Azeotropic Behavior in the System Methanol + Methyl 1,1-Dimethylethyl Ether

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Vapor−liquid equilibrium for the binary system methanol + methyl 1,1-dimethylethyl ether has been measured at 50, 78.4, and 94 kPa. The system presents a minimum boiling point azeotrope that is enriched in the ether when the pressure decreases. The activity coefficients and boiling points of the solutions were correlated with its composition by the Wohl, Wilson, UNIQUAC, NRTL, and Wisniak−Tamir equations.

Introduction

Environmental legislation around the world has forced the use of oxygenates for gasoline blending to phase out the lead additives and to reduce the reactive evaporative and exhaust emissions. The U.S. Clean Air Act Amendments of 1990 set forth the basic guidelines for future transportation fuel composition and require the manufacture of oxygenated and reformulated gasolines. Methyl 1,1-dimethylethyl ether (MTBE) is the primary oxygenated compound being used to reformulate gasolines to improve their octane rating and pollution-reducing capability.

MTBE is produced by the reaction of methanol with isobutylene in the liquid phase over a strongly acidic ion-exchange resin catalyst. Excess concentration of methanol up to about 20% of the stoichiometric amount are generally used to achieve high conversions (Chase, 1984). The use of excess methanol, however, causes a purification problem because methanol forms a minimum-boiling azeotrope with MTBE at an approximate composition of 14 wt % methanol at 760 mmHg. The conventional separation process (Bitar et al., 1984) is both capital and energy intensive. Pervaporation has been considered as an alternative separation technique (Farnand and Noh, 1989; Park et al., 1995). The possibility of a hybrid distillation-pervaporation process, in which pervaporation is used only in a limited area of separation such as for breaking the azeotrope, can be demonstrated by the total recovery improvement for MTBE (TRIM) process which has been developed by Air Products & Chemicals using cellulose acetate membranes (Chen et al., 1989).

Another potential technique for separation of MTBE from methanol is distillation at pressures other than atmospheric, to enrich the azeotrope in one of the components. Hence, it is of interest to consider the distillation behavior of the reactor effluent (MTBE with excess methanol) under different pressures in order to obtain a richer azeotropic mixture in one of the components. Vapor−liquid equilibrium (VLE) for the binary system methanol + MTBE has been measured by Churkin et al. (1979), Aim and Ciprian (1980), Zong et al. (1987), and Arce et al. (1996) at 101.33 kPa, by Acosta et al. (1980) at 78.4 kPa, and by Wang et al. (1989) at 0.5 MPa and 1 MPa. Isothermal VLE data for the system has been determined by Yu et al. (1984) at 313 K, by Mullins et al. (1989) at 303 K, 313 K, and 323 K, by Park and Lee (1995) at 313 K, by Farkova et al. (1995) at 315 K and 325 K, by Fischer et al. (1996) at 363 K, and by Coto et al. (1996) at six temperatures between 298 K and 338 K. Toghiani et al. (1996) have reported isobaric data at 53.33 kPa and 101.33 kPa and isothermal data at 313 K and 333 K. Gmehling et al. (1995) determined experimental azeotropic data for the MTBE−methanol system at different conditions. VLE data and infinite dilution activity coefficients have been measured by Lee et al. (1994, 1995) at 318.15 K and 338.15 K using headspace gas chromatography. Activity coefficients of the system at 298.15 K and 1 atm were measured by Gao et al. (1986) using headspace gas chromatography. The activity coefficients at infinite dilution of the binary system have measured by Pividal et al. (1992) at 288.15 K and by Delcros et al. (1995) at 323.15 K. The literature also contains VLE measurements for MTBE + methanol mixtures subject to the salt effect (Velasco et al., 1992); the results show that addition of salt has a favorable effect on the separation of the mixture components.

The present work was undertaken to measure VLE data for the title system at 94 kPa, 78.4 kPa, and 50 kPa, for which isobaric data are not available or are incomplete, as well as to study the mobility of the azeotropic composition with the pressure and temperature.

Experimental Section

Materials. MTBE (99.8 mass %, HPLC grade) and methanol (99.9+ mass %, HPLC grade) were purchased from Aldrich and used without further purification, after gas chromatography failed to show any significant impurities. The properties and purity (as determined by GLC) of the pure components appear in Table 1. Appropriate precautions were taken when handling MTBE in order to avoid peroxide formation.

