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

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The first part of this paper is a review of experimental methods and the high-pressure phase behavior of dimethyl ether systems for which data have been published between 1932 and 1999. For the systems investigated, the references, temperatures, pressures, cell volumes, and experimental procedures are reported. The second part of this paper is high-pressure vapor−liquid equilibrium (VLE) data for the systems dimethyl ether (DME) + ethanol at (332.95, 353.25, and 373.15) K and dimethyl ether + ethanol + water at (333.55, 353.55, and 373.65) K. The experimental data are correlated using the Elliott−Suresh−Donohue (ESD-EOS) and Peng Robinson (PR-EOS) equations of state.

Introduction

This paper is a continuation of a research program to provide vapor−liquid equilibrium (VLE) results on binary and ternary mixtures valuable to the design of high-pressure processes. In our previous paper we reported vapor−liquid equilibrium data for the systems carbon dioxide + methanol, carbon dioxide + ethanol, chlorodifluoromethane (R-22) + ethanol, and chlorodifluoromethane + ethanol + water (Elbaccouch et al., 2000). In this paper we report vapor−liquid equilibrium data for the binary system dimethyl ether (DME) + ethanol at (332.95, 353.25, and 373.15) K and the ternary system dimethyl ether + ethanol + water at (333.55, 353.55, and 373.65) K, where the feed composition of ethanol to water is 95.6% to 4.4% by mass on a dimethyl ether free basis (azeotropic composition).

Dimethyl ether is made from methanol by a dehydration process (Hansen et al., 1995) and is used primarily as a propellant for spray cans, as a fuel in engines, as a replacement for diesel oil (Jonasson et al., 1995a), and as a raw material in the synthesis of light olefins, such as ethylene and propylene (Sardesai, 1997). Our goal is to explore the properties of dimethyl ether as a near-critical solvent or a supercritical solvent or a cosolvent and compare them to those of chlorodifluoromethane and propane.

Review of Published Data on Dimethyl Ether Systems

Phase behavior data can be generated through a variety of techniques. Review articles describing methods and techniques of phase behavior measurements were published by Tsiklis (1968), Schneider (1975), Eubank et al. (1980), Deiters and Schneider (1986), Fornari et al. (1990), and Dohrn and Brunner (1995). Several authors have published detailed compilations of high-pressure vapor−liquid equilibrium data. Hicks et al. (1978) and Knapp et al. (1981) covered the period from 1900 to 1980. Fornari et al. (1990) covered the period from 1978 to 1987. Dohrn and Brunner (1995) covered the period from 1987 to 1993. This paper summarizes data from these sources and from the literature.

Table 1 lists dimethyl ether systems for which high-pressure phase equilibrium data have been published between 1932 and 1999. The table lists the maximum pressure corresponding to each isotherm reported for each system. Also, Table 1 explains the differences between the compiled systems in terms of cell type, mixing procedure, and sampling technique. The various symbols used in Table 1 are explained in Table 2.

A review of Table 1 leads to the following observations. Experimental methods for phase behavior can be classified as analytical methods or synthetic methods. The analytical methods are classified as dynamic or static. Analytical methods involve the determination of the compositions of the coexisting phases by taking samples from each phase and analyzing them outside the equilibrium cell via a gas chromatograph (GC) or a wet test meter. Dynamic methods require the circulation of at least one of the phases to and from the cell. The static method does not involve the circulation of any of the phases. Mixing in the static method is accomplished via stirring or rocking. Sampling in the dynamic method is done using sampling loops connected to special sampling valves, whereas sampling in the static method is done using capillaries.

Some analytical methods use a homogenizer while sampling the coexisting phases in which the condensed phase is evaporated and homogenized prior to on-line gas chromatographic analysis. In our previous paper (Elbaccouch et al., 2000) we reported VLE data for the systems CO_2 + methanol and CO_2 + ethanol, without using a homogenizer. These were very consistent with the data of Suzuki and Sue (1990), who used a homogenizer in their VLE measurements.

In the case of the synthetic methods, the compositions of the coexisting phases are determined stoichiometrically. Visible cells are essential in the stoichiometric methods because the measurements are based on mass balances coupled with either measuring the height of each phase or adjusting the temperature, pressure, or composition in such a way that one phase exists in excess compared to the other phases.

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Table 1. Review of Dimethyl Ether (DME) Published Systems

