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Measurement and Correlation of Vapor−Liquid Equilibria at $T = 333.15$ K and Excess Molar Volumes at $T = 298.15$ K for Ethanol + Dimethyl Carbonate (DMC), DMC + 1-Propanol, and DMC + 1-Butanol

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Isothermal vapor−liquid equilibrium (VLE) data are measured for ethanol + dimethyl carbonate (DMC), DMC + 1-propanol, and DMC + 1-butanol at $T = 333.15$ K by a using headspace gas chromatography (HSGC) method. The binary systems containing ethanol and 1-propanol have minimum boiling azeotropes. The experimental binary VLE data were correlated with common g^E model equations. Excess molar volumes (V^E) of ethanol + DMC, 1-propanol + DMC, and 1-butanol + DMC are obtained from the measured densities at $T = 298.15$ K by using a digital vibrating tube densimeter. All measured V^E are shown positive deviation from ideal mixing and are correlated with the five-parameter Redlich−Kister polynomial.

Introduction

Dimethyl carbonate (DMC) is an environmentally benign and biodegradable chemical. DMC is mainly produced by the oxidative carbonylation of methanol over a CuCl catalyst. The current worldwide production capacity of DMC is much less than the demand because it is a versatile reagent and solvent and is nontoxic to humans and the environment, as indicated by its toxicological and ecotoxicological properties.[1] DMC is a strong contender to assist the refining industry in meeting the Clean Air Act specifications for oxygen in gasoline. DMC has about 3 times the oxygen content as methyl *tert*-butyl ether (MTBE). It does not phase separate in a water stream as some alcohols do, and it has both low toxicity and relatively quick biodegradablity.[2,3]

In this work, isothermal VLE were measured for ethanol (1) + dimethyl carbonate (DMC) (2), DMC (1) + 1-propanol (2), and DMC (1) + 1-butanol (2) at $T = 333.15$ K. The excess molar volumes for ethanol (1) + DMC (2), 1-propanol (1) + DMC (2), and 1-butanol (1) + DMC (2) were determined at $T = 298.15$ K. The experimental VLE data were correlated with the g^E model equations; Margules, van Laar, Wilson, NRTL, and UNIQUAC. The excess molar volumes were correlated by the Redlich−Kister polynomial.

Experimental Section

Materials. DMC was obtained from Aldrich Chemical Co., and the others were supplied by Merck Co. All the chemicals had a purity of better than $w = 99.8$ %, and these values were verified with gas chromatography. The reagent were used without further purification. The measured densities of all chemicals, literature values, and Antoine constants are listed in Table 1.

Apparatus and Procedure. Binary isothermal VLE data have been measured by using headspace gas chromatography (HSGC). The HSGC system consists of a commercial gas chromatography (Agilent 6890N) and a headspace sampler (HP19395A), which has an electropneumatic sampling system and a precision thermostat, having an uncertainty of in temperature of ± 0.1 K. HP-FFAP (Hewlett-Packard, poly(ethylene glycol)-TPA modified, 50 m × 0.2 mm × 0.3 μm) capillary column fitted with a thermal conductivity detector was used for the analysis. All the sample mixtures (of volume about 3 cm^3) were prepared directly in a 10 cm^3 glass vial that was the equilibrium cell, using a digital microbalance (AND Co. HA-202M) with an uncertainty of $\pm 1 \times 10^{-5}$ g. With the HSGC method, the equilibrated vapor phase is automatically analyzed with a electropneumatic sampling system, while the liquid-phase compositions were calculated from the thermodynamic relations and the mass balance was calculated from the feed compositions. According to the HSGC method used in this work, total pressure is not measured but calculated using the chromatogram peak area along with thermodynamic relations. The detailed procedure of the calculation method is described in our previous work.[4−7]

Table 1. Measured Densities at 298.15 K and Antoine Constants of Pure Components

	density/g·cm^{-3}		Antoine constants[a,b]		
chemicals	present study	lit. value[a]	*A*	*B*	*C*
DMC	1.06319	1.06328	6.15885	1253.59	211.600
ethanol	0.78520	0.7850	7.23710	1952.86	226.184
1-propanol	0.79975	0.7997	6.87377	1440.74	198.806
1-butanol	0.80604	0.8060	7.04974	1617.52	203.296

[a] Data from Dortmund Data Bank.[8] [b] $\log_{10} P_i^{\mathrm{sat}}/\mathrm{kPa} = A - [B/(t/°\mathrm{C} + C)]$.

