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Density of Methanol + Water between 250 K and 440 K and up to 40 MPa and Vapor−Liquid Equilibria from 363 K to 440 K

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The density of methanol + water has been measured between 257.3 K and 442.15 K as a function of pressure at five compositions by means of a high-pressure apparatus implementing a metal bellows as a simple cell. Bubble pressures have been determined at five temperatures between 363.15 K and 442.15 K. They are compared with literature data that have been correlated by using the "excess function-equation of state" model.

Introduction

A knowledge of the thermodynamic properties of the methanol + water system is very important in order to improve the prediction of phase equilibria. Numerous vapor-liquid equilibria, excess enthalpies, and excess volumes at atmospheric pressure have been measured at temperatures between 298.15 K and 333.15 K (McGlashan and Williamson, 1976; Benson and Kiyohara, 1980; Patel and Sandler, 1985). Few data exist above these temperatures and under pressure. Excess volumes have been reported by Easteal and Woolf (1985) between 278 K to 323 K at pressures to 280 MPa and recently by Xiao et al. (1997) between 323 K and 573 K at two pressures of 7 MPa and 13.5 MPa. On the other hand, vapor−liquid equilibria have been measured by Griswold and Wong (1952) at four temperatures between 373 K and 523 K, by Schroder (1958) at 413.15 K, and by Hirata and Suda (1967) and Hirata et al. (1975) at pressures of 0.3 MPa and 0.5 MPa.

In this work, densities are reported as a function of pressure for methanol + water over a wide range of temperature and composition. We have also determined bubble pressures at five temperatures between 373 K and 423 K.

Experimental Section

Materials. Methanol provided by Prolabo (Paris, France) had a stated minimum purity of 99%. It was purified by fractional distillation on a 60-plate Oldershaw type column and was controlled by gas-chromatographic analysis (purity > 99.90%). The main impurity was water (<0.10%). Water used was distilled twice.

Apparatus and Procedure. A schematic diagram of the apparatus is shown in Figure 1, and a more detailed description is given elsewhere (Hocq, 1994; Hocq et al., 1995).

The apparatus consists mainly of an equilibrium cell that includes a bellows and two sapphire windows for visual observation, a constant-temperature air bath, a high-pressure recirculation pump, a micrometric table, pressure and temperature transducers, and regulation and vacuum systems. Figure 2 shows a cross-sectional view of the metal bellows whose length varies from 8 cm to 32 cm.

Pressure is measured by using five Schenk extensiometric gauge pressure transducers (type P3MA) and controlled by a digital Heise gauge (model 901B) calibrated to NIST standards before use. The pressure measurements were estimated to be accurate to within ±0.01 MPa.

The temperature of the air bath is kept constant with an uncertainty of ±0.05 K by an electronic controller. The temperature was determined with three platinum resistance thermometers inserted into the cell with an estimated accuracy of ± 0.05 K.

The displacement bellows is detected by a magnetic core whose position is measured by means of a micrometric table. The bellows was calibrated by measuring the *PVT* properties of toluene and methanol at various temperatures between 240 K and 450 K in the range of pressures from 0.4 MPa to 64 MPa covering the bellows displacement from 8 cm to 32 cm, which corresponds to the volume variation from 30 cm^3 to 150 cm^3. Densities of methanol and toluene were calculated with the Goodwin (1987, 1989) equations of state. A calibration equation, established between the volume and the number of micrometric steps, reproduces data within 0.2%.

The first step in the experimental procedure is to introduce into the filling cell a known amount of the first component using a syringue. After degassing, the sample is transferred from the filling into the bellows by distillation using liquified nitrogen. The filling cell is weighed before and after sample transfer. The mass measurements were reproducible to within 0.0001 g. The second component was added using the same technique.

The rest of the operation was managed by a computer. It consisted of adjusting the working temperature and increasing the pressure up to 70 MPa, the micrometric table being initialized by moving to its mechanical zero. When the equilibrium state is reached in about 20 min, temperature, pressure, and bellows position were recorded. The volume of the mixture was calculated with the calibration equation. In the single-phase region, the measurements were carried out in intervals of pressure of 1.5 MPa for the given temperature. In the two-phase region, these

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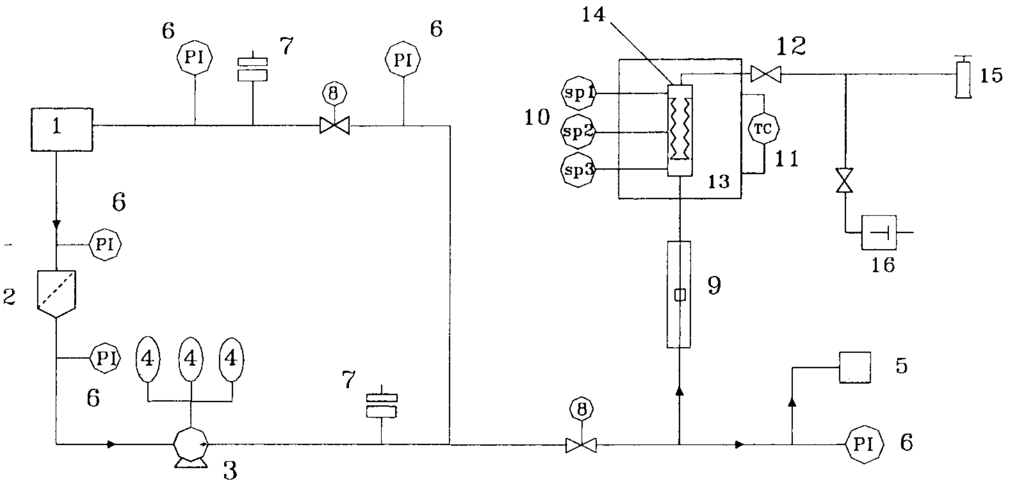