Apparatus and Procedure. An all glass vapor−liquid equilibrium apparatus model 602, manufactured by Fischer Labor und Verfahrenstechnik was used in the equilibrium determinations. General details of the experimental equipment and procedure appear in another publication (Wisniak et al., 1997). The equilibrium temperature was

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Table 1. Purities (mass %), Densities *d*, Refractive Index n_D, and Normal Boiling Points T_b of Pure Components

component (purity/mass %)	d(298.15 K)/(g·cm^{-3})		n_D (298.15 K)		T_b (101.3 kPa)/K	
	exptl[a]	lit.	exptl[a]	lit.	exptl[a]	lit.
methanol (99.9+)	0.787 32	0.787 30[b]	1.3270	1.3267[b]	337.84	337.65[b]
MTBE (99.8)	0.735 20	0.735 28[c]	1.3664	1.3663[d]	327.83	327.83[e]

[a] Measured. [b] *TRC Tables*, a-5030. [c] Daubert and Danner (1989). [d] *TRC Tables*, a-6040. [e] Reich et al. (1998).

Table 2. Experimental Vapor−Liquid Equilibrium Data for Methanol (1) + MTBE (2) at 50 kPa

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$/(cm^3·mol^{-1})	$-B_{22}$/(cm^3·mol^{-1})	$-B_{12}$/(cm^3·mol^{-1})
307.47	0.0386	0.0670	3.2844	0.9934	2258	1290	862
307.04	0.0696	0.1047	2.8935	1.0016	2281	1295	865
306.71	0.1073	0.1474	2.6792	1.0069	2299	1298	867
306.53	0.1293	0.1660	2.5235	1.0170	2308	1301	868
306.34	0.1788	0.2070	2.2902	1.0334	2318	1303	870
306.33	0.2160	0.2296	2.1004	1.0525	2319	1303	870
306.30	0.2501	0.2498	1.9743	1.0731	2321	1303	870
306.33	0.2980	0.2734	1.8088	1.1095	2319	1303	870
306.35	0.3330	0.2903	1.7157	1.1400	2318	1303	869
306.42	0.3604	0.3035	1.6511	1.1638	2314	1302	869
306.67	0.4276	0.3272	1.4801	1.2451	2301	1299	867
306.97	0.4846	0.3553	1.3965	1.3107	2285	1296	865
307.49	0.5589	0.3835	1.2730	1.4370	2257	1290	862
307.79	0.5941	0.3993	1.2284	1.5051	2242	1286	859
307.97	0.6154	0.4151	1.2217	1.5366	2232	1284	858
308.85	0.6857	0.4533	1.1469	1.7020	2188	1274	852
309.62	0.7380	0.4853	1.0990	1.8698	2150	1266	847
310.61	0.7715	0.5163	1.0671	1.9432	2102	1255	840
311.37	0.8108	0.5662	1.0733	2.0507	2066	1247	835
313.35	0.8742	0.6356	1.0191	2.4154	1977	1226	823
314.19	0.9024	0.6847	1.0228	2.6178	1941	1217	817
315.85	0.9349	0.7572	1.0125	2.8551	1872	1200	807
316.84	0.9484	0.7964	1.0043	2.9176	1833	1190	801
317.77	0.9649	0.8453	1.0051	3.1609	1797	1181	795

Table 3. Experimental Vapor−Liquid Equilibrium Data for Methanol (1) + MTBE (2) at 78.4 KPa

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$/(cm^3·mol^{-1})	$-B_{22}$/(cm^3·mol^{-1})	$-B_{12}$/(cm^3·mol^{-1})
319.67	0.0289	0.0607	3.5258	0.9887	1726	1163	783
318.97	0.0620	0.1129	3.1447	0.9904	1751	1169	788
318.33	0.1082	0.1673	2.7357	1.0003	1775	1176	792
317.93	0.1582	0.2083	2.3660	1.0221	1790	1179	794
317.74	0.1940	0.2377	2.2157	1.0352	1798	1181	795
317.61	0.2401	0.2627	1.9874	1.0673	1803	1183	796
317.59	0.2695	0.2801	1.8867	1.0854	1804	1183	796
317.62	0.3089	0.3017	1.7694	1.1120	1802	1183	796
317.63	0.3568	0.3249	1.6465	1.1555	1802	1182	796
317.71	0.4045	0.3483	1.5495	1.2022	1799	1182	795
317.87	0.4540	0.3677	1.4455	1.2660	1793	1180	794
318.02	0.5019	0.3864	1.3640	1.3403	1787	1179	793
318.24	0.5453	0.4055	1.3038	1.4124	1779	1176	792
318.53	0.5865	0.4255	1.2547	1.4870	1768	1174	790
319.26	0.6650	0.4583	1.1530	1.6896	1741	1167	786
320.22	0.7205	0.5011	1.1146	1.8072	1706	1157	780
320.95	0.7695	0.5362	1.0808	1.9906	1680	1150	776
321.86	0.8104	0.5732	1.0542	2.1626	1649	1142	771
323.21	0.8642	0.6367	1.0355	2.4627	1604	1130	763
325.49	0.9263	0.7475	1.0293	2.9373	1532	1109	750
328.10	0.9687	0.8695	1.0277	3.2979	1454	1086	736
329.64	0.9853	0.9381	1.0241	3.1910	1411	1073	728