DME +	ref	temp/K	pressure/MPa	method	cell vol/cm^3
aniline	Rowley and Powell, 1991	363.15, 313.15	2.723, 0.891	Sto-Sti-Con nVis-Liq	n.a.
n-butane	Fernandez et al., 1992	282.96, 297.86, 312.98, 328.01, 343.07, 357.65, 372.87, 387.22, 402.71, 405.16, 414.50	0.372, 0.586, 0.882, 1.285, 1.807, 2.449, 3.286, 4.261, 4.820, 4.705, 4.295	Dyn-Vcir-Vis Air&Liq	n.a.
1-butene	Fernandez et al., 1987	283.6, 303.47, 322.47, 342.80, 369.33	0.376, 0.674, 1.091, 1.777, 2.999	Dyn-Vcir-Con Vis-Air&Liq nHom	n.a.
CH_3Cl	Holldorff and Knapp, 1988a	253.20, 322.49	0.115, 1.082	Sta-Sti-nVar Vis-Liq-Hom	n.a.
CH_3Cl + CH_3OH	Holldorff and Knapp, 1988a	293.15, 323.15	0.262, 0.786	Sta -sti-Con Vis-Liq-Hom	n.a.
CH_3OH	Chang et al., 1982	273.15, 293.15, 313.15, 333.15, 353.15, 373.15, 393.15, 413.15, 433.15, 453.15	0.255, 0.521, 0.900, 1.461, 2.243, 3.256, 4.663, 5.481, 6.081, 6.674	Dyn-Vcir-Con Liq-Hom	75
CH_3OH	Holldorff and Knapp, 1988b	253.52, 352.68	0.035, 1.042	Sta-Sti-Con Vis-nHom	512
CH_4	Sanchez et al., 1987	382.9, 313.3, 343.8	12.36, 12.16, 10.66	Sta-Sti-Con nHom	n.a.
CO	Jonasson et al., 1995a	288.15, 306.15, 316.15	7.70, 7.35, 6.92	Sta-Sti-Con nVis-Liq-nHom	700
CO_2	Jonasson et al., 1995a	282.20, 308.65, 320.12	4.12, 6.33, 6.79	Sta-Sti-Con nVis-Liq-nHom	700
CO_2	Tsang and Street, 1981	273.15, 288.2, 308.65, 320.06, 335.17, 350.2, 360.07, 370.13, 377.57, 386.56	3.10, 4.41, 6.26, 7.25, 7.93, 7.39, 7.11, 6.61, 6.37, 5.70	Dyn-Vcir-Con Liq-Hom	n.a.
CO_2	Winkler and Maass, 1932	307.15, 327.55	5.478, 4.57	volumetric	n.a.
ethylformate	Rowley and Powell, 1991	353.15, 273.15	2.211, 0.268	Sto-Sti-Con nVis-Liq	n.a.
H_2	Jonasson et al., 1995b	288.15, 306.15, 316.15	7.14, 7.99, 6.84	Sta-Sti-Con nVis-Liq-nHom	700
H_2O	Holldorff and Knapp, 1988c	273.04, 322.53	0.016, 1.118	volumetric	n.a.
H_2O	Pozo and Streett, 1984	323.15, 48.15, 373.26, 94.21, 403.26, 414, 423.5, 433.2, 453.3, 473.6, 493.16	1.027, 1.8, 2.848, 4.054, 4.661, 5.454, 6.219, 5.959, 21.01, 17.31, 14.82	Dyn-Vcir-Con Vis-Air-Hom	n.a.
methylamine	Rowley and Powell, 1991	353.15, 273.15	2.211, 0.268	Sto-Sti-Con nVis-Liq	n.a.
phenol	Rowley and Powell, 1991	353.15, 319.15	2.211, 1.023	Sto-Sti-Con nVis	n.a.
propylene	Winkler and Maass, 1932	336.15, 392.55	1.157, 3.634	volumetric	n.a.
R-22	Noles and Zollweg, 1992	283.15, 323.15, 363.15, 373.01, 383.00, 395.0	0.681, 1.947, 4.451, 4.847, 4.813, 4.979	Dyn-VLcir Con Vis-Liq-Hom	50
SO_2	Noles and Zollweg, 1991	283.15, 323.59, 363.15, 405.0, 415.0, 425.0	0.371, 1.160, 2.729, 5.425, 5.71, 6.186	Dyn-VLcir-Vis Air-Hom	n.a.
SO_2	Pupezin et al., 1966	248.15, 243.15, 238.15, 233.15	9.522, 0.635, 6.053, 4.746	volumetric	n.a.
SO_2	Zawisza amd Glowka, 1970	323.15, 363.15, 393.15	1.148, 2.695, 4.734	n.a.	n.a.

[a] n.a. = not applicable.

Table 2. Explanation of Symbols Used in Table 1

symbol	meaning	symbol	meaning
Sti	stirring	Sto	stoichiometry
Roc	rocking	Hom	homogeneous
Con	constant volume	nHom	nonhomogeneous
Var	variable volume	VLcir	vapor liquid circulation
Vis	visible window	Vcir	vapor circulation
nVis	non-visible window	Liq	liquid bath
Sta	static	Air	air bath
Dyn	dynamic		

Experimental Section

Our experimental apparatus is a dynamic circulation continuous flow type where the vapor and the liquid are circulated inside the equilibrium cell thoroughly and continuously at a constant temperature until vapor−liquid equilibrium is achieved. The apparatus is shown in Figure 1, and it consists mainly of an equilibrium cell, two magnetic pumps, two sampling valves, two hand pumps, an air bath, and a gas chromatograph (GC). A detailed description of the apparatus, calibration methods, and measurement techniques has been published elsewhere (Elbaccouch et al., 2000).

Our measurements utilize a 40 cm^3 constant volume cell with visible windows. The liquid and vapor samples are withdrawn from the cell through 0.5 and 31.0 μL sample loops, respectively. Data are analyzed using a Hewlett-Packard gas chromatograph (model 5890) and an integrator (model 3390 A). The oven temperature, the thermal conductivity detector (TCD) temperature, and the injection temperature of the gas chromatograph are set to 145, 250, and 200 °C, respectively. An 8 ft Porapak Q packed column was used for this study, and the flow rate of the carrier gas (helium) was set to 25.93 mL·min^{-1}.