Figure 1. Schematic diagram of the experimental apparatus: (1) oil tank; (2) filter; (3) piston pump; (4) shock absorber; (5) pressure gauge “Heise”; (6) pressure gauges; (7) breaking disk; (8) regulation valves; (9) micrometric table; (10) platinum resistance thermometer; (11) thermic regulation; (12) product introduction valve; (13) climatic fence; (14) autoclave and bellows; (15) filling cell; (16) vacuum pump.

are carried out at given intervals of density in adjusting the number of micrometric steps. The experiment continues by decompressing the cell to the next pressure by opening and closing regulation valves (8). A measurement for a single isotherm took 1 day.

Experimental Results

Table 1 lists the density and pressure measurements of methanol (1) + water (2) for five compositions at nine temperatures ranging from 257.3 K to 442.15 K. For the mole fractions of methanol of 0.1061 and 0.2872, the *PVT* properties have not been measured along the isotherm of 257 K on account of the vicinity of melting points of methanol + water.

In Figure 3, the volume is plotted as a function of pressure at constant composition ($x_1 = 0.4980$). The bubble pressure corresponds to the intersection of the curves representing the one-phase and two-phase regions. The bubble pressure and composition data at five temperatures (from 363.15 K to 442.15 K) are presented in Table 2. We have not reported bubble pressures at lower temperatures since the values are too small.

Results and Discussion

It was difficult to compare directly our P, ρ, T data with those reported in the literature since they are few in number and are often outside the temperatures and pressures studied. Recently, Xiao et al. (1997) developed a modified corresponding-states model based on their measurements and available at temperatures between 323 K and 573 K and pressures between 7 MPa and 13.5 MPa. To evaluate our data, this model was used. The mean relative deviation and the mean relative bias between experimental and calculated densities defined by

$$\Delta\rho/\rho(\%) = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{\rho_{\mathrm{exp},i} - \rho_{\mathrm{cal},i}}{\rho_{\mathrm{exp},i}}\right| \tag{1}$$

$$\beta_{\mathrm{r}}(\rho) = \frac{100}{N}\sum_{i=1}^{N}\frac{\rho_{\mathrm{exp},i} - \rho_{\mathrm{cal},i}}{\rho_{\mathrm{exp},i}} \tag{2}$$

are presented in Table 3. Agreement seems quite acceptable.

For vapor−liquid equilibria, the methanol + water data were correlated using the model “excess function-equation of state” described previously (Péneloux et al., 1989). To represent the properties of pure compounds a volume-translated Peng−Robinson equation of state was adopted:

$$P = \frac{RT}{\tilde{v} - \tilde{b}} - \frac{a(T)}{\tilde{v}(\tilde{v} + \gamma\tilde{b})} \quad \text{with} \quad \gamma = 2(\sqrt{2} + 1) \tag{3}$$

The pseudo-covolume $\tilde{b}$ was calculated from critical constants, and the dependent-temperature function $a(T)$ is given by

$$a(T) = a(T_{\mathrm{b}})\left\{1 + m_1\left[1 - \left(\frac{T}{T_{\mathrm{b}}}\right)^{0.05}\right] - m_2\left(1 - \frac{T}{T_{\mathrm{b}}}\right)\right\} \tag{4}$$

where $a(T_{\mathrm{b}})$ is the value of parameter a at the normal boiling temperature T_{b}. Parameters m_1 and m_2 were adjusted in accordance with vapor pressures of pure components. Their values are listed in Table 4.

The excess function is defined at packing fraction ($\eta = \tilde{b}/\tilde{v}$), and the mixture equation has the following form

$$z = \frac{1}{1 - \eta} - \sum_{i=1}^{p}\frac{x_i a_i}{RTb_i}Q'(\eta) + \frac{1}{2}\sum_{i=1}^{p}\sum_{j=1}^{p}\frac{\tilde{b}_i\tilde{b}_j x_i x_j}{\sum_{i=1}^{p} x_i\tilde{b}_i}\frac{E_{ij}(T)}{RT}Q'(\eta) \tag{5}$$

with

$$Q'(\eta) = \frac{\eta}{1 + \gamma\eta}$$

E_{ij} denotes the binary energy parameter and varies with temperature according to

$$E_{ij} = E^{\circ}_{ij}\left(\frac{T^{\circ}}{T}\right)^{r} \qquad T^{\circ} = 298.15\ \mathrm{K} \tag{6}$$

E°_{ij} and r are two parameters adjusted using vapor−liquid equilibrium data. The isothermal VLE values betwwen 243 K and 473 K and isobaric VLE values at atmospheric pressure reported in the literature and given in Table 5 were selected for this evaluation. We find $E^{\circ}_{ij} = 365.8$ J cm^{-3} and $r = -1.823$. It should be noted that we have not taken into account our measurements in adjustment.