Table 4. Experimental Vapor−Liquid Equilibrium Data for Methanol (1) + MTBE (2) at 94 KPa

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$/(cm^3·mol^{-1})	$-B_{22}$/(cm^3·mol^{-1})	$-B_{12}$/(cm^3·mol^{-1})
324.83	0.0223	0.0584	4.2099	0.9874	1552	1115	754
324.27	0.0461	0.1020	3.6384	0.9832	1570	1120	757
323.32	0.0950	0.1638	2.9365	0.9963	1600	1129	762
322.99	0.1358	0.2033	2.5795	1.0055	1611	1132	764
322.67	0.1915	0.2468	2.2446	1.0278	1622	1134	766
322.49	0.2523	0.2840	1.9706	1.0638	1628	1136	767
322.48	0.2695	0.2937	1.9072	1.0747	1628	1136	767
322.45	0.2847	0.3005	1.8488	1.0883	1629	1136	767
322.48	0.3037	0.3121	1.7970	1.0986	1628	1136	767
322.54	0.3351	0.3252	1.6911	1.1268	1626	1136	767
322.58	0.4141	0.3614	1.5152	1.2098	1625	1135	767
322.74	0.5058	0.3999	1.3607	1.3422	1619	1134	766
322.83	0.5185	0.4036	1.3344	1.3652	1616	1133	765
323.01	0.5720	0.4281	1.2717	1.4652	1611	1131	764
323.63	0.6169	0.4495	1.2051	1.5448	1590	1126	761
323.88	0.6926	0.4849	1.1440	1.7892	1582	1123	759
325.28	0.7547	0.5195	1.0599	2.0001	1538	1111	751
325.66	0.7854	0.5354	1.0328	2.1841	1526	1107	749
327.18	0.8501	0.6002	1.0031	2.5674	1481	1094	741
329.23	0.9076	0.6870	0.9877	3.0674	1423	1077	730
329.60	0.9176	0.7072	0.9905	3.1819	1412	1073	728
332.09	0.9634	0.8371	1.0100	3.7105	1346	1053	715

measured with an accuracy of 0.02 K using a Lauda thermometer, model R42/2, provided with a 4 mm diameter Pt-100 temperature sensor. The total pressure of the system was controlled by a vacuum pump capable of working at pressures down to 0.25 kPa. The pressure was measured by a Vac Probs pressure transducer with an accuracy of 0.07 kPa; a 5 L Erlenmeyer flask connected between the separating chamber and the Vac Probs dampens the pressure variations to no more than 0.01 kPa. The overall accuracy of the pressure is ±0.1 kPa. On the average the system reached equilibrium conditions after 60 min operation. Samples, taken by syringing 1.0 μL after the system had achieved equilibrium, were analyzed by gas chromatography on a Gow-Mac series 550P apparatus provided with a thermal conductivity detector and a Spectra Physics model SP 4290 electronic integrator. The column was 3 m long and 0.2 cm in diameter, packed with SE-30. Column, injector, and detector temperatures were 348.15 K, 493.15 K, and 543.15 K. Very good separation was achieved under these conditions, and calibration analyses were carried out to convert the peak ratio to the mass composition of the sample. The pertinent polynomial fit had a correlation coefficient R^2 better than 0.99. Concentration measurements were accurate to better than ±0.001 mole fraction.