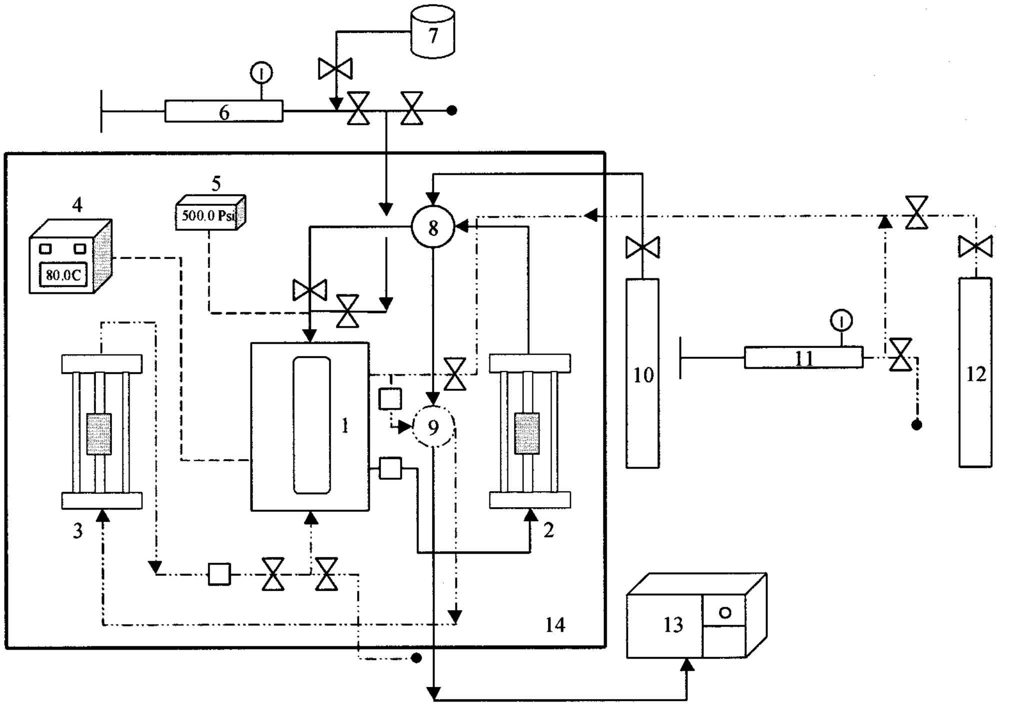

Figure 1. Schematic diagram of the VLE experimental apparatus: 1, equilibrium cell; 2, liquid magnetic circulation pump; 3, vapor magnetic circulation pump; 4, cell temperature indicator; 5, cell pressure indicator; 6, liquid feed high-pressure pump; 7, liquid reservoir; 8, liquid sampling valve; 9, vapor sampling valve; 10, helium cylinder; 11, gas feed high-pressure pump; 12, gas cylinder; 13, gas chromatograph; 14, constant temperature air bath; solid arrow, liquid line; dashed–dotted arrow, vapor line; dotted arrow, helium line; ●, vacuum line; - - -, temperature or pressure probe; bow tie, valve; □, filter.

Table 3. Vapor–Liquid Equilibria of the DME (1) + Ethanol (2) System

T/K	*P*/MPa	*x*(1)	*y*(1)	*T*/K	*P*/MPa	*x*(1)	*y*(1)
332.85	0.191	0.6350	0.7575	373.15	0.339	0.0345	0.3570
332.65	0.382	0.1874	0.8986	373.15	0.817	0.1963	0.7483
332.75	0.514	0.2747	0.9292	373.15	1.248	0.3429	0.8328
332.75	0.595	0.3318	0.9396	373.15	1.476	0.4221	0.8557
333.05	0.752	0.4446	0.9536	373.25	1.835	0.5485	0.8849
332.85	0.823	0.4940	0.9589	373.35	2.121	0.6502	0.9046
333.05	0.874	0.5389	0.9619	373.35	2.342	0.7281	0.9199
332.85	0.987	0.6429	0.9683	373.55	2.518	0.7828	0.9290
333.25	1.032	0.6816	0.9717	373.05	2.581	0.8128	0.9377
333.25	1.066	0.6991	0.9714	373.05	2.727	0.8553	0.9483
333.25	1.095	0.7220	0.9730	373.05	2.885	0.8981	0.9601
332.95	1.112	0.7430	0.9750	373.15	3.160	0.9638	0.9833
332.15	1.123	0.7512	0.9756				
333.05	1.135	0.7613	0.9762				
332.95	1.173	0.7914	0.9781				
333.05	1.253	0.8569	0.9831				
353.35	0.576	0.2087	0.8442				
353.25	0.809	0.3176	0.8874				
353.35	0.921	0.3680	0.9033				
353.25	0.981	0.3997	0.9102				
353.25	1.084	0.4494	0.9184				
353.25	1.155	0.4849	0.9238				
353.35	1.243	0.5389	0.9309				
353.25	1.330	0.5742	0.9353				
353.25	1.361	0.5912	0.9378				
353.25	1.446	0.6359	0.9427				
353.15	1.511	0.6680	0.9460				
353.15	1.616	0.7245	0.9531				
352.85	1.649	0.7479	0.9567				
352.85	1.706	0.7757	0.9597				
352.85	1.739	0.7957	0.9620				
353.35	1.772	0.8038	0.9625				

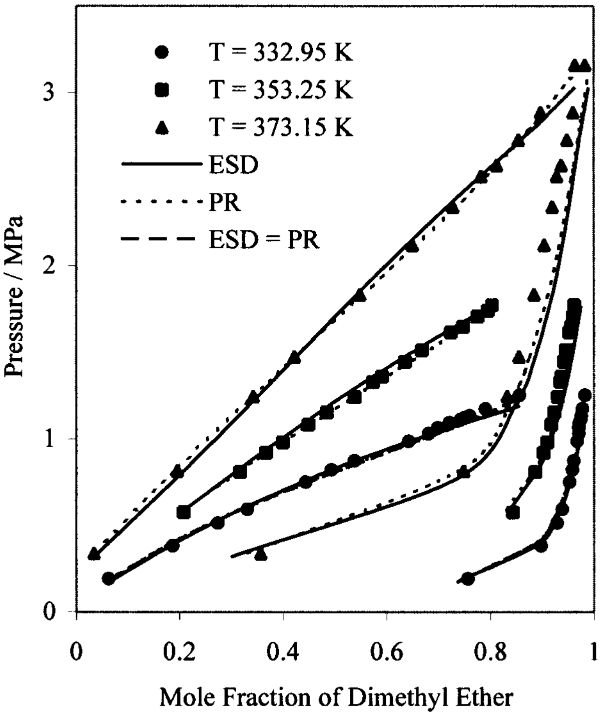

Figure 2. $P-T-x$ diagram of the DME (1) + ethanol (2) system: (●, ■, ▲) this work. ESD = PR only for the 332.95 K isotherm. From the graph it is difficult to distinguish the ESD = PR line from the PR line.