The relative mean deviation in the bubble-point pressure and absolute mean deviation in the vapor-phase composi-

Table 1. P, ρ Data for Methanol (1) + Water (2) at Different Temperatures

P/MPa	ρ /moL^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ /moL^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}
$x_1 = 0.1061$															
$T = 272.46$ K		$T = 302.60$ K		$T = 332.55$ K		$T = 363.17$ K		$T = 383.57$ K		$T = 403.52$ K		$T = 424.05$ K		$T = 443.49$ K	
17.355	52.3000	40.145	51.4514	37.121	49.0102	40.523	47.5560	29.198	45.6890	37.837	45.0270	28.986	43.4205	28.519	42.3008
15.863	52.2032	38.746	51.3544	35.653	48.9295	39.104	47.4764	27.703	45.6076	36.356	44.9517	27.598	43.3495	27.081	42.2324
14.346	52.1246	37.269	51.2799	34.171	48.8406	37.538	47.3855	26.201	45.5273	34.853	44.8806	26.151	43.2738	25.627	42.1678
12.905	52.0356	35.815	51.1904	32.735	48.7498	36.052	47.3090	24.723	45.4574	33.334	44.8032	24.659	43.1963	24.152	42.0993
11.482	51.9425	34.348	51.1072	31.233	48.6613	34.548	47.2250	23.272	45.3919	31.826	44.7247	23.158	43.1320	22.701	42.0337
9.949	51.8667	32.827	51.0249	29.745	48.5769	33.049	47.1382	21.813	45.3292	30.333	44.6445	21.773	43.0586	21.293	41.9751
8.476	51.7925	31.337	50.9375	28.268	48.4973	31.565	47.0473	20.441	45.2438	28.905	44.5616	20.368	42.9806	19.888	41.9182
7.021	51.7151	29.847	50.8400	26.757	48.4252	30.025	46.9689	19.079	45.1697	27.494	44.4835	18.902	42.9089	18.358	41.8444
5.601	51.6315	28.391	50.7448	25.266	48.3427	28.509	46.8831	17.598	45.0952	26.122	44.4024	17.362	42.8359	16.884	41.7733
4.077	51.5441	27.043	50.6649	23.902	48.2615	26.997	46.8021	16.131	45.0165	24.694	44.3273	15.842	42.7695	15.381	41.7031
2.596	51.4678	25.511	50.5900	22.435	48.1765	25.534	46.7254	14.686	44.9455	23.183	44.2589	14.343	42.7096	13.944	41.6344
1.128	51.3988	24.029	50.4983	21.009	48.0871	24.059	46.6468	13.375	44.8743	21.774	44.1626	12.937	42.6513	12.494	41.5766
		22.501	50.4026	19.506	48.0048	22.661	46.5739	12.005	44.8016	20.292	44.0865	11.401	42.5866	10.993	41.5127
		21.009	50.3123	18.055	47.9235	21.240	46.4950	10.641	44.7327	18.907	44.0191	9.926	42.5177	9.516	41.4552
		19.582	50.2236	16.588	47.8504	19.719	46.4122	9.334	44.6556	17.554	43.9426	8.423	42.4626	8.053	41.3906
		18.119	50.1485	15.230	47.7787	18.324	46.3355	7.894	44.5886	16.051	43.8673	6.935	42.3993	6.658	41.3371
		16.682	50.0708	13.751	47.7000	16.893	46.2602	6.492	44.5250	14.628	43.8131	5.566	42.3370	5.274	41.2804
		15.302	49.9821	12.323	47.6207	15.416	46.1876	5.141	44.4570	13.188	43.7382	4.134	42.2759	3.864	41.2186
		13.828	49.8892	10.931	47.5385	13.928	46.1188	3.816	44.4005	11.904	43.6678	2.747	42.2175	2.473	41.1474
		12.311	49.7985	9.598	47.4634	12.396	46.0542	2.519	44.3280	10.585	43.5991	1.199	40.9851	1.342	37.9460
		10.808	49.7160	8.113	47.3937	11.049	45.9800	1.255	44.2651	9.110	43.5257	0.784	37.1590	1.193	33.4167
		9.367	49.6361	6.712	47.3218	9.695	45.9021	0.464	41.6114	7.730	43.4633	0.732	33.7583	1.166	29.6370
		7.985	49.5624	5.269	47.2477	8.275	45.8338	0.423	39.7382	6.379	43.3917	0.708	29.9020	1.177	26.7206
		6.648	49.4886	3.889	47.1728	6.817	45.7665	0.318	33.8429	5.082	43.3240	0.679	26.9269	1.173	24.4234
		5.206	49.4055	2.564	47.1052	5.382	45.6896	0.287	29.9431	3.734	43.2580	0.681	24.5923	1.159	22.5790
		3.777	49.3208	1.206	47.0266	3.994	45.6208	0.255	26.9359	2.416	43.2033	0.669	22.7125	1.155	21.0424
		2.456	49.2504			2.624	45.5423	0.239	24.5851	1.123	43.1462	0.646	21.1582	1.111	19.7261
		1.087	49.1642			1.172	45.4772	0.228	22.6978	0.640	37.9061	0.660	19.8057	1.132	18.5419
						0.303	44.0695	0.243	20.8539	0.548	33.5597	0.682	18.6035	1.140	17.4350
						0.254	41.0485	0.238	19.5241	0.463	29.7931	0.624	17.4884	1.105	16.3584
						0.211	35.4289	0.230	18.3388	0.495	26.8609	0.654	16.4035	1.123	15.2750
						0.166	31.1505	0.215	17.2248	0.475	24.5511	0.655	15.3170	1.092	14.1606
						0.183	27.8672	0.231	16.1348	0.473	22.6819	0.648	14.2039	1.077	13.0241
						0.150	24.8712	0.224	15.0163	0.449	21.1392	0.619	13.0596		
						0.159	22.8799	0.210	13.8605	0.437	19.8100				
						0.153	21.2366	0.208	12.6830	0.420	18.6181				
						0.191	19.8334			0.440	17.5121				
						0.104	18.6029			0.397	16.4346				
						0.125	17.4196			0.382	15.3565				
						0.108	16.2964			0.421	14.2456				
						0.107	15.1308			0.382	13.1053				