Results

The temperature T and liquid-phase x_i and vapor-phase y_i mole fraction at 50 kPa, 78.4 kPa, and 94 kPa are reported in Tables 2−4, and in Figure 1 for the system methanol (1) + MTBE (2) at 78.4 kPa. In this figure appear the experimental data obtained together with the data of Acosta et al. (1980); we can observe the scarce experimental information in their work. The activity coefficients γ_i were calculated from the following equation (Van Ness and Abbott, 1982):

$$\ln \gamma_i = \ln\left(\frac{y_i P}{x_i P_i^{\,0}}\right) + \frac{(B_{ii} - V_i^{\mathrm{L}})(P - P_i^{\,0})}{RT} + y_j^{\,2}\,\frac{\delta_{ij}P}{RT} \quad (1)$$

where T and P are the boiling point and the total pressure, V_i^{L} is the molar liquid volume of component i, B_{ii} and B_{jj}

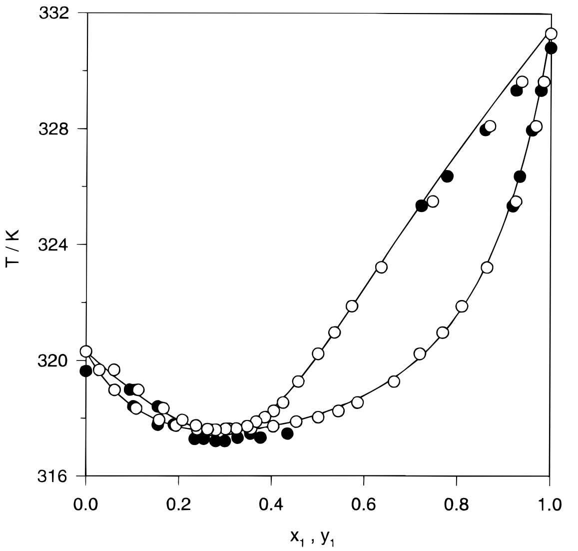

Figure 1. Boiling temperature diagram for the system methanol (1) + MTBE (2) at 78.4 kPa: experimental data (filled circle); experimental data of Acosta et al. (open circle); smoothed with the Wilson model (line).

Table 5. Antoine Coefficients, Equation 3

compound	A_i	B_i	C_i
methanol[a]	7.8975	1474.08	229.13
MTBE[b]	6.7359	1032.99	213.27

[a] *TRC Tables*, a-5030. [b] Reich et al. (1998)

are the second virial coefficients of the pure gases, B_{ij} the cross second virial coefficient, and

$$d_{ij} = 2B_{ij} - B_{jj} - B_{ii} \tag{2}$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Equation 1 is valid at low and moderate pressures when the virial equation of state truncated after the second coefficient is adequate to describing the vapor phase of the pure components and their mixtures, and liquid volumes of the pure components are incompressible over the pressure range under consideration. The molar virial coefficients B_{ii} and B_{ij} were estimated by the method of Hayden and O'Connell (1975) using the molecular parameters suggested by Prausnitz et al. (1980). Critical properties of all components were taken from DIPPR (Daubert and Danner, 1989) The last two terms in eq 1., particularly the second one that expresses the correction due to the nonideal behavior of the vapor phase, contributed less than 3% to the activity coefficients. The vapor pressures of the pure compounds $P_i°$ were expressed by the Antoine equation:

$$\log(P_i°/\text{mmHg}) = A_i - \frac{B_i}{(T/°\text{C}) + C_i} \tag{3}$$

The constants A_i, B_i, and C_i were taken from the literature, *TRC Tables* (1974) for methanol and Reich et al. (1998) for MTBE; the values are reported in Table 5. The calculated activity coefficients reported in Tables 2−4 are estimated accurate to within ±3%. The results reported in these tables indicate that the measured system exhibits positive deviations from ideal behavior and presents a minimum boiling azeotrope at the three pressures. The experimental azeotropic points are summarized in Table 6 along with a comparison with literature values. Azeotropic compositions were obtained, in all cases, by determining the x_1 values that make zero the best polynomial fit of the function $(x_1 - y_1) = f(x_1)$. Azeotropic temperatures or pressures have been obtained from the best polynomial fit for $T = f(x_1)$ or for $P = f(x_1)$, using the x_1 values previously determined.