Five samples from each phase were taken for analysis by the gas chromatograph, and the reported compositions were the result of averaging those values together. The standard deviation of the binary liquid dimethyl ether phase compositions was not more than ±0.0025 mole fraction, and that of the vapor phase compositions was not more than ±0.0062. The standard deviations of the composition of dimethyl ether and water in the ternary system were not more than ±0.0016 and ±0.0036 mole fraction, respectively, and those of the vapor-phase composition were not more than ±0.0017 and 0.000 97, respectively. The maximum pressure drop in the system after

Table 4. Vapor−Liquid Equilibria of the DME (1) + Ethanol (2) + Water (3) System

T/K	P/MPa	$x(1)$	$x(2)$	$x(3)$	$y(1)$	$y(2)$	$y(3)$	α_{21}[a]	α_{31}
333.55	0.273	0.2155	0.7134	0.0711	0.9150	0.0793	0.0057	0.0262	0.0189
333.55	0.409	0.2747	0.6596	0.0657	0.9316	0.0633	0.0051	0.0283	0.0229
333.45	0.675	0.4394	0.5110	0.0496	0.9546	0.0418	0.0036	0.0377	0.0334
333.55	0.987	0.7077	0.2679	0.0244	0.9741	0.0234	0.0025	0.0635	0.0744
333.45	1.063	0.7882	0.1951	0.0167	0.9790	0.0188	0.0022	0.0776	0.1061
333.55	1.164	0.8594	0.1299	0.0107	0.9843	0.0142	0.0015	0.0954	0.1224
333.45	1.244	0.8946	0.0980	0.0074	0.9879	0.0109	0.0012	0.1007	0.1468
333.45	1.295	0.9214	0.0727	0.0059	0.9962	0.0026	0.0012	0.0331	0.1881
353.45	0.330	0.0911	0.8260	0.0829	0.7220	0.2572	0.0208	0.0393	0.0317
353.45	0.485	0.1583	0.7658	0.0759	0.8179	0.1688	0.0133	0.0427	0.0339
353.55	0.725	0.2628	0.6715	0.0657	0.8767	0.1138	0.0095	0.0508	0.0433
353.55	1.083	0.4310	0.5194	0.0496	0.9194	0.0744	0.0062	0.0671	0.0586
353.45	1.221	0.5007	0.4565	0.0428	0.9296	0.0644	0.0060	0.0760	0.0755
353.55	1.338	0.5634	0.3992	0.0374	0.9367	0.0577	0.0056	0.0869	0.0901
353.45	1.494	0.6458	0.3246	0.0296	0.9457	0.0492	0.0051	0.1035	0.1177
353.55	1.585	0.6920	0.2820	0.0260	0.9505	0.0447	0.0048	0.1154	0.1344
353.55	1.748	0.7868	0.1961	0.0171	0.9612	0.0346	0.0042	0.1444	0.2010
353.45	1.855	0.8357	0.1541	0.0102	0.9672	0.0292	0.0036	0.1637	0.3050
353.55	1.920	0.8637	0.1260	0.0103	0.9712	0.0256	0.0032	0.1807	0.2763
353.65	1.970	0.8852	0.1067	0.0081	0.9741	0.0229	0.0030	0.1950	0.3366
353.35	2.023	0.9114	0.0821	0.0065	0.9789	0.0186	0.0025	0.2109	0.3581
373.55	0.633	0.1261	0.7948	0.0791	0.6740	0.3007	0.0253	0.0708	0.0598
373.45	0.912	0.2153	0.7148	0.0699	0.7702	0.2119	0.0179	0.0829	0.0716
373.95	1.377	0.3690	0.5171	0.0539	0.8444	0.1431	0.0125	0.1084	0.1013
373.85	1.645	0.4612	0.4920	0.0468	0.8702	0.1187	0.0111	0.1279	0.1257
373.55	2.073	0.6212	0.3466	0.0322	0.9025	0.0883	0.0920	0.1754	0.1967
373.55	2.247	0.6824	0.2912	0.0264	0.9131	0.0785	0.0084	0.2015	0.2378
373.65	2.413	0.7394	0.2396	0.0210	0.9231	0.0691	0.0078	0.2310	0.2975
373.55	2.541	0.7883	0.1945	0.0172	0.9325	0.0603	0.0072	0.2621	0.3539

[a] $\alpha_{21} \equiv$ relative volatility of ethanol with respect to DME.

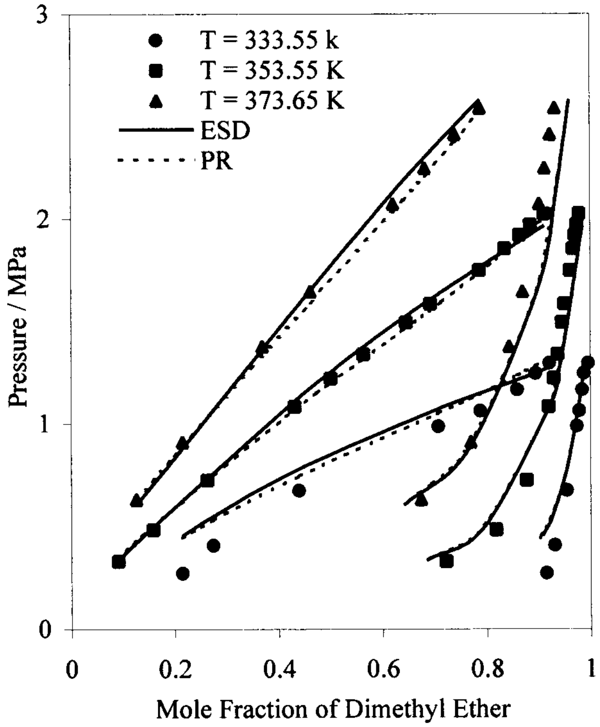

Figure 3. $P-T-x$ diagram of the DME (1) + ethanol (2) + water (3) system: (●, ■, ▲) this work.