Densities of the pure components and each binary mixtures were determined with an Anton Paar digital vibrating-tube densimeter (DMA 5000) at $T = 298.15$ K with an uncertainty of $\pm 1 \times 10^{-5}$ g·cm^{-3}. Bidistilled water and dry air were used to verify the calibration of the densimeter.

Results and Discussion

The pure component properties, stored in the DDB,[8] were used to calculate the true liquid compositions with SRK equation.[9] Vapor pressures of the pure component at $T = 333.15$ K were calculated from the Antoine equation. The used Antoine constants are listed also in Table 1.

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Table 2. Isothermal VLE for Binary Systems of Ethanol (1) + DMC (2), DMC (1) + 1-Propanol (2), and DMC (1) + 1-Butanol (2) at 333.15K

P(calcd)/kPa	x_1	y_1	γ_1	γ_2	P(calcd)/kPa	x_1	y_1	γ_1	γ_2
				Ethanol (1) + DMC (2)					
36.75	0.0170	0.0649	3.0001	1.0005	54.91	0.5995	0.6303	1.2307	1.4510
38.38	0.0343	0.1194	2.8475	1.0018	55.01	0.6502	0.6529	1.1777	1.5625
43.40	0.1004	0.2673	2.4622	1.0119	54.95	0.7002	0.6620	1.1076	1.7733
46.49	0.1492	0.3468	2.3039	1.0215	54.45	0.7500	0.7132	1.1037	1.7881
48.50	0.1994	0.3963	2.0552	1.0469	54.05	0.7999	0.7472	1.0764	1.9551
49.53	0.2495	0.4236	1.7930	1.0888	53.50	0.8501	0.7756	1.0406	2.2927
51.13	0.3001	0.4697	1.7060	1.1088	52.30	0.9002	0.8226	1.0188	2.6614
52.66	0.3492	0.5134	1.6503	1.1270	50.34	0.9502	0.8877	1.0027	3.2504
53.58	0.4496	0.5453	1.3855	1.2669	49.41	0.9659	0.9174	1.0003	3.4285
54.15	0.5003	0.5766	1.3304	1.3135	48.16	0.9831	0.9576	1.0001	3.4667
54.71	0.5499	0.6115	1.2967	1.3519					
				DMC (1) + 1-Propanol (2)					
22.17	0.0169	0.1004	3.7646	1.0006	37.28	0.5498	0.6405	1.2431	1.4687
23.81	0.0337	0.1754	3.5466	1.0021	37.41	0.5998	0.6516	1.1632	1.6062
25.11	0.0497	0.2287	3.3100	1.0051	37.64	0.6502	0.6843	1.1338	1.6755
28.41	0.0999	0.3461	2.8164	1.0181	37.74	0.6998	0.7093	1.0948	1.8026
30.63	0.1497	0.4150	2.4304	1.0397	37.73	0.7501	0.7388	1.0636	1.9450
32.40	0.1998	0.4669	2.1671	1.0650	37.59	0.8002	0.7733	1.0398	2.1032
33.64	0.2496	0.5023	1.9379	1.1006	37.28	0.8498	0.8143	1.0226	2.2735
33.92	0.2997	0.5115	1.6570	1.1671	36.79	0.9000	0.8642	1.0113	2.4647
35.42	0.3496	0.5623	1.6307	1.1757	36.02	0.9498	0.9231	1.0021	2.7212
35.98	0.3997	0.5813	1.4974	1.2379	35.69	0.9662	0.9488	1.0031	2.6709
36.65	0.4496	0.6077	1.4179	1.2886	35.38	0.9830	0.9715	1.0008	2.9335
36.97	0.4999	0.6224	1.3175	1.3772					
				DMC (1) + 1-Butanol (2)					
9.83	0.0169	0.1935	3.2141	1.0001	29.09	0.5515	0.8270	1.2483	1.3919
11.66	0.0340	0.3319	3.2617	0.9999	29.90	0.6015	0.8418	1.1980	1.4725
12.44	0.0500	0.3795	2.7018	1.0083	30.56	0.6514	0.8543	1.1472	1.5839
16.91	0.0980	0.5688	2.8093	1.0026	31.10	0.7014	0.8659	1.0990	1.7318
18.60	0.1505	0.6168	2.1829	1.0411	31.84	0.7512	0.8833	1.0716	1.8519
20.38	0.2007	0.6624	1.9250	1.0682	32.39	0.8012	0.8983	1.0397	2.0548
21.98	0.2511	0.6984	1.7498	1.0984	33.23	0.8509	0.9228	1.0315	2.1347
23.93	0.3012	0.7373	1.6768	1.1156	33.72	0.9006	0.9397	1.0070	2.5389
26.11	0.3513	0.7745	1.6476	1.1261	34.25	0.9505	0.9677	0.9981	2.7730
26.08	0.4015	0.7739	1.4386	1.2223	34.49	0.9663	0.9793	1.0004	2.6319
27.42	0.4514	0.7976	1.3869	1.2553	34.71	0.9830	0.9894	1.0000	2.6758
28.08	0.5014	0.8089	1.2967	1.3349					

