}_{23*} + V^{\mathrm{E}}_{13*} + x_1 x_2 x_3 (A_1 + A_2 x_1 + A_3 x_2) \tag{7}$$

where V^{E}_{12*}, V^{E}_{23*}, and V^{E}_{13*} represent the excess molar volumes of each combination and x_1, x_2, and x_3 are the mole fractions of PVE (1), 1-propanol (2), and toluene (3). The correlated values agreed relatively well with the experimental data with standard deviations of 0.0169 $\mathrm{cm^3{\cdot}mol^{-1}}$ (V^{E}). The isoclines were

Table 5. Fitted G^{E} Model Parameters and Standard Deviations for the Ternary System {PVE (1) + 1-Propanol (2) + Toluene (3)} at 323.15 K

G^{E} model	A_{ij} ($\mathrm{J{\cdot}mol^{-1}}$)	A_{ji} ($\mathrm{J{\cdot}mol^{-1}}$)	α	Δ*y*
		Wilson		
1 + 2	1257.566	4252.806	–	0.0114
2 + 3	4128.423	3401.135		
1 + 3	89.400	193.464		
		NRTL		
1 + 2	4000.673	676.839	0.200	0.0110
2 + 3	4263.089	3235.475	0.500	
1 + 3	859.447	−700.246	0.100	
		UNIQUAC		
1 + 2	2557.912	−637.445	–	0.0138
2 + 3	400.796	1447.560		
1 + 3	929.387	−825.938		

Table 6. Densities and Excess Molar Volumes for the Binary System {PVE (1) + Toluene (2)} at 298.15 K

x_1	ρ ($g\cdot cm^{-3}$)	V^E ($cm^3\cdot mol^{-1}$)	x_1	ρ ($g\cdot cm^{-3}$)	V^E ($cm^3\cdot mol^{-1}$)
		PVE (1) + Toluene (2)			
0.0494	0.85730	−0.0313	0.5999	0.80377	−0.3528
0.1002	0.85246	−0.0890	0.6998	0.79365	−0.3120
0.1995	0.84305	−0.2004	0.7999	0.78369	−0.2776
0.2999	0.83340	−0.2842	0.8993	0.77356	−0.1938
0.3993	0.82366	−0.3331	0.9500	0.76831	−0.1329
0.5002	0.81373	−0.3599			

Table 7. Densities and Excess Molar Volumes for the Ternary System {PVE (1) + 1-Propanol (2) + Toluene (3)} at 298.15 K

x_1	x_2	ρ ($g\cdot cm^{-3}$)	V^E ($cm^3\cdot mol^{-1}$)	x_1	x_2	ρ ($g\cdot cm^{-3}$)	V^E ($cm^3\cdot mol^{-1}$)
0.0595	0.5401	0.82726	−0.0225	0.1994	0.5999	0.80710	−0.1365
0.0498	0.4502	0.83357	0.0227	0.1504	0.6996	0.80579	−0.1234
0.0395	0.3601	0.83969	0.0549	0.1010	0.7995	0.80388	−0.0557
0.0295	0.2713	0.84531	0.0936	0.4201	0.4000	0.79577	−0.1833
0.1796	0.4194	0.82121	−0.0944	0.3499	0.5002	0.79640	−0.1502
0.1496	0.3499	0.82856	−0.0552	0.2800	0.5999	0.79710	−0.1188
0.1199	0.2796	0.83563	−0.0180	0.2098	0.7001	0.79793	−0.0940
0.0900	0.2099	0.84233	0.0259	0.5402	0.4000	0.78197	−0.1325
0.0295	0.0698	0.85536	0.0770	0.4495	0.4999	0.78474	−0.1345
0.3003	0.2994	0.81544	−0.1477	0.3599	0.6001	0.78741	−0.1152
0.2493	0.2507	0.82384	−0.1316	0.2702	0.6996	0.79037	−0.0953
0.1996	0.1996	0.83180	−0.0856	0.4000	0.0595	0.81990	−0.2744
0.1495	0.1511	0.83946	−0.0423	0.5002	0.0498	0.81060	−0.3220
0.1006	0.0995	0.84700	−0.0026	0.5999	0.0404	0.80113	−0.3217
0.3496	0.1509	0.81935	−0.1951	0.6996	0.0304	0.79164	−0.2914
0.2795	0.1200	0.82828	−0.1696	0.8006	0.0192	0.78220	−0.2526
0.2099	0.0902	0.83684	−0.1241	0.4001	0.1801	0.81247	−0.2177
0.0699	0.0291	0.85351	0.0084	0.5995	0.1203	0.79579	−0.2622
0.3593	0.0401	0.82498	−0.2553	0.6999	0.0906	0.78750	−0.2532
0.2702	0.0294	0.83439	−0.2133	0.4003	0.3000	0.80465	−0.1794
0.1800	0.0195	0.84369	−0.1461	0.4985	0.2514	0.79740	−0.2019
0.0404	0.6001	0.82572	−0.0201	0.5999	0.2000	0.79026	−0.2192
0.0302	0.6999	0.82050	−0.0472	0.7005	0.1497	0.78311	−0.1950
0.0203	0.7994	0.81465	−0.0548	0.8006	0.1000	0.77640	−0.1891
0.1505	0.4996	0.81951	−0.0941	0.5003	0.3499	0.79023	−0.1658
0.1208	0.5992	0.81646	−0.0939	0.6002	0.2803	0.78427	−0.1589
0.0899	0.6997	0.81320	−0.0887	0.7006	0.2096	0.77878	−0.1662
0.0295	0.9007	0.80533	−0.0462	0.7000	0.2698	0.77432	−0.1340
0.2998	0.4002	0.80914	−0.1565	0.8005	0.1801	0.77011	−0.0877
0.2505	0.4993	0.80810	−0.1458				

Table 8. Fitted Redlich−Kister (Binary System) or Cibulka (Ternary System) Parameters and Standard Deviations of Fits for the Mixture {PVE (1) + 1-Propanol (2) + Toluene (3)} at 298.15 K

system ($cm^3\cdot mol^{-1}$)	A_1	A_2	A_3	A_4	σ_{st}
(1) + (2)[a]	−0.3690	0.2576	0.0981	−0.1637	0.0028
(2) + (3)[b]	0.0373	−0.4597	0.3868	−0.1653	0.0033
(1) + (3)	−1.4194	−0.0280	−0.1784	−1.0776	0.0058
(1) + (2) + (3)	5.4962	−7.2455	−6.7479	−	0.0169

[a] Parameters taken from ref 8. [b] Parameters taken from ref 11.

calculated using eq 7 and represented in Figure 5, which shows negative V^E at almost all the compositions as can be expected from the binary V^E data. Only the narrow toluene-rich concentration region shows positive V^E.

The adjusted parameters of the Redlich−Kister and Cibulka equations are given in Table 8 along with standard deviations between calculated and experimental data.

Conclusion

Isothermal vapor−liquid equilibrium data at 323.15 K and excess molar volumes (V^E) at 298.15 K were experimentally determined for the ternary system {PVE + 1-propanol + toluene} and its binary subsystems. Only the binary VLE of {1-propanol + toluene} shows a minimum boiling azeotrope. The NRTL model provided the best correlation results for measured binary and ternary VLE data. The binary V^E data of {PVE + toluene} show negative deviations from ideal behavior and correlated well with the Redlich−Kister equation. The Cibulka equation was applied reliably for the ternary V^E data. The isoclines of ternary V^E data show negative values for almost all the composition ranges of the ternary mixture except a narrow concentration region of the {1-propanol + toluene} mixture.

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