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High-Pressure Vapor−Liquid Equilibrium for Dimethyl Ether + 2-Propanol and Dimethyl Ether + 2-Propanol + Water

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We report vapor−liquid equilibrium data for the system dimethyl ether (DME) + 2-propanol at 323.45, 348.45, and 373.45 K and for the system dimethyl ether + 2-propanol + water at 323.25, 348.05, and 373.15 K. The experimental data are correlated using the Peng−Robinson equation of state and the Elliott−Suresh−Donohue equation of state. We explore the properties of dimethyl ether in the ternary system as a near-critical or supercritical solvent or cosolvent. The data for the dimethyl ether solutions are compared to literature data for ternary systems containing propylene or propane + 2-propanol + water. Dimethyl ether exhibits relatively higher solubility in the aqueous phase, leading to enhanced volatility of water at relatively low pressures compared to the case for propane. On the other hand, dimethyl ether also becomes completely soluble in the aqueous solution at relatively low pressures, precluding two-phase mass transfer under certain conditions.

Introduction

This is our second report on vapor−liquid equilibrium measurements in binary and ternary systems involving dimethyl ether (DME). Earlier studies included measurements of phase equilibria in mixtures of dimethyl ether with ethanol, and dimethyl ether with ethanol and water.[1] The measurements for those systems covered three different isotherms and pressures up to the vicinity of the critical locus of the mixture.

This study presents phase equilibrium measurements for the system dimethyl ether + 2-propanol at 323.45, 348.45, and 373.45 K and for the system dimethyl ether + 2-propanol + water at 323.25, 348.05, and 373.15 K, where the feed ratio of 2-propanol to water is near the azeotropic ratio on a dimethyl ether free basis (68 mol of alcohol to 32 mol of water). The experimental data are correlated using the Peng−Robinson equation of state[2] and the Elliott−Suresh−Donohue equation of state.[3,4] In this study we report the properties of dimethyl ether in the dimethyl ether + 2-propanol + water system as a near-critical or supercritical solvent or cosolvent and compare them to those of propylene and propane in ternary systems containing propylene or propane + 2-propanol + water. This study complements prior work on dehydrating binary azeotropes by probing a heavier alcohol and a stronger proton-accepting solvent than those in previous studies.

Experimental Section

The experimental apparatus is a dynamic circulation flow type apparatus where the vapor and the liquid are circulated inside the equilibrium cell. The details of the experimental equipment, calibrations, and operating procedures have been presented previously[1,5] and therefore will only be briefly described here.

Table 1. Vapor−Liquid Equilibria of the DME (1) + 2-Propanol (2) System

T/K	*P*/MPa	*x*(1)	*y*(1)	*T*/K	*P*/MPa	*x*(1)	*y*(1)
323.35	0.129	0.0802	0.8113	348.75	1.574	0.7907	0.9720
323.15	0.271	0.2025	0.9175	348.65	1.641	0.8257	0.9761
323.45	0.478	0.3809	0.9563	348.45	1.718	0.8614	0.9804
323.45	0.573	0.4659	0.9647	348.45	1.838	0.9148	0.9872
323.55	0.739	0.6221	0.9766	348.45	1.902	0.9386	0.9900
323.55	0.837	0.7163	0.9816	348.45	1.930	0.9526	0.9923
323.45	0.922	0.7971	0.9861	373.15	0.531	0.1349	0.6573
323.45	0.961	0.8321	0.9881	373.25	0.915	0.2786	0.8092
348.85	0.274	0.1089	0.7381	373.45	1.483	0.4768	0.8892
348.55	0.549	0.2554	0.8733	373.45	1.717	0.5511	0.9065
348.55	1.003	0.4961	0.9365	373.55	1.948	0.6244	0.9220
348.55	1.147	0.5702	0.9472	373.45	2.084	0.6673	0.9300
348.65	1.294	0.6464	0.9566	373.45	2.514	0.7940	0.9525
348.55	1.430	0.7206	0.9647	373.65	2.621	0.8232	0.9581
348.65	1.520	0.7631	0.9693				

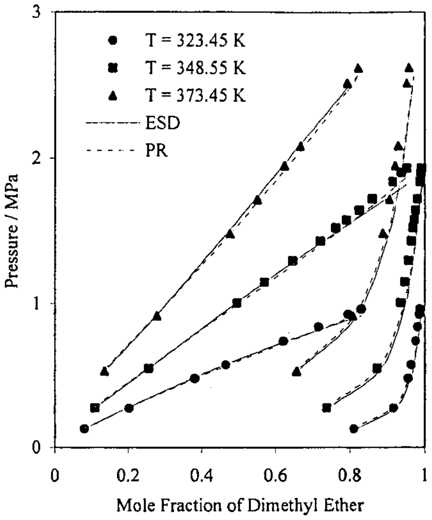

Figure 1. *P*−*T*−*x* diagram of DME (1) + 2-propanol (2) system: (●, ■, ▲) this work.