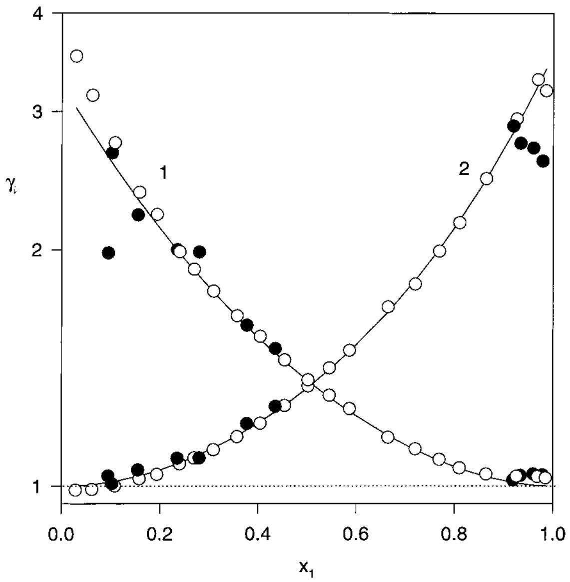

Figure 2. Activity coefficient plot for the system methanol (1) + MTBE (2) at 78.4 kPa: experimental data (filled circle); data from Acosta et al. (open circle); smoothed with the Wilson model (line).

Table 6. Azeotropic Points for MTBE (1) + Methanol (2)

x_1	T/K	P/kPa	ref
0.7994	296.15	32.84	Gmehling et al., 1995
0.804	298.15	35.27	Velasco et al., 1992
0.795	298.15	36.00	Coto et al., 1996
0.7865	300.15	39.36	Gmehling et al., 1995
0.770	303.15	43.75	Mullins et al., 1989
0.776	303.15	44.53	Coto et al., 1996
0.755	306.49	50.00	this work
0.769	307.64	53.33	Toghiani et al., 1996
0.759	308.15	54.48	Coto et al., 1996
0.750	313.15	64.36	Park and Lee, 1995
0.738	313.15	65.69	Mullins et al., 1989
0.757	313.15	66.27	Toghiani et al., 1996
0.7341	313.15	66.57	Gmehling et al., 1995
0.726	315.00	71.11	Farkova et al., 1995
0.749	317.49	74.37	Gao et al., 1986
0.788	317.55	74.37	Yu et al., 1984
0.692	317.20	78.40	Acosta et al., 1980
0.711	317.58	78.40	this work
0.727	318.15	79.63	Lee et al., 1994
0.717	318.15	80.26	Coto et al., 1996
0.686	322.48	94.00	this work
0.732	323.15	95.52	Mullins et al., 1989
0.678	324.91	100.00	Zong et al., 1987
0.6994	323.95	100.50	Gmehling et al., 1995
0.700	324.75	101.32	Churkin et al., 1979
0.688	324.39	101.32	Aim and Ciprian, 1980
0.688	324.33	101.32	Gao et al., 1986
0.694	324.32	101.32	Arce et al., 1996
0.703	324.39	101.33	Toghiani et al., 1996
0.695	325.00	103.15	Farkova et al., 1995
0.681	328.15	115.85	Coto et al., 1996
0.662	333.15	138.09	Toghiani et al., 1996
0.637	338.15	162.23	Coto et al., 1996
0.639	338.15	164.40	Lee et al., 1994
0.458	363.54	354.60	Fischer et al., 1996
0.496	374.93	500.00	Wang et al., 1989
0.412	403.42	1000.00	Wang et al., 1989

Table 7. Consistency Test for the System Methanol (1) + MTBE (2) at 50 kPa, 78.4 kPa, and 94 KPa

pressure/kPa	A^a	100AAD $(y_1)^b$	AAD$(P)^c$/kPa
50.0	1.172	0.59	0.25
78.4	1.229	0.54	0.91
94.0	1.229	0.96	1.12

[a] Zero order Legendre polynomial (or Porter model) parameter in equation 4. [b] Average absolute deviation in vapor phase composition. [c] Average absolute deviation in pressure.

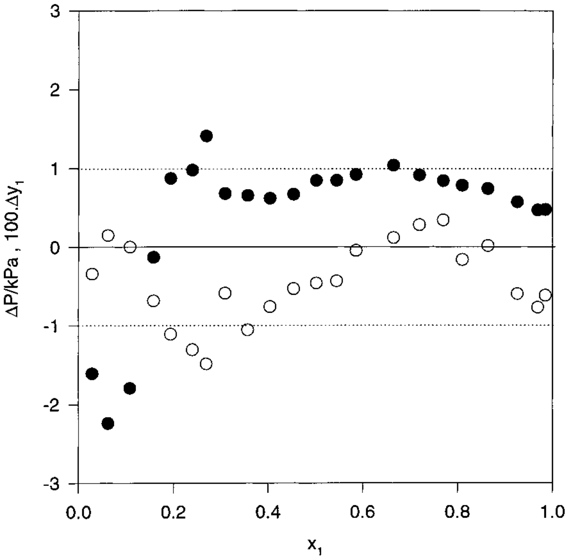

Figure 3. Consistency residuals plot for the system methanol (1) + MTBE (2) at 78.4 kPa: ΔP/kPa (filled circle); $100\Delta y_1$ (open circle).