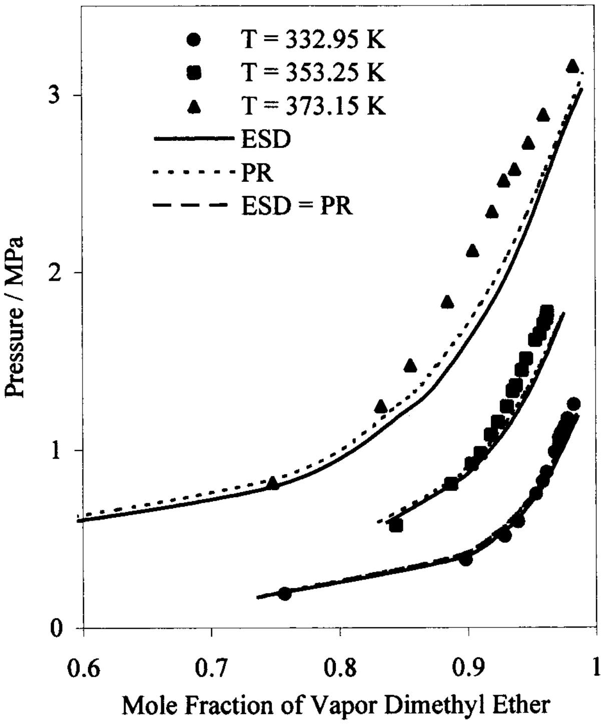

Figure 4. Pressure versus vapor mole fraction of DME for the DME (1) + ethanol (2) system: (●, ■, ▲) this work. ESD = PR only for the 332.95 K isotherm. From the graph it is difficult to distinguish the ESD = PR line from the PR line.

withdrawing five samples from each phase was less than 0.69 kPa.

The calibration methods for dimethyl ether, ethanol, and water were similar to the methods described in our previous paper. The average deviations in each of the dimethyl ether, ethanol, and water calibrations were within 0.3%, 4%, and 3%, respectively. Those percentages were based on the error between the correlated number of moles and the experimental number of moles. Every composition point in the calibrated curves was a result of averaging five samples together. The data were fit with quadratic equations for which the y-intercepts were set equal to zero. The density of dimethyl ether, used for the dimethyl ether calibration, was obtained from the Lee−Kesler equation of state. The accuracy of the Lee−Kesler equation of state was checked by comparing its dimethyl ether vapor pres-

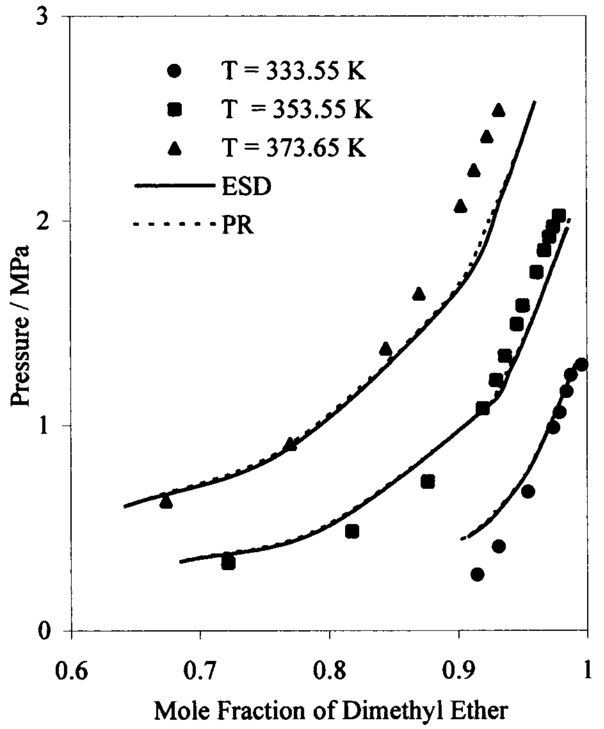

Figure 5. Pressure versus vapor mole fraction of DME for the DME (1) + ethanol (2) + water (3) system: (●, ■, ▲) this work.

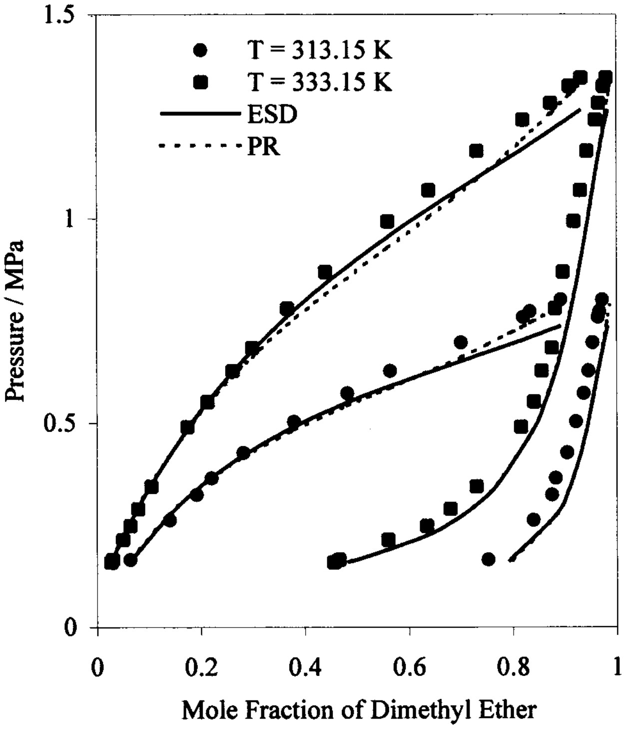

Figure 6. $P-T-x$ diagram of the DME (1) + methanol (2) system: (●, ■) Chang et al. (1982).

sure between (130 and 400) K to that of the AIChE DIPPR correlation, and an average error of 2% was found.