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 333.15 K

model equation	A_{12}	A_{21}	α	Δy_1[a]
		Ethanol (1) + DMC (2)		
Margules	1.0682	1.2073		0.0078
van Laar	1.0687	1.2147		0.0077
Wilson	592.8773	316.6633		0.0066
NRTL	611.1014	478.7729	0.7953	0.0052
UNIQUAC	35.8916	346.2100		0.0075
		DMC (1) + 1-Propanol (2)		
Margules	1.3185	1.0675		0.0041
van Laar	1.3333	1.0762		0.0037
Wilson	589.0039	394.1021		0.0032
NRTL	336.1559	647.3597	0.5027	0.0031
UNIQUAC	90.3822	230.9768		0.0036
		DMC (1) + 1-Butanol (2)		
Margules	1.1435	1.0689		0.0073
van Laar	1.1454	1.0689		0.0072
Wilson	546.5437	325.5268		0.0066
NRTL	435.0474	515.2689	0.6649	0.0062
UNIQUAC	31.0459	238.7980		0.0072

[a] $\Delta y_1 = |y_{1,\mathrm{exp}} - y_{1,\mathrm{calcd}}|/N$; N = number of data.

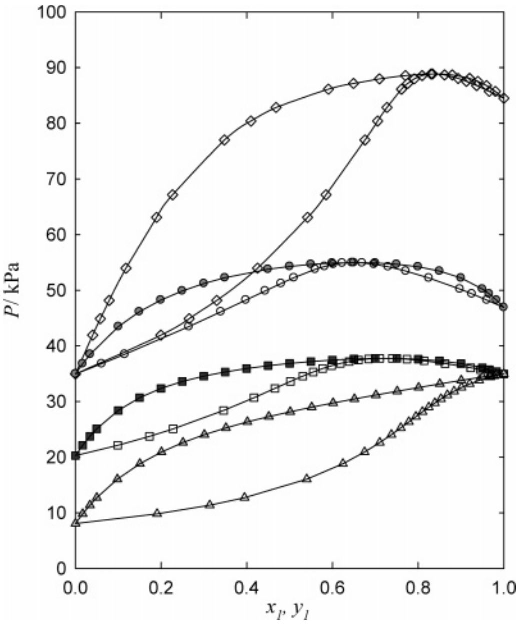

Figure 1. Isothermal VLE for the ●, ethanol + DMC; ■, DMC + 1-propanol; and ▲, DMC + 1-butanol at 333.15 K. Solid lines, correlated values from NRTL equation. ◇, methanol + DMC taken from ref 12.

Table 2 gives experimental values of calculated total pressures, equilibrium liquid and vapor compositions, and activity coefficients for the binary systems. The total pressures reported in this work are calculated values. Although the total pressure is the calculated value, the calculated total pressure of this HSGC method has been shown to be in good agreement with direct measurement within experimental error.[10] The objective function used to calculate the activity coefficient is

$$\text{objective function} = \sum\left(1 - \frac{\gamma_{\text{calcd}}}{\gamma_{\text{exp}}}\right)^2 \le \epsilon \qquad (1)$$

Table 4. Measured Densities and Excess Molar Volumes of Ethanol (1) + DMC (2), 1-Propanol (1) + DMC (2), and 1-Butanol (1) + DMC (2) at 298.15 K