Table 1. (Continued)

P/MPa	ρ /moL^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ /moL^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}
$x_1 = 0.2872$															
$T = 272.36$ K		$T = 302.32$ K		$T = 332.81$ K		$T = 363.00$ K		$T = 383.52$ K		$T = 403.52$ K		$T = 424.29$ K		$T = 442.71$ K	
15.193	41.8476	27.442	40.9851	31.872	39.7126	38.941	38.6364	36.860	37.8328	38.835	36.8795	38.419	36.2004	28.831	35.0195
13.663	41.7896	25.976	40.9228	30.436	39.6629	37.551	38.5856	35.373	37.7823	37.246	36.8365	36.823	36.1508	27.220	34.9801
12.207	41.7327	24.619	40.8068	28.952	39.6132	36.164	38.5290	33.772	37.7319	35.664	36.7963	35.212	36.1110	25.617	34.9442
10.736	41.6688	23.118	40.7473	27.478	39.5625	34.761	38.4712	32.210	37.6796	34.123	36.7462	33.609	36.0757	24.029	34.9032
9.232	41.6102	21.641	40.6929	25.986	39.5102	33.435	38.4215	30.636	37.6331	32.554	36.7034	32.019	36.0286	22.384	34.8560
7.776	41.5529	20.121	40.6256	24.518	39.4609	31.933	38.3749	29.062	37.5788	30.951	36.6643	30.406	35.9888	20.795	34.8160
6.350	41.4966	18.689	40.5881	23.082	39.4100	30.452	38.3311	27.468	37.5256	29.436	36.6235	28.805	35.9424	19.188	34.7731
4.877	41.4289	17.284	40.5305	21.648	39.3636	28.981	38.2849	25.944	37.4716	27.968	36.5798	27.217	35.8932	17.584	34.7370
3.501	41.3884	15.853	40.4741	20.242	39.3116	27.511	38.2394	24.415	37.4260	26.401	36.5359	25.605	35.8433	15.986	34.6950
2.114	41.3293	14.387	40.4233	18.773	39.2623	26.026	38.1928	22.937	37.3874	24.862	36.4869	24.002	35.7974	143.84	34.6547
1.115	41.2802	12.993	40.3807	17.287	39.2118	24.557	38.1450	21.403	37.3406	23.313	36.4415	22.403	35.7543	12.763	34.6177
		11.602	40.3375	15.876	39.1645	23.080	38.0994	19.944	37.2891	21.733	36.3995	20.810	35.7019	11.158	34.5818
		10.186	40.2843	14.445	39.1239	21.579	38.0555	18.401	37.2379	20.168	36.3530	19.214	35.6547	9.557	34.5429
		8.730	40.2241	12.981	39.0618	20.062	38.0077	16.837	37.1910	18.672	36.3089	17.606	35.6125	7.940	34.5058
		7.306	40.1691	11.503	39.0143	18.572	37.9618	15.301	37.0887	17.069	36.2677	15.986	35.5683	6.308	34.4661
		5.817	40.1209	10.080	38.9554	17.129	37.9168	13.797	37.0395	15.488	36.2242	14.419	35.5270	4.770	34.4307
		4.411	40.0702	8.579	38.9161	15.667	37.8690	12.315	36.9894	14.001	36.1851	12.821	35.4842	3.444	34.3856
		3.031	40.0114	7.110	38.8687	14.255	37.8268	10.841	36.9470	12.426	36.1407	11.216	35.4378	2.432	34.2961
		1.631	39.9581	5.148	38.8174	12.809	37.7829	9.357	36.8991	10.939	36.0951	9.659	35.3952	1.714	30.6800
		1.158	39.9016	3.725	38.7673	11.388	37.7334	7.868	36.8575	9.430	36.0527	8.010	35.3557	1.603	27.8430
				2.397	38.7103	9.931	37.6873	6.365	36.8125	7.906	36.0172	6.414	35.3147	1.532	25.5861
				1.150	38.6650	8.531	37.6405	4.882	36.7663	6.302	35.9786	4.824	35.2769	1.479	23.7606
						7.067	37.5976	3.432	36.7163	4.789	35.9312	3.365	35.2096	1.506	22.2162
						5.589	37.5569	2.078	36.6552	3.401	35.8883	2.307	35.1677	1.485	20.8676
						4.137	37.5064	0.990	33.9100	2.108	35.8345	1.107	32.8230	1.479	19.6492
						2.674	37.4597	0.395	30.4580	0.937	33.2874	1.009	29.5311	1.436	18.4868
						1.312	37.4068	0.389	27.6454	0.713	29.8836	0.977	26.9424	1.440	17.3446
						0.925	37.3046	0.322	25.4014	0.627	27.1880	0.961	24.8622	1.444	16.1813
						0.635	33.4597	0.287	23.5835	0.590	25.0391	0.916	23.1514	1.438	14.9858
						0.485	32.8309	0.253	22.0486	0.549	23.2849	0.937	21.6925	1.429	13.5202
						0.259	29.5600	0.287	20.7117	0.588	21.7973	0.873	20.4005		
						0.182	26.9367	0.225	19.4903	0.564	20.2565	0.900	19.2097		
						0.129	24.8407	0.253	18.3268	0.548	19.0668	0.883	18.0584		
						0.151	23.1167	0.254	17.1747	0.538	17.9135	0.845	16.9016		
						0.125	21.6509	0.253	16.0046	0.494	16.7597	0.852	15.7255		
						0.139	20.1183	0.240	14.7970	0.518	15.5809	0.855	14.5181		
						0.136	18.9252			0.501	14.3665				
						0.111	17.7723								
						0.104	16.6126								
						0.108	15.4246								
						0.101	14.1744								