The vapor−liquid equilibria data reported in Tables 2−4 were found to be thermodynamically consistent by the point-to-point method of Van Ness et al. (1973) as modified by Fredenslund et al. (1977). Consistency criteria ($\Delta y \leq 10^{-2}$) were met using a zero-order Legendre polynomial, which is equivalent to the symmetric regular solution model given by

$$G^E/RT = Ax_1x_2 \tag{4}$$

The variation of activity coefficients with composition appears in Figure 2 for the system at 78.4 kPa, together with the values from Acosta et al. (1980). This figure shows a symmetric behavior of the activity coefficients with an intersection around the composition $x_1 = 0.5$. Thus the activity coefficients are reasonably represented by eq 4.

The pertinent consistency statistics together with the parameter A in eq 4 are shown in Table 7. Residuals of the Fredenslund test are represented in Figure 3 for the system at 78.4 kPa. The activity coefficients were correlated with the Wohl, Wilson, NRTL, and UNIQUAC equations (Walas, 1985). The parameters of these equations were obtained by minimizing the following objective function (OF)

$$OF = \sum_{i=1}^{N} 100\left(\left|\frac{P_i^{\text{exptl}} - P_i^{\text{calcd}}}{P_i^{\text{exptl}}}\right| + \left|y_i^{\text{exptl}} - y_i^{\text{calcd}}\right|\right) \tag{5}$$

and are reported in Table 8, together with the pertinent statistics of VLE interpolation. Inspection of the results given in Table 8 shows that all the models fitted well the methanol + MTBE system, the best fit corresponding to the Wilson model.

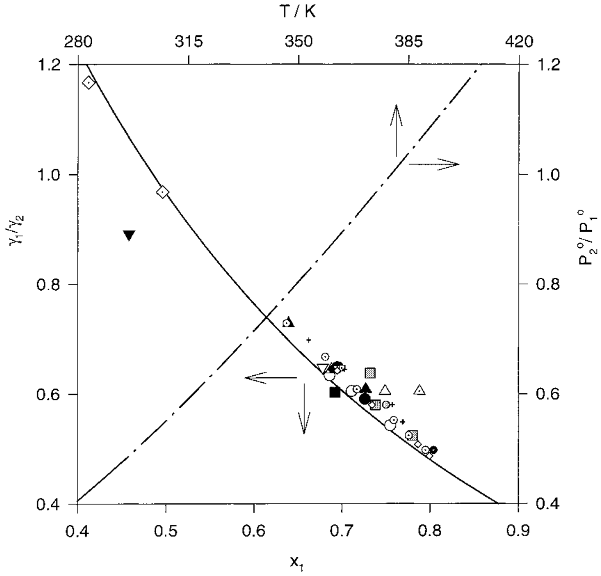

Figure 4. Activity coefficient and vapor pressure ratios vs composition and temperature. This work (open circle); Farkova et al. (filled circle); Gao et al. (open triangle, pointed up); Lee et al. (filled triangle, pointed up); Wang et al. (dotted diamond); Zong et al. (open triangle, pointed down); Arce et al. (open square); Aim and Ciprian (filled diamond); Acosta et al. (filled square); Churkin et al. (dotted square); Mullins et al. (shaded square); Yu et al. (dotted triangle); Gmehling et al. (open diamond); Fischer et al. (filled triangle, pointed down); Coto et al. (dotted circle); Velasco et al. (dotted circle); Toghiani et al. (plus); Park and Lee (shaded circle); Wilson model (solid line); Antoine equations (dotted−dashed line).