x_1	ρ_m/g·cm^{-3}	v^E/cm^3·mol^{-1}	x_1	ρ_m/g·cm^{-3}	v^E/cm^3·mol^{-1}	x_1	ρ_m/g·cm^{-3}	v^E/cm^3·mol^{-1}
				Ethanol (1) + DMC (2)				
0.0000	1.06319	0.0000	0.3501	0.98568	0.1503	0.6999	0.88989	0.1201
0.0501	1.05275	0.0484	0.4002	0.97328	0.1553	0.7499	0.87410	0.1073
0.1000	1.04229	0.0773	0.4499	0.96059	0.1560	0.8001	0.85771	0.0892
0.1501	1.03154	0.1034	0.5000	0.94740	0.1539	0.8498	0.84070	0.0766
0.1998	1.02064	0.1189	0.5500	0.93374	0.1501	0.8998	0.82298	0.0540
0.2498	1.00934	0.1336	0.6001	0.91957	0.1457	0.9500	0.80445	0.0289
0.2998	0.99773	0.1415	0.6500	0.90500	0.1348	1.0000	0.78520	0.0000
				1-Propanol (1) + DMC (2)				
0.0000	1.06319	0.0000	0.3498	0.97439	0.3085	0.7001	0.88218	0.2982
0.0501	1.05050	0.0743	0.3998	0.96145	0.3281	0.7500	0.86868	0.2694
0.1002	1.03773	0.1426	0.4499	0.94847	0.3365	0.8002	0.85515	0.2233
0.1498	1.02544	0.1750	0.5001	0.93529	0.3452	0.8501	0.84136	0.1901
0.1999	1.01247	0.2391	0.5500	0.92219	0.3420	0.9002	0.82759	0.1314
0.2502	0.99985	0.2625	0.6000	0.90892	0.3357	0.9502	0.81383	0.0584
0.2999	0.98713	0.2922	0.6501	0.89557	0.3217	1.0000	0.79975	0.0000
				1-Butanol (1) + DMC (2)				
0.0000	1.06319	0.0000	0.3499	0.96339	0.4492	0.7000	0.87468	0.4256
0.0502	1.04797	0.1018	0.4000	0.95013	0.4704	0.7499	0.86298	0.3648
0.0999	1.03324	0.1882	0.4501	0.93702	0.4870	0.7999	0.85107	0.3336
0.1499	1.01851	0.2837	0.5000	0.92420	0.4916	0.8500	0.83953	0.2670
0.2003	1.00453	0.3157	0.5500	0.91158	0.4852	0.8999	0.82811	0.2017
0.2501	0.99053	0.3765	0.6000	0.89907	0.4766	0.9499	0.81700	0.1066
0.2998	0.97690	0.4166	0.6500	0.88683	0.4515	1.0000	0.80604	0.0000

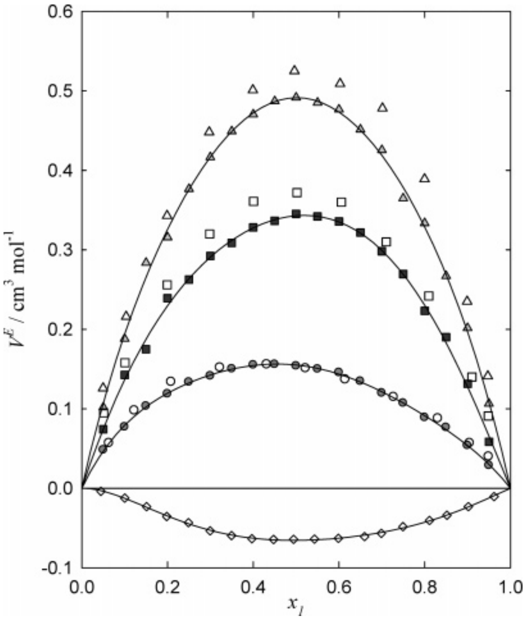

Figure 2. Excess molar volumes for the ●, ethanol + DMC; ■, 1-propanol + DMC; and ▲, 1-butanol + DMC at 298.15 K; ◇, methanol + DMC taken from ref 12; ○, ethanol + DMC; □, 1-propanol + DMC; and △, 1-butanol + DMC taken from ref 13. Solid lines, calculated values from Redlich−Kister equation.

The ethanol (1) + DMC (2), DMC (1) + 1-propanol (2), and DMC (1) + 1-butanol (2) all show miscibility over the entire compositions. Ethanol (1) + DMC (2) and DMC (1) + 1-propanol (2) exhibit the minimum boiling azeotropes, while DMC (1) + 1-butanol (2) has no azeotropic point. The azeotropic points were $x_1 = 0.6535$ for the ethanol (1) + DMC (2) and $x_1 = 0.7228$ for the DMC (1) + 1-propanol (2), which were determined by interpolation of the measured VLE data. The total pressures at these points are 55.01 kPa and 37.74 kPa, respectively.

The activity coefficients of the experimental binary systems were correlated with the most common g^E models (that are Margules, van Laar, Wilson, NRTL, and UNIQUAC). The activity coefficients so determined are listed in Table 3 together with the correlated g^E model parameters. The mean deviation of vapor-phase mole fraction (Δy_1) means

$$\Delta y_1 = |y_{1,\mathrm{exp}} - y_{1,\mathrm{calcd}}|/N \qquad (2)$$

where N is the number of experimental data.