Table 1. (Continued)

P/MPa	ρ /moL^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ /moL^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}
								$x_1 = 0.4980$									
$T = 256.87$ K		$T = 272.39$ K		$T = 301.67$ K		$T = 332.82$ K		$T = 363.14$ K		$T = 383.25$ K		$T = 403.64$ K		$T = 424.34$ K		$T = 442.72$ K	
14.026	38.8674	18.459	38.0520	39.013	37.1646	34.153	35.1638	39.095	33.8206	38.128	32.5884	38.223	31.6585	34.959	30.6603	14.043	28.9217
12.519	38.7965	16.955	37.9798	37.625	37.0993	32.695	35.1029	37.716	33.7629	36.775	32.5371	36.859	31.6046	33.676	30.6126	9.146	28.7329
11.059	38.7274	15.423	37.9116	36.151	37.0413	31.197	35.0458	36.315	33.7024	35.372	32.4856	35.446	31.5514	32.417	30.5653	7.814	28.6879
9.582	38.6638	13.925	37.8488	34.649	36.9643	29.694	34.9800	34.917	33.6408	33.985	32.4388	34.077	31.4995	31.136	30.5148	6.663	28.6384
8.049	38.5902	12.457	37.7806	33.194	36.9047	28.240	34.9167	33.530	33.5839	32.661	32.3925	32.693	31.4456	29.839	30.4637	5.353	28.5922
6.614	38.5192	11.021	37.7079	31.795	36.8453	26.762	34.8348	32.128	33.5263	31.280	32.3444	31.276	31.3930	28.581	30.4140	4.054	28.5470
5.094	38.4752	9.587	37.6411	30.368	36.8067	25.249	34.7921	30.690	33.4685	29.922	32.2996	29.865	31.3390	27.277	30.3641	2.810	28.4974
3.734	38.3995	8.125	37.5677	28.836	36.7557	23.743	34.7344	29.326	33.4090	28.520	32.2492	28.491	31.2906	26.018	30.3176	2.142	26.8161
2.217	38.2449	6.683	37.4999	27.372	36.7045	22.246	34.6789	27.952	33.3488	27.185	32.2003	27.129	31.2383	24.723	30.2684	1.881	24.4609
		5.230	37.4279	25.940	36.5701	20.765	34.6192	26.551	33.2928	25.807	32.1531	25.673	31.1875	23.477	30.2229	1.753	21.3522
		3.799	37.3662	24.454	36.5134	19.261	34.5536	25.172	33.2357	24.408	32.1049	24.272	31.1406	22.192	30.1745	1.702	18.9826
		2.366	37.2980	22.986	36.4423	17.796	34.4855	23.767	33.1762	23.019	32.0569	22.894	31.0892	20.918	30.1301	1.674	17.1491
				21.556	36.3696	16.317	34.4238	22.411	33.1221	21.665	32.0105	21.487	31.0378	19.650	30.0815	1.643	15.7025
				20.104	36.2855	14.816	34.3612	21.112	33.0627	20.300	31.9614	20.040	30.9907	18.350	30.0307	1.637	14.5364
				18.625	36.2294	13.319	34.3004	19.713	33.0070	18.899	31.9102	18.605	30.9407	17.081	29.9833	1.636	13.5681
				17.122	36.1654	11.896	34.2366	18.334	32.9553	17.520	31.8639	17.208	30.8933	15.834	29.9358	1.627	12.7266
				15.669	36.0869	10.331	34.1786	16.926	32.8973	16.133	31.8143	15.743	30.8421	14.599	29.8897	1.622	11.9744
				14.199	36.0219	8.799	34.1233	15.539	32.8355	14.727	31.7710	14.332	30.7921	13.321	29.8447	1.608	11.2704
				12.775	35.9419	7.297	34.0701	14.148	32.7782	13.349	31.7291	12.896	30.7464	12.031	29.8008	1.592	10.5835
				11.321	35.8645	5.808	34.0100	12.838	32.7221	11.990	31.6823	11.490	30.6988	10.795	29.7537	1.565	9.8893
				9.842	35.7936	4.245	33.9449	11.443	32.6656	10.587	31.6366	10.142	30.6491	9.560	29.7057	1.595	9.1787
				8.386	35.7277	2.867	33.8872	10.024	32.6064	9.293	31.5891	8.892	30.5996	8.296	29.6623	1.581	8.3584
				6.885	35.6605			8.678	32.5502	7.973	31.5480	7.563	30.5532	7.033	29.6175		
				5.453	35.6225			7.508	32.4926	6.703	31.5095	6.261	30.5050	5.741	29.5695		
				4.037	35.5847			6.199	32.4436	5.330	31.4568	4.938	30.4598	4.497	29.5260		
				2.746	35.4797			4.759	32.3907	4.047	31.4144	3.617	30.4128	3.197	29.4823		
								3.493	32.3407	2.771	31.3662	2.286	30.3687	2.126	29.4705		
								2.224	32.2892	1.617	30.9101	1.348	29.3962	1.119	19.4846		
								1.033	31.5473	1.017	29.9495	1.068	28.2593	1.065	17.5204		
								0.365	25.6849	0.568	25.5891	0.757	24.1331	1.041	15.9810		
								0.254	22.3322	0.436	22.1267	0.692	2.10064	1.012	14.7572		
								0.212	19.6228	0.378	19.4623	0.648	18.6451	1.021	13.7428		
								0.211	17.5868	0.346	17.4660	0.652	16.5538	0.999	12.7321		
								0.162	16.0050	0.305	15.9236	0.578	15.2078	0.975	11.9734		
								0.109	14.7545	0.319	14.7024	0.598	14.1196	0.983	11.2631		
								0.149	13.7332	0.278	13.6966	0.550	13.2013	0.981	10.5754		
								0.119	12.7010	0.260	12.8332	0.575	12.3966	0.948	9.8790		
								0.105	11.9298	0.289	11.9230	0.555	11.6613	0.961	9.1610		
								0.122	11.2172	0.278	11.2126	0.537	10.9647	0.948	8.4296		
								0.107	10.5236	0.276	10.5181	0.551	10.2772				
								0.109	9.6868	0.273	9.8173	0.550	9.4003				
								0.104	8.9597	0.265	9.0985	0.544	8.6698				
								0.102	8.2197	0.234	8.3612						