We can follow a simple procedure to determine the variation of the azeotropic point with pressure and composition. If at low pressures the vapor phase is assumed to behave ideally, then the activity coefficients can be calculated from the following simplified relation:

$$\gamma_i = y_iP/x_iP_i^\circ \tag{6}$$

For a binary system at the azeotropic point we have

$$\gamma_1/\gamma_2 = P_2^\circ/P_1^\circ \tag{7}$$

The first term of eq 7 can be obtained from any activity coefficients model and the second one from the Antoine equation for each of the components. So, knowing the azeotropic temperature or pressure and the parameters of a model (for instance Wilson), it is possible to obtain the azeotropic composition. In Figure 4 are represented the curves $P_2^\circ/P_1^\circ = f(T)$, using the Antoine constants given in Table 5, and γ_1/γ_2, using the parameters of the Wilson model at 94 kPa given in Table 8. In Figure 5 appear azeotropic temperatures and pressures as a function of azeotropic compositions. In these figures component 1 is MTBE and component 2 is methanol. All the values in Table 6 are represented in both figures and show the dispersion of the information available in the literature. Some workers measured the liquid-phase composition and equilibrium temperature and calculated the vapor-phase composition (Churkin et al., 1979; Wang et al., 1989; Fischer et al., 1996; Coto et al., 1996). Gao et al. (1986) calculated VLE data at 74.37 kPa and 101.33 kPa from measured values of the activity coefficients at 298.15 K and 1 atm. Velasco et al. (1992) measured the liquid- and vapor-

Table 8. Parameters and Deviations between Experimental and Calculated Values for Different G^E Models

						bubble-point pressures		dew-point pressures	
model	pressure kPa	A_{ij}	A_{ji}	q_i/q_j	α_{ij}	ΔP^a/%	$100\Delta y^b$	ΔP^a/%	$100\Delta y^b$
Wohl	50.0	1.1579	1.1821	0.9229		0.56	0.55	0.62	0.74
	78.4	1.1528	1.2443	0.9229		0.53	0.41	0.52	0.46
	94.0	1.1657	1.3250	0.9229		0.96	0.79	1.19	0.81
Wilson[d]	50.0	4758.19[c]	−1117.82[c]			0.39	0.46	0.47	0.64
	78.4	4772.06[c]	−925.77[c]			0.51	0.36	0.58	0.42
	94.0	4843.70[c]	−687.62[c]			1.03	0.71	1.43	0.69
NRTL	50.0	1935.94[c]	1288.10[c]		0.2	0.54	0.49	0.52	0.60
	78.4	2410.05[c]	1036.14[c]		0.2	0.54	0.43	0.53	0.50
	94.0	2839.93[c]	852.48[c]		0.2	1.13	0.83	1.36	0.90
UNIQUAC[e]	50.0	−523.50[c]	3262.68[c]			0.55	0.50	0.57	0.65
	78.4	−471.30[c]	3297.00[c]			0.52	0.41	0.52	0.48
	94.0	−409.22[c]	3316.82[c]			1.05	0.80	1.31	0.83

[a] Average percentual deviation in bubble pressure $\Delta P = 100/N \sum_i^N |P_i^{\text{exptl}} - P_i^{\text{calcd}}|/P_i^{\text{exptl}}$ (N, number of data points). [b] Average absolute deviation in vapor phase composition. [c] Parameters in joules per mol^{-1}. [d] Liquid volumes have been estimated from the Rackett equation (Rackett, 1970). [e] Volume and surface parameters calculated from Prausnitz et al. (1980).

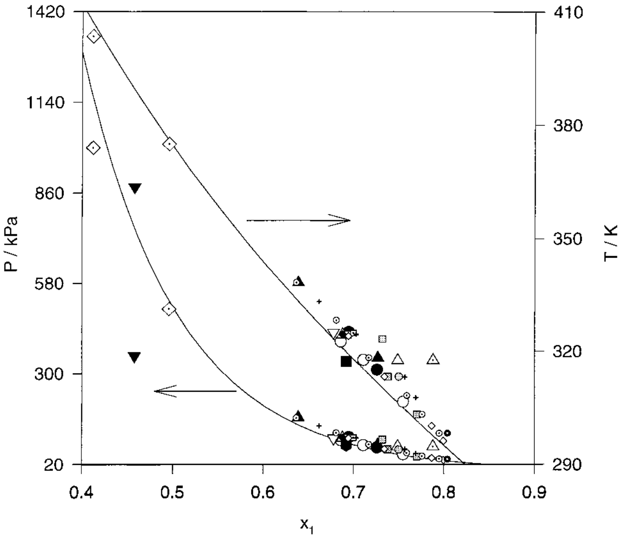

Figure 5. Azeotropic pressures and temperatures vs azeotropic compositions: this work (open circle); Farkova et al. (filled circle); Gao et al. (open triangle, pointed up); Lee et al. (filled triangle, pointed up); Wang et al. (dotted diamond); Zong et al. (open triangle, pointed down); Arce et al. (open square); Aim and Ciprian (filled diamond); Acosta et al. (filled square); Churkin et al. (dotted square); Mullins et al. (shaded square); Yu et al. (dotted triangle); Gmehling et al. (open diamond); Fischer et al. (filled triangle, pointed down); Coto et al. (dotted circle); Velasco et al. (dotted circle); Toghiani et al. (plus); Park and Lee (shaded circle); smoothed data using eq 7 (line).