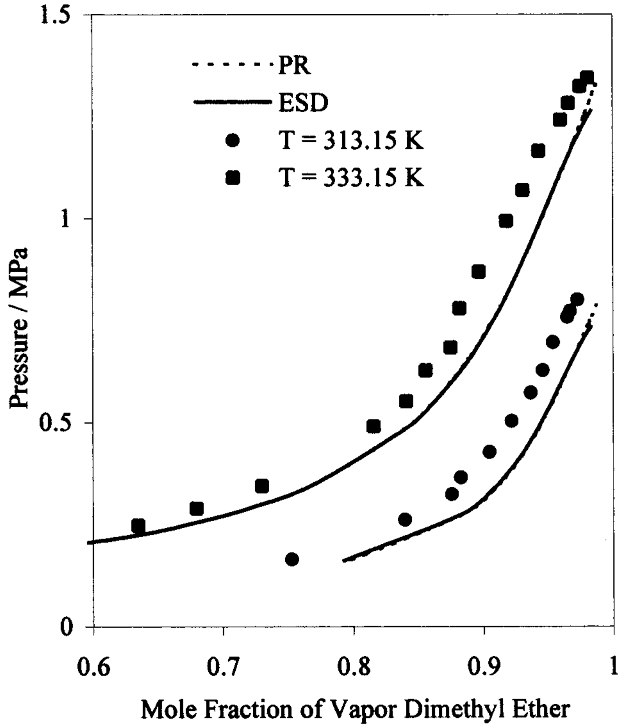

Figure 7. Pressure versus vapor mole fraction for the DME (1) + methanol (2) system: (●, ■) Chang et al. (1982).

Chemicals

Dimethyl ether of purity 99.95% was obtained from Praxair Corporation. Absolute ethanol (200 proof) was obtained from Quantum Chemical Corporation. Distilled water was obtained from the chemistry department at the University of Akron. All chemicals were used without any further purification.

Results and Discussions

Vapor−liquid equilibrium data for dimethyl ether + ethanol at (332.95, 353.25, and 373.15) K are presented in Table 3, and isothermal vapor−liquid equilibria are plotted in Figure 2. Vapor−liquid equilibrium data for dimethyl ether + ethanol + water at (333.55, 353.55, and 373.65) K are presented in Table 4, and isothermal vaopr−liquid equilibria are plotted in Figure 3. The vapor mole fraction of dimethyl ether versus pressure for the binary and ternary systems on a scale from 0.60 to 1.0 is plotted in Figures 4 and 5, respectively.

In the VLE data reported by Wagner and Pavlicek (1994) for the system CO_2 + ethyl acetate at 323.25 K, both vapor and liquid mole fractions of CO_2 versus pressure are plotted on a scale from 0 to 1. When we plotted the vapor mole fraction versus pressure on a scale from 0.98 to 1.0 in., a degree scatter in their data was apparent. This problem can be due to an error in either the calibration method, the time of equilibration, or the method of sampling. Detailed discussions of these factors were presented in our previous paper (Elbaccouch et al., 2000).

Table 5. k_{ij} Binary Interactions

system	k_{ij}° ESD	k_{ij}^{T} ESD	k_{ij}° PR	k_{ij}^{T} PR	%PAAD[a]	%PAAD
DME + ethanol	−0.2958	99.4852	−0.1886	63.492	2.25	1.61
DME + methanol	−0.1158	47.9076	−0.0024	1.6832	3.59	3.53
ethanol + H_2O	0.1497	0.0773	0.0130	−35.6733	2.01	4.12
DME + H_2O	0.1737	−49.3047	0.0859	−115.968	6.24	15.48

[a] %PAAD ≡ percent pressure average absolute deviation.