The apparatus is based on a 40 cm^3 constant volume cell with windows on opposite sides for visual observation of experimental conditions. A 31 μL vapor-sampling loop and 0.5 μL liquid-sampling loop were used in this study for sampling. An air bath was used to maintain the temperature of the cell, and a gas chromatograph (GC) was used

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Table 2. Vapor−Liquid Equilibria of the DME (1) + 2-Propanol (2) + Water (3) System

T/K	P/MPa	x(1)	x(2)	x(3)	y(1)	y(2)	y(3)	α31	α21
323.35	0.141	0.0843	0.6300	0.2857	0.8434	0.1248	0.0318	0.0111	0.0198
323.25	0.235	0.157	0.5784	0.2646	0.9123	0.0698	0.0179	0.0116	0.0208
323.25	0.330	0.2281	0.5331	0.2388	0.9408	0.0460	0.0132	0.0134	0.0209
323.25	0.418	0.2959	0.4869	0.2172	0.9536	0.0360	0.0104	0.0149	0.0229
323.25	0.501	0.3611	0.4429	0.1960	0.9617	0.0298	0.0085	0.0163	0.0253
323.15	0.577	0.4275	0.3994	0.1731	0.9673	0.0245	0.0082	0.0209	0.0271
323.15	0.662	0.5037	0.3484	0.1479	0.9732	0.0200	0.0068	0.0238	0.0297
323.25	0.739	0.5773	0.2985	0.1242	0.9771	0.0168	0.0061	0.0290	0.0333
323.15	0.779	0.6257	0.2668	0.1075	0.9788	0.0150	0.0062	0.0369	0.0359
323.25	0.817	0.6468	0.2515	0.1017	0.9802	0.0138	0.0060	0.0389	0.0362
348.35	0.221	0.0578	0.6442	0.2980	0.6316	0.2761	0.0923	0.0283	0.0392
348.25	0.468	0.1783	0.5653	0.2564	0.8474	0.1135	0.0391	0.0321	0.0422
348.05	0.669	0.2755	0.5049	0.2196	0.8986	0.0754	0.0260	0.0363	0.0458
347.95	0.834	0.3557	0.4516	0.1927	0.9201	0.0581	0.0218	0.0437	0.0497
348.05	1.049	0.4655	0.3782	0.1563	0.9388	0.0435	0.0177	0.0562	0.0570
348.05	1.166	0.5280	0.3355	0.1365	0.9464	0.0374	0.0162	0.0662	0.0622
348.05	1.251	0.5755	0.3024	0.1221	0.9514	0.0334	0.0152	0.0753	0.0668
348.05	1.338	0.6272	0.2665	0.1063	0.9570	0.0292	0.0138	0.0851	0.0718
348.05	1.562	0.7641	0.1717	0.0642	0.9684	0.0203	0.0113	0.1389	0.0933
347.95	1.618	0.7930	0.1511	0.0559	0.9711	0.0182	0.0107	0.1563	0.0984
348.05	1.787	0.8862	0.0854	0.0284	0.9805	0.0115	0.0080	0.2546	0.1217
348.05	1.813	0.8989	0.0757	0.0254	0.9820	0.0106	0.0074	0.2667	0.1282
348.05	1.852	0.9173	0.0618	0.0209	0.9843	0.0090	0.0067	0.2988	0.1357
348.05	1.873	0.9282	0.0554	0.0164	0.9862	0.0081	0.0057	0.3271	0.1376
372.95	0.762	0.1738	0.5697	0.2565	0.7529	0.1747	0.0724	0.0652	0.0708
372.85	1.103	0.2804	0.5001	0.2195	0.8332	0.116	0.0508	0.0779	0.0781
373.05	1.416	0.3819	0.4334	0.1847	0.8718	0.0876	0.0406	0.0963	0.0885
373.05	1.678	0.4694	0.3751	0.1555	0.894	0.0708	0.0352	0.1189	0.0991
372.95	1.814	0.5137	0.3441	0.1422	0.9029	0.0643	0.0328	0.1312	0.1063
373.15	2.095	0.6117	0.2773	0.111	0.9197	0.0517	0.0286	0.1714	0.1240
373.15	2.207	0.6516	0.2502	0.0982	0.9252	0.0475	0.0273	0.1958	0.1337
373.15	2.344	0.7103	0.2153	0.0744	0.9273	0.0457	0.027	0.2780	0.1626
373.15	2.444	0.7388	0.1897	0.0715	0.9378	0.0382	0.024	0.2644	0.1586