phase compositions and calculated the values of the pressure. In all cases, the azeotropic points were determined in the way described before, using the variables reported as calculated values in the pertinent papers. In general, good agreement is observed between the calculated curve and the experimental points.

An alternative procedure for determining the azeotropic conditions is to use the fact that the solution behaves regularly. In this case we have

$$\ln \gamma_1 = A\, x_2^{\,2} \tag{8}$$

$$\ln \gamma_2 = A\, x_1^{\,2} \tag{9}$$

and, assuming ideal behavior for the vapor phase,

$$P = x_1 P_1^\circ \gamma_1 + x_2 P_2^\circ \gamma_2 \tag{10}$$

For the azeotropic point we have

Table 9. Azeotropic Compositions Obtained Using Equation 11 for the System MTBE (1) + Methanol (2) at 50 kPa, 78.4 kPa, and 94 kPa

pressure/ kPa	temp/ K	Azeotropic compositions (x_1)			
		exptl	$A = 1.229^a$	$A = 1.172^a$	$A = 1.210^b$
50.0	306.49	0.755	0.749	0.761	0.753
78.4	317.58	0.711	0.705	0.715	0.708
94.0	322.48	0.686	0.686	0.695	0.689

[a] Values of parameter *A* (regular model) in Table 7. [b] Average value of parameter *A* in Table 7.

Table 10. Coefficients in Correlation of Boiling Points, Equation 13, Average Deviation, and Root Mean Square Deviations in Temperature (rmsd)

pressure/ kPa	C_0	C_1	C_2	C_3	max dev^a/K	avg dev^b/K	rmsd^c/ K
50.0	−28.24	−9.60	−27.17	−17.77	0.43	0.20	0.051
78.4	−27.95	−3.14	−38.90	−33.60	1.01	0.43	0.113
94.0	−28.90	−9.37	−41.59	−18.98	0.90	0.40	0.101

[a] Maximum deviation. [b] Average deviation. [c] Root-mean-square deviation.

$$\mathrm{d}P/\mathrm{d}x_1 = [1 - 2x_1x_2A][P_1^\circ \exp(Ax_2^{\,2}) - P_2^\circ \exp(Ax_1^{\,2})] = 0 \tag{11}$$

From eq 11 it is possible to obtain azeotropic compositions for different azeotropic temperatures. The values of the azeotropic compositions obtained by this procedure are reported in Table 9, together with the experimental values, and again very good agreement is observed.

From Figure 5 we see that a decrease in the operating pressure causes an increase in the concentration of MTBE. According to Malesinski (1965),

$$\frac{\mathrm{d}x_2}{\mathrm{d}P} = \frac{\Delta\bar{V}_2\Delta\bar{H}_1 - \Delta\bar{V}_1\Delta\bar{H}_2}{x_1\Delta\bar{H}_1 + x_2\Delta\bar{H}_2}\left(\frac{\partial^2 G^E}{\partial x_2^{\,2}}\right)^{-1}_{T,P} \tag{12}$$

where $\Delta\bar{V}_i$ is the partial molar vaporization volume (i.e., $\bar{V}_i^V - V_i^L$), and $\Delta\bar{H}_i$ is the partial molar vaporization enthalpy (i.e., $\bar{H}_i^V - \bar{H}_i^L$), both positive quantities. For a minimum boling temperature azeotrope, if pressure rises, azeotrope becomes enriched in the component that has the largest vaporization enthalpy, which in this case is the methanol.

The boiling point of the solution was correlated with its composition by the equation proposed by Wisniak and Tamir (1976):

$$T/\mathrm{K} = x_1T_1^\circ + x_2T_2^\circ + x_1x_2\sum_{k=1}^{m}C_k(x_1 - x_2)^k \qquad (13)$$

In this equation T_i°/K is the boiling point of the pure component i and m is the number of terms in the series expansion of $(x_1 - x_2)$. The various constants of eq 13 are reported in Table 10, which also contains information indicating the degree of goodness of the correlation.

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