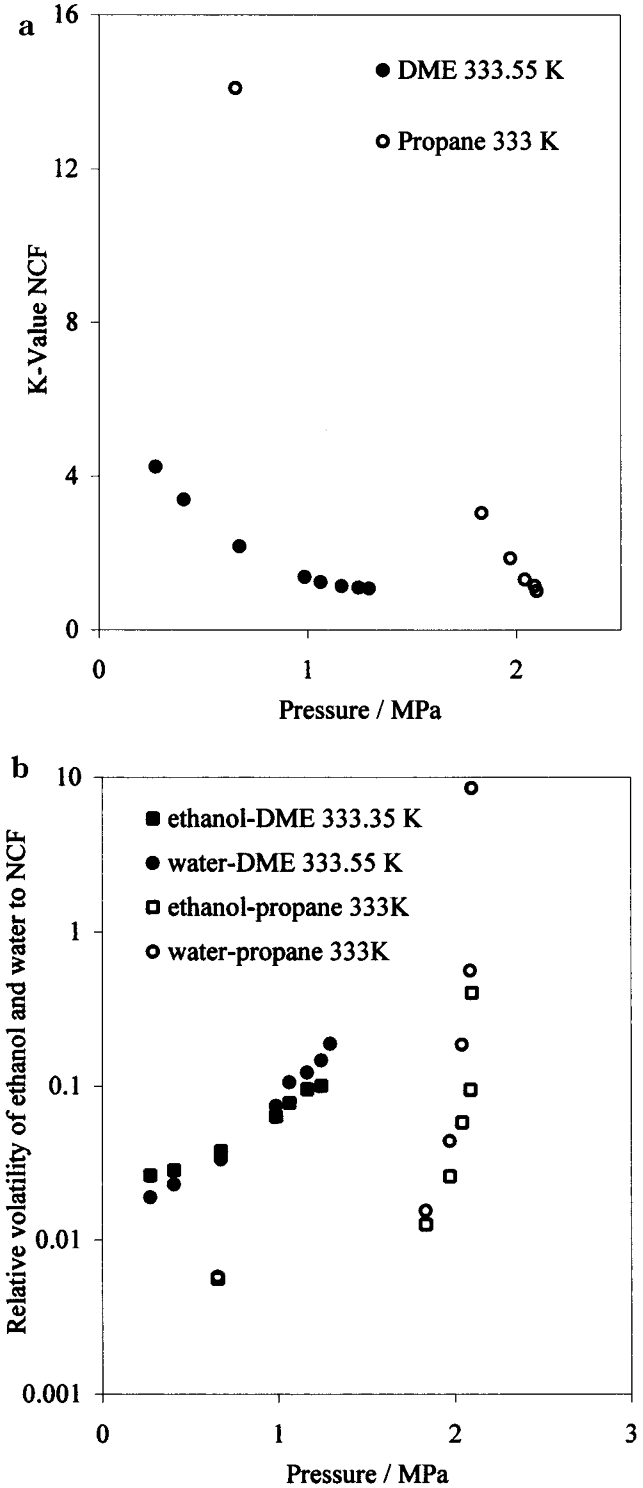

Figure 8. (a) K values of DME in the DME + ethanol + water system at 333.55 K and of propane in the propane + ethanol + water system at 333 K in 95.6% ethanol by weight on a solvent free-basis: ○, Horizoe et al. (1993); ●, this work. (b) Relative volatilities of ethanol and water with respect to DME at 333.55 K and of propane at 333 K in 95.6% ethanol by weight on a solvent free-basis: O and □, Horizoe et al. (1993); ● and ■, this work.

The experimental data were correlated using the Peng−Robinson equation of state (PR-EOS) (Peng and Robinson, 1976) and the Elliott−Suresh−Donohue equation of state (ESD-EOS) (Elliott et al., 1990; Suresh and Elliott, 1992). The ESD-EOS accounts for self-association and cross-association for systems with multiple associating species. Table 5 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 systems ethanol + water and dimethyl ether + water, which were used to model the ternary system, were obtained by regressing the experimental data reported by Gmehling et al. (1981) and Pozo and Streett (1984), respectively. A temperature-dependent function of the binary interaction parameter was used for the vapor−liquid equilibrium calculation. This function is given by $k_{ij} = k_{ij}^{\circ} + k_{ij}^{T}/T$. T is the temperature in Kelvin, and k_{ij}° and k_{ij}^{T} are constants characterizing the temperature dependence. For the systems dimethyl ether + ethanol, dimethyl ether + methanol (Chang et al., 1982), and dimethyl ether + water, the ESD-EOS was fit with a cross-association of hydrogen bonding equal to 6.65 kJ·mol^{-1}. For the ternary system dimethyl ether + ethanol + water, the cross-association between the dimethyl ether + ethanol system and the dimehtyl + water system was tuned to 6.65 kJ·mol^{-1}.

Note that the ESD-EOS should behave similarly to the PR-EOS when the solvating parameter of the dimethyl ether is not implemented. This is illustrated in Figure 2 for the isotherm 332.95 K. In Figures 2 and 3 the ESD-EOS with and without solvating and the PR-EOS agree well with our reported liquid mole fractions of dimethyl ether but deviate from our measured vapor mole fractions of dimethyl ether. A similar trend is shown in Figures 6 and 7 in the vapor mole fraction of dimethyl ether for the system dimethyl ether + methanol at 313.15 and 333.15 K reported by Chang et al. (1982). In Figures 6 and 7, the ESD-EOS and PR-EOS agree well with the liquid mole fraction of dimethyl ether and deviate from the vapor mole fraction of dimethyl ether.

The relative volatility of water and ethanol with respect to dimethyl ether as a near critical fluid (NCF) is reported in Table 4. Comparisons of the K value and the relative volatility between these data and the data for propane of Horizoe et al. (1993) for the isotherm 333.5 K are shown in parts a and b of Figure 8, respectively. Also, comparisons between the K value and the relative volatility between our dimethyl ether ternary data and chlorodifluoromethane ternary data for the isotherms (353.55 and 373.65) K are shown in parts a−c of Figure 9, respectively.

In Figure 8a, the K value for dimethyl ether is lower than the K value for propane because propane has a higher vapor pressure than dimethyl ether and the polar nature of dimethyl ether makes it more compatible than propane with water. A similar result can be observed in Figure 9a, where the K value for dimethyl ether is lower than the K value for chlorodifluoromethane, but we must note that chlorodifluoromethane has a higher vapor pressure than dimethyl ether. As a crude measure of compatibility for a given solvent, we can define a "pseudo" activity coefficient by $\gamma_i = K_i P / P_i^{\mathrm{sat}}$. Considering the data at $P \approx 1.9$ MPa and $T \approx 372$ K, $\gamma_{\mathrm{R-22}} \approx 1.06$ while $\gamma_{\mathrm{DME}} \approx 1.23$. By this measure, chlorodifluoromethane is more compatible with ethanol and water than dimethyl ether is. On the other hand, the higher vapor pressure of chlorodifluoromethane means that a higher pressure is necessary to achieve the same volatility enhancement of the ethanol and water that can be achieved with dimethyl ether at a given pressure.