Table 1. (Continued)

P/MPa	ρ /moL^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ /moL^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}
								$x_1 = 0.6876$									
T = 257.34 K		T = 272.91 K		T = 302.47 K		T = 333.14 K		T = 363.05 K		T = 383.29 K		T = 403.43 K		T = 423.26 K		T = 443.02 K	
15.762	34.9700	28.559	34.6884	36.268	33.4872	39.659	31.9314	38.622	30.3356	36.281	29.3954	38.996	28.6290	38.939	27.8557	32.887	27.0253
14.417	34.9069	27.219	34.6306	34.907	33.4294	38.252	31.8773	37.091	30.2882	34.687	29.3492	37.547	28.5867	37.353	27.8074	31.368	27.0082
13.118	34.8471	25.854	34.5698	33.593	33.3669	36.757	31.8177	35.568	30.2390	33.122	29.3013	36.080	28.5412	35.776	27.7642	29.803	26.9544
11.826	34.7852	24.543	34.5092	32.283	33.3053	35.269	31.7535	34.088	30.1881	31.640	29.2520	34.571	28.4934	34.173	27.7152	28.235	26.9091
10.515	34.7190	23.253	34.4429	30.958	33.2474	33.709	31.7035	32.581	30.1389	30.118	29.2074	33.050	28.4487	32.553	27.6717	26.618	26.8666
9.211	34.6582	21.892	34.3839	29.635	33.1942	32.254	31.6484	31.112	30.0875	28.617	29.1648	31.559	28.4057	30.940	27.6239	25.008	26.8213
7.943	34.5966	20.567	34.3286	28.328	33.1366	30.781	31.5889	29.582	30.0389	27.127	29.1216	30.028	28.3661	29.356	27.5758	23.417	26.7798
6.622	34.5326	19.212	34.2658	26.963	33.0795	29.367	31.5384	28.035	29.9948	25.605	29.0790	28.553	28.3236	27.734	27.5290	21.830	26.7355
5.372	34.4651	17.910	34.2054	25.641	33.0214	27.898	31.4810	26.534	29.9406	24.110	29.0346	27.063	28.2795	26.093	27.4865	20.283	26.6942
4.032	34.4099	16.576	34.1419	24.321	32.9588	26.367	31.4269	25.070	29.9012	22.607	28.9929	25.549	28.2367	24.482	27.4429	18.646	26.6543
2.698	34.3496	15.199	34.0815	22.980	32.9045	24.901	31.3748	23.531	29.8579	21.119	28.9551	24.027	28.1954	22.858	27.3964	17.142	26.6085
1.457	34.3007	13.902	34.0206	21.616	32.8490	23.377	31.3181	22.020	29.8041	19.632	28.9112	22.553	28.1488	21.260	27.3533	15.581	26.5664
		12.591	33.9614	20.312	32.7913	21.887	31.2642	20.549	29.7551	18.120	28.8646	20.989	28.1030	19.655	27.3067	13.972	26.5256
		112.88	33.8974	18.980	32.7318	20.422	31.2054	19.063	29.7163	16.606	28.8186	19.468	28.0586	18.061	27.2657	12.327	26.4812
		9.820	33.8389	17.620	32.6751	18.889	31.1443	17.560	29.6744	15.086	28.7718	17.965	28.0181	16.494	27.2236	10.740	26.4390