Table 3. Binary Interaction Parameters

system	$k_{ij}°$ ESD	k_{ij}^T ESD	$k_{ij}°$ PR	k_{ij}^T PR	%PAAD[a] ESD	%PAAD[a] PR	ref
2-propanol + water	0.2078	−58.13	−0.0170	−52.10	0.76	6.58	6
DME + water	0.1737	−49.30	0.0859	−116.0	6.24	15.48	7
DME + 2-propanol	−0.1644	53.31	−0.1414	49.31	1.02	1.99	this work

[a] %PAAD = percent average absolute deviation in the bubble pressure.

for data analysis. The oven temperature, the thermal conductivity detector (TCD) temperature, and the injection temperature of the GC were set to 160 °C, 250 °C, and 200 °C, respectively. An 8 ft long Pora Pak Q packed column was used in this study, and the flow rate of the carrier gas of the GC was set to 10.06 $cm^3 \cdot min^{-1}$, which was the average of 10 measurements taken while the reference gas was off. Helium was used as the carrier gas.

The dimethyl ether calibration was conducted using the vapor-sampling loop and the control system of the experimental apparatus. The typical deviation in the dimethyl ether calibration was within 0.3%. The 2-propanol and water calibrations were conducted using a 1.0 μL precision liquid-sampling syringe. The typical deviations in the 2-propanol and water calibrations were within 3%. These percentages were based on the variances between the correlated number of moles and the experimental number of moles.

Results and Discussion

Vapor−liquid equilibrium measurements for dimethyl ether + 2-propanol at 323.45, 348.45, and 373.45 K are reported in Table 1, and isothermal VLE are plotted in Figure 1. Vapor−liquid equilibrium data for dimethyl ether + 2-propanol + water at 323.25, 348.05, and 373.15 K are reported in Table 2, and isothermal VLE are plotted in Figure 2. The pressures versus the vapor mole fraction of dimethyl ether for the binary and ternary systems are plotted in Figures 3 and 4, respectively. The standard deviation of the binary liquid dimethyl ether phase compositions was not more than +0.003 mole fraction, and that of the vapor-phase compositions was not more than +0.009 mole fraction. The standard deviation of the ternary liquid dimethyl ether and water phase compositions was not more than +0.004 mole fraction, and those of the vapor-phase compositions were not more than +0.002 and +0.0067 mole

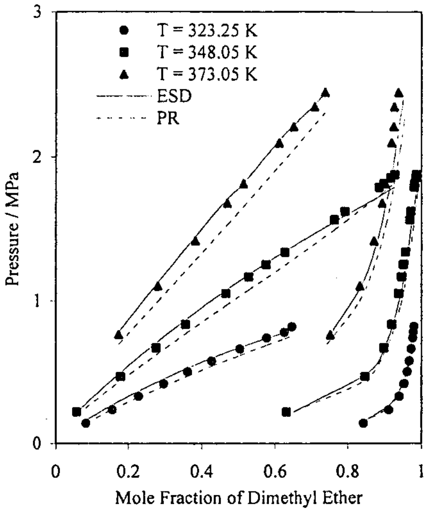

Figure 2. $P-T-x$ diagram of DME (1) + 2-propanol (2) + water (3) system: (●, ■, ▲) this work.

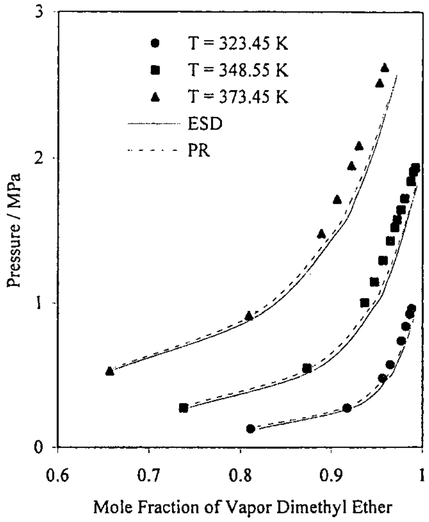

Figure 3. Pressure versus vapor mole fraction of DME for the DME (1) + 2-propanol (2) system: (●, ■, ▲) this work.