Wilson, NRTL, and UNIQUAC parameters (A_{ij}) for the binary systems are as follows: Wilson, $A_{ij} = (\lambda_{ij} - \lambda_{ii})$ cal·mol^{-1}; NRTL, $A_{ij} = (g_{ij} - g_{jj})$ cal·mol^{-1}; and UNIQUAC, $A_{ij} = (u_{ij} - u_{jj})$ cal·mol^{-1}.

The mean deviations between calculated and experimental vapor compositions, Δy_1, are less than 1 mol % for almost all g^E equations. These small deviations are an indication of the quality of the measured data. To check the consistency of the measured VLE, Redlich−Kister thermodynamic consistency tests[11] have been applied. These showed good agreement within ± 1 %. The equilibrium pressures and compositions ($P-x-y$) for each binary system at $T = 333.15$ K are shown in Figure 1 together with the results of Han and Park[12] for methanol + DMC. The solid lines in Figure 1 are those calculated by the best correlated equation as NRTL for all the binary systems.

The excess molar volumes for the binary mixtures were calculated from the measured densities of the pure substances and mixtures using

$$V^E/\mathrm{cm^3{\cdot}mol^{-1}} = \frac{(x_1M_1 + x_2M_2)}{\rho_m} - \left(\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right) \qquad (3)$$

where x_i, M_i, ρ_i, and ρ_m are the mole fraction, molar mass, and pure component density of i component and mixture density, respectively. The experimental densities and excess molar volumes at $T = 298.15$ K for the binary systems of ethanol (1) + DMC (2), 1-propanol (1) + DMC (2), and 1-butanol (1) + DMC (2) are listed in Table 4 and shown in Figure 2 with the values reported by Rodríguez et al.[13] All the measured excess molar volumes showed positive deviations from the ideal behavior and a symmetric figure. The more carbon numbers that are in alcohol resulted in a larger deviation from ideality. The maximum deviations from ideal mixing were 0.1560, 0.3452, and 0.4916 cm^3·mol^{-1}, respectively. For 1-propanol (1) + DMC (2) and 1-butanol (1) + DMC (2), our experimental

Table 5. Fitted Redlich−Kister Parameters and Standard Deviations for Excess Molar Volumes of Ethanol (1) + DMC (2), 1-Propanol (1) + DMC (2), and 1-Butanol (1) + DMC (2) at 298.15 K

	A_1	A_2	A_3	A_4	A_5	$\sigma_{st}/cm^3 \cdot mol^{-1}$
ethanol (1) + DMC (2)	0.6205	−0.1086	0.0068	−0.1062	0.2795	0.0016
1-propanol (1) + DMC (2)	1.3716	0.0877	0.2279	−0.2334	−0.1214	0.0058
1-butanol (1) + DMC (2)	1.9656	0.0103	0.0963	0.0153	0.3478	0.0076

data are slightly smaller than those reported by Rodríguez et al. In Figure 2, excess molar volumes of methanol (1) + DMC (2) reported by Han and Park[12] are also plotted. For the methanol (1) + DMC (2), the excess molar volume showed a negative deviation from ideality.

The measured data were correlated with a five-parameter Redlich−Kister polynomial:[11]

$$V^E/\mathrm{cm}^3\cdot\mathrm{mol}^{-1} = x_1 x_2 \sum_{i=1}^{5} A_i (x_1 - x_2)^{i-1} \tag{4}$$

where A_i values are the adjustable parameters. The standard deviation of fit (σ_{st}) is defined by

$$\sigma_{st}/\mathrm{cm}^3\cdot\mathrm{mol}^{-1} = \left[\frac{\sum_i (v^E_{calcd} - v^E_{exp})_i^2}{N - n}\right]^{1/2} \tag{5}$$

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

The fitted parameters of the Redlich−Kister polynomial and standard deviations are listed in Table 5. With a standard deviation of less than 0.1 %, the correlated values are in good agreement with the experimental data. In Figure 2, the solid lines represent the calculated values with the fitted Redlich−Kister polynomial.

Conclusions

Isothermal VLE data at $T = 333.15$ K for ethanol + DMC, DMC + 1-propanol, and DMC + 1-butanol were obtained with the HSGC method. VLE data showed positive deviations from Raoult's law. The binary systems containing ethanol and 1-propanol had minimum boiling azeotropes. All the binary systems could be correlated well with common g^E model equations within deviations of the vapor mole fraction of 1 %. Excess molar volumes were obtained from the measured densities at $T = 298.15$ K for ethanol + DMC, 1-propanol + DMC, and 1-butanol + DMC. All measured V^E had positive deviations from ideal mixing. Measured V^E values were correlated by five-parameter Redlich−Kister polynomial, and their deviations between measured and calculated values were less than 1 %.

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