		8.466	33.7841	16.314	32.6145	17.391	31.0856	16.065	29.6319	13.563	28.7262	16.526	27.9768	14.871	27.1775	9.206	26.4021
		7.141	33.7242	14.990	32.5550	15.913	31.0288	14.526	29.5935	12.029	28.6840	15.019	27.9363	13.240	27.1400	7.475	26.3620
		5.905	33.6610	13.685	32.4997	14.426	30.9751	13.052	29.5498	10.526	28.6391	13.486	27.8929	11.654	27.1069	5.848	26.3230
		4.550	33.5964	12.322	32.4429	13.020	30.9214	11.545	29.4992	9.045	28.5980	11.999	27.8531	9.975	27.0647	4.300	26.2783
		3.264	33.5380	10.675	32.3860	11.593	30.8667	10.024	29.4509	7.513	28.5532	10.533	27.8110	8.345	27.0198	2.783	26.2388
		1.900	33.4853	9.664	32.2734	10.137	30.8165	8.539	29.4088	5.985	28.5116	9.060	27.7720	6.834	26.9785	1.936	21.3294
		1.172	33.4260	8.340	32.2255	8.540	30.7640	7.047	29.3696	4.459	28.4654	7.636	27.7270	5.295	26.9332	1.922	18.8876
				7.015	32.1692	6.947	30.7079	5.537	29.3253	3.110	28.4174	6.040	27.6846	4.852	26.8956	1.876	16.9983
				5.637	32.1116	5.488	30.6633	4.345	29.2828	1.731	28.3720	4.584	27.6472	2.549	26.8507	1.913	15.5124
				4.316	32.0516	4.128	30.6115	2.634	29.2301	0.995	28.3309	3.104	27.6020	1.332	25.4545	1.855	14.3215
				2.938	32.0027	2.753	30.5616	1.197	29.1871	0.391	24.3320	1.772	27.5595	1.264	23.1957	1.865	13.3379
				1.688	31.9490	1.420	30.5212	1.061	29.1560	0.388	21.0257	0.942	27.5290	1.193	20.3163	1.879	12.4982
								0.329	25.6237	0.385	18.6454	0.705	23.3363	1.169	18.1122	1.857	11.7535
								0.280	22.2194	0.387	17.1958	0.695	20.1435	1.183	16.3999	1.854	11.0627
								0.225	19.6062	0.380	15.4494	0.692	17.6431	1.203	15.0410	1.886	10.2655
								0.255	17.2365	0.369	14.2648	0.729	16.0273	1.188	13.9368	1.837	9.5975
								0.209	15.7073	0.381	13.2855	0.698	14.7389	1.147	13.0120	1.859	8.9122
								0.206	14.4824	0.392	12.4489	0.691	13.6819	1.192	12.2120	1.872	8.2096
								0.180	13.4720	0.347	11.7066	0.681	12.7947	1.166	11.4859		
								0.167	12.6137	0.376	11.0143	0.693	12.0167	1.188	10.8064		
								0.183	11.8534	0.358	10.3438	0.679	11.3079	1.166	10.1416		
								0.161	11.1552	0.324	9.6721	0.659	10.6332	1.145	9.4699		
								0.162	10.4832	0.288	8.9867	0.702	9.9676	1.145	8.7844		
								0.140	9.8148	0.219	8.2833	0.704	9.2898	1.161	8.0775		
								0.169	9.1332			0.669	8.5935				
								0.161	8.3450			0.602	7.8781				
								0.158	7.7911								

Table 1. (Continued)