With regard to the dehydration of ethanol solutions, Figures 8b, 9b, and 9c provide several valuable insights. For example, the water and ethanol volatilities are higher with dimethyl ether than with propane or chlorodifluoromethane at all the conditions that we studied, seeming to favor dimethyl ether. On the other hand, the relative

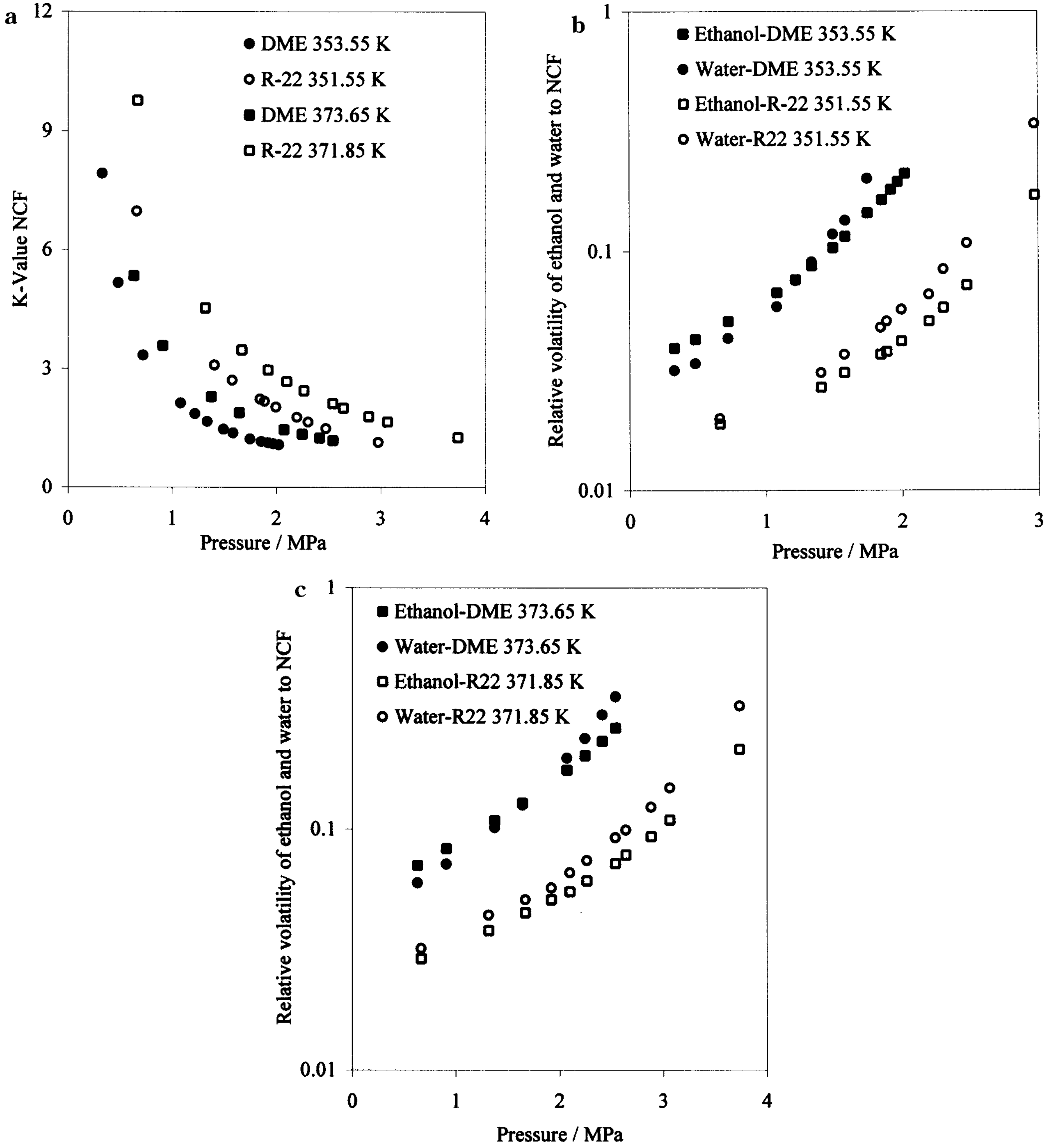

Figure 9. (a) *K* values of DME in the DME + ethanol + water system at 353.55 and 373.65 K and of R-22 in R-22 + the ethanol + water system at 351.55 and 371.85 K in 95.6% ethanol by weight on a solvent free-basis: ○ and □, Elbaccouch et al. (2000); ● and ■, this work. (b) Relative volatilities of ethanol and water with respect to DME at 353.55 K and of R-22 at 351.55 K in 95.6% ethanol by weight on a solvent free-basis: ○ and □, Elbaccouch et al. (2000); ● and ■, this work. (c) Relative volatilities of ethanol and water with respect to DME at 373.65 K and of R-22 at 371.85 K in 95.6% ethanol by weight on a solvent free-basis: ○ and □, Elbaccouch et al. (2000); ● and ■, this work.

volatility of water to dimethyl ether was always less than unity, making dimethyl ether infeasible for dehydration. It might be conjectured that further raising the pressure would promote water volatilities greater than unity, but pressures higher than those reported here led to single phases as all of the NCF solvent was dissolved. Recognizing this leads to the important insight that the propane solvent works by generating a different type of solvent-rich phase at high pressures. The high-pressure propane system is more like a liquid−liquid equilibrium, whereas the dimethyl ether and chlorodifluoromethane systems always exhibit vapor−liquid equilibrium, owing to their greater compatibility with polar components. In this context, liquid instability seems to be an essential aspect of the NCF dehydration process. Hence, it is unfortunate that dimethyl ether fails to exhibit liquid instability at high pressures. This observation suggests exploring compositions richer in water to see if a second liquid phase could be formed and whether the liquid−liquid partitioning in dimethyl ether might be more favorable than that in propane.

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