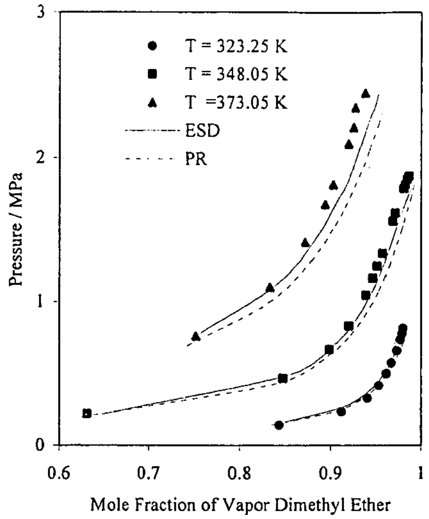

Figure 4. Pressure versus vapor mole fraction of DME for the DME (1) + 2-propanol (2) + water (3) system: (●, ■, ▲) this work.

fraction, respectively. Throughout this study, the maximum pressure drop in the system after withdrawing five samples was 0.0069 MPa.

The experimental data were correlated using the Peng–Robinson equation of state (PR-EOS) and the Elliott–Suresh–Donohue equation of state (ESD-EOS). Table 3 contains the binary interaction parameters (k_{ij}) and the percentage error in the bubble point pressure (PAAD) for the ESD-EOS and the PR-EOS. The interaction parameters of the system 2-propanol + water and dimethyl ether + water, which were used to model the ternary system, were obtained by regressing the experimental data reported by Kobayashi and Katz[6] and Pozo and Streett,[7] respectively. A temperature-dependent function for the binary interaction parameter was used for the vapor–liquid calculations. This function is given by $k_{ij} = k_{ij}^{\circ} + k_{ij}^{T}/T$, where T is the temperature in Kelvin and k_{ij}° and k_{ij}^{T} are constants characterizing the temperature dependence. The ESD-EOS was fit with a proton acceptor energy of hydrogen bonding equal to 16.65 kJ·mol^{-1} and a bonding volume of 0.398 cm^3·mol^{-1} for dimethyl ether. The cross-association (solvation) energy was computed as $\Delta H_{Dj} = (16.65 + \Delta H_{jj})/2$ in all binary combinations involving DME.

The relative volatility of water and 2-propanol with respect to dimethyl ether as a near critical fluid (NCF) is reported in Table 2. The data from Tables 1 and 2 show that the presence of water has minimal impact on the relative volatility of 2-propanol to DME as long as similar liquid mole fractions of DME are compared. This comparison of the K-value and relative volatility of dimethyl ether with the data for propylene and propane of Zabaloy et al.[8] for the isotherm 348 K is shown in Figure 5. Propylene has a higher vapor pressure than propane and dimethyl ether, and propane has a higher vapor pressure than dimethyl ether. Dimethyl ether is more polar than both propylene and propane. Thus, in Figure 5a, the K-value for dimethyl ether is lower than the K-value for propane and propylene. In addition, the polarity of dimethyl ether makes it more compatible with water than propylene and propane. This observation agrees with our previous observation for the system dimethyl ether + ethanol + water.[1] Also, we reported that the K-value of R-22 for the system chlorodifluoromethane (R-22) + ethanol + water was lower than that for propane in the propane + ethanol + water system despite the fact that R-22 has a higher vapor pressure than propane.[5] Again, polarity plays a major role

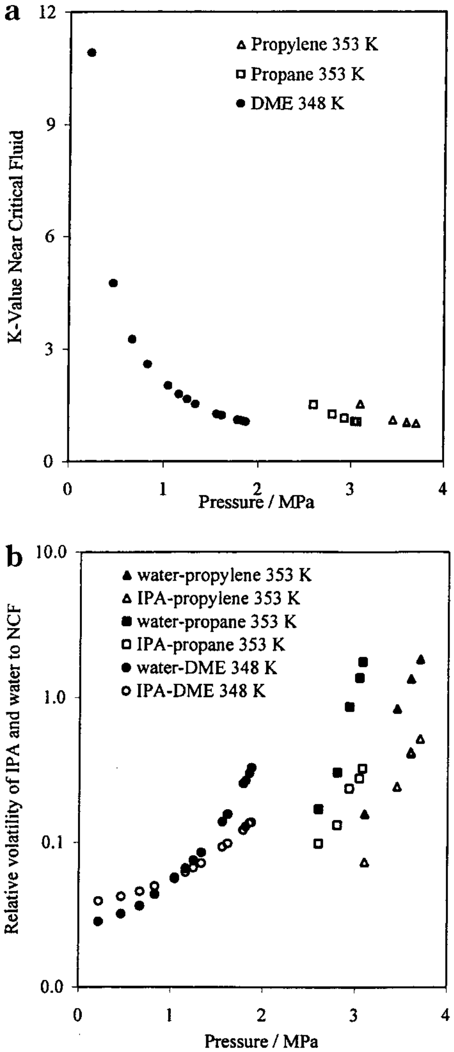

Figure 5. (a) K-value of DME in the DME + 2-propanol + water system at 348.05 K, in the propane in propane + 2-propanol + water system at 353 K, and in the propylene in propylene + 2-propanol + water system at 353 K at the azeotropic composition on a solvent free-basis: (□, △) Zabaloy et al.;[8] (●) this work. (b) Relative volatility of 2-propanol and water with respect to DME at 348.05 K, propane at 353 K, and propylene at 353 K at the azeotropic composition: (□, △, ■, ▲) Zabaloy et al.;[8] (●, ○) this work.

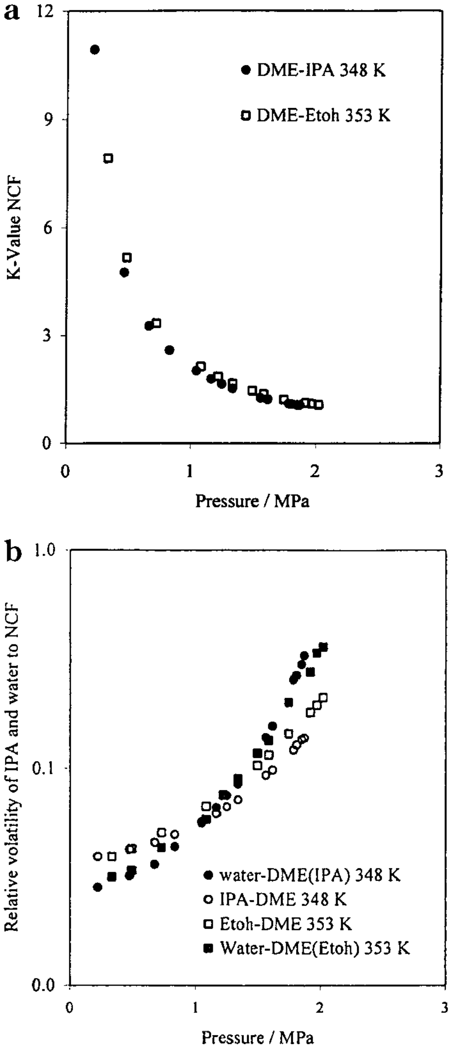

Figure 6. (a) *K*-value of DME in the DME + ethanol + water system at 353.55 K and in the DME + 2-propanol + water system at 348.05 K at the azeotropic composition: (□) Elbaccouch et al.;[5] (●) this work. (b) Relative volatility of ethanol and water with respect to DME at 353.55 K and of 2-propanol and water with respect to DME at 348.05 K at the azeotropic composition: (■, □) Elbaccouch et al.;[5] (●, ○) this work.

in making the more polar solvent more soluble in the liquid phase.

In Figure 5b, it seems that the relative volatilities of water and 2-propanol are higher with dimethyl ether than with propylene and propane at the pressures that we studied. However, the relative volatility of water needs to be larger than unity in order for dimethyl ether to be feasible for dehydration.[8] The same phenomenon was observed for the relative volatility of our previously studied chlorodifluoromethane + ethanol + water and dimethyl ether + ethanol + water systems, when we compared them to the data of Horizoe et al.[9] for the system propane + ethanol + water. Dehydrations and extractions appear to rely on the formation of LLE at very high pressures. It may be possible to form a second liquid phase at higher pressure and higher water composition, but we have studied only water to 2-propanol ratios at the composition of the binary azeotrope.

The *K*-values for the systems dimethyl ether + ethanol + water at 353 K and dimethyl ether + 2-propanol + water at 348 K are plotted in Figure 6a and the relative volatilities of ethanol, 2-propanol, and water with respect to dimethyl ether are plotted in Figure 6b. Apparently, increasing the molecular weight of the alcohol altered the solubility and the relative volatilities of the water and dimethyl ether to only a minor extent.

Conclusions

Similar to our previous finding for dimethyl ether + ethanol + water, the application of dimethyl ether as a cosolvent leads to systems that exhibit VLE. The VLE terminate when the pressure exceeds the bubble point in the presence of the dimethyl ether. Despite the higher degree of hydrocarbon nature in 2-propanol relative to ethanol, we observed no indication of LLE in this system over the range of compositions and pressures studied. Relative volatilities of water to dimethyl ether (0.01 to 0.33) were generally higher than those of ethanol to water (0.02 to 0.16), especially at 348 K. Nevertheless, the relative volatility of water in this system was less than unity, making dimethyl ether unsuitable as a dehydration solvent for this system.

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