P/MPa	ρ /moL^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ /moL^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}	P/MPa	ρ/mol L^{-1}
$x_1 = 0.9061$																	
$T = 257.51$ K		$T = 272.93$ K		$T = 302.40$ K		$T = 332.99$ K		$T = 363.27$ K		$T = 383.59$ K		$T = 404.03$ K		$T = 424.40$ K		$T = 442.56$ K	
18.914	30.2487	19.059	29.6063	28.993	28.5177	38.459	27.5613	38.268	26.2995	39.094	25.5514	40.274	24.8076	38.844	24.1122	19.764	22.9994
17.493	30.2016	17.594	29.5571	27.516	28.4681	36.978	27.5053	36.841	26.2491	37.625	25.5058	38.788	24.7622	37.376	24.0690	18.307	22.9592
16.060	30.1587	16.123	29.5089	26.062	28.4153	35.537	27.4526	35.359	26.2044	36.117	25.4582	37.311	24.7193	35.882	24.0250	16.801	22.9246
14.648	30.1194	14.635	29.4520	24.598	28.3584	34.076	27.3981	33.886	26.1526	34.657	25.4145	35.790	24.6736	34.414	23.9801	15.307	22.8851
13.225	30.0784	13.155	29.4040	23.165	28.3060	32.651	27.3443	32.385	26.1079	33.245	25.3792	34.276	24.6294	32.939	23.9369	13.776	22.8447
11.788	30.0253	11.678	29.3572	21.695	28.2485	31.196	27.2954	30.947	26.0611	31.734	25.3401	32.788	24.5826	31.417	23.8973	12.302	22.8089
10.326	29.9779	10.242	29.2986	20.239	28.1926	29.727	27.2408	29.480	26.0177	30.269	25.2950	313.19	24.5374	29.886	23.8558	10.781	22.7747
8.852	29.9342	8.747	29.2417	18.774	28.1381	28.248	27.1897	27.981	25.9724	28.798	25.2473	29.851	24.4944	28.384	23.8192	9.322	22.7370
7.416	29.8912	7.269	29.1875	17.289	28.0842	26.779	27.1364	26.501	25.9228	27.297	25.2009	28.350	24.4538	26.923	23.7800	7.781	22.6980
6.032	29.8523	5.817	29.1337	15.817	28.0382	25.321	27.0908	25.024	25.8749	25.863	25.1573	26.816	24.4162	25.466	23.7400	6.360	22.6621
4.587	29.8090	4.390	29.0874	14.353	27.9871	23.830	27.0409	23.562	25.8275	24.401	25.1128	25.341	24.3708	23.971	23.7039	5.001	22.6290
3.224	29.7625	2.747	28.9781	12.882	27.9351	22.394	26.9868	22.078	25.7886	22.942	25.0730	23.842	24.3267	22.437	23.6635	3.666	22.5985
				11.416	27.8850	20.958	26.9366	20.620	25.7472	21.465	25.0353	22.376	24.2870	21.009	23.6248	2.411	22.5662
				9.960	27.8397	19.456	26.8974	19.116	25.7097	20.062	24.9914	20.872	24.2439	19.559	23.5865	2.281	20.2275
				8.560	27.7918	18.030	26.8532	17.617	25.6711	18.655	24.9443	19.364	24.2018	18.136	23.5488	2.222	17.2814
				7.251	27.7489	16.552	26.8133	16.141	25.6213	17.210	24.9003	17.899	24.1609	16.665	23.5096	2.202	15.3245
				5.782	27.7098	15.100	26.7669	14.639	25.5772	15.863	24.8584	16.404	24.1186	15.199	23.4699	2.209	13.8082
				4.412	27.6643	13.659	26.7167	13.181	25.5340	14.475	24.8157	14.949	24.0753	13.715	23.4328	2.175	12.5915
				3.066	27.6200	12.202	26.6721	11.692	25.4882	13.039	24.7741	13.491	24.0321	12.213	23.3989	2.164	11.6220
				1.689	27.5759	10.797	26.6307	10.215	25.4462	11.683	24.7284	12.012	23.9921	10.736	23.3582	2.177	10.8165
				1.149	27.5239	9.343	26.5910	8.758	25.3992	10.616	24.6877	10.594	23.9512	9.284	23.3195	2.159	10.1322
						7.866	26.5418	7.404	25.3558	9.284	24.6426	9.188	23.9116	7.872	23.2817	2.185	9.5219
						6.412	26.4972	6.045	25.3155	7.948	24.6057	7.815	23.8737	6.410	23.2436	2.147	8.9521
						5.064	26.4568	4.699	25.2744	6.666	24.5649	6.364	23.8374	5.018	23.2035	2.153	8.4053
						3.618	26.4181	3.340	25.2362	5.284	24.5226	4.960	23.8064	3.615	23.1644	2.156	7.8570
						2.236	26.3812	2.035	25.1996	3.999	24.4768	3.685	23.7673	2.283	23.1274	2.131	7.2937
						1.162	26.3354	1.151	25.1354	2.757	24.4393	2.320	23.7305	1.284	18.5580	2.133	6.7156
								0.137	19.9433	1.424	24.0876	1.177	23.4754	1.271	16.0603		
								0.131	17.1104	1.140	23.9545	0.924	20.8107	1.264	14.0741		
								0.125	14.9253	0.493	21.3949	0.915	17.8252	1.259	12.6164		
								0.120	13.4632	0.490	18.5063	0.911	15.7721	1.256	11.5497		
								0.102	12.3107	0.485	16.0653	0.882	14.1463	1.260	10.6796		
								0.117	11.3832	0.491	14.3747	0.910	12.8706	1.254	10.0002		
								0.108	10.6155	0.468	13.0483	0.884	11.8512	1.248	9.3563		
								0.120	9.9527	0.445	11.9854	0.868	11.0121	1.246	8.7982		
								0.134	9.3513	0.451	11.1194	0.863	10.3009	1.228	8.2545		
								0.120	8.7902	0.450	10.3901	0.854	9.6773	1.195	7.7078		
								0.109	8.2387	0.423	9.7495	0.866	9.1032	1.229	7.1414		
								0.108	7.6822	0.450	9.1692	0.863	8.5547	1.223	6.5635		
								0.108	7.1080	0.430	8.6170	0.845	7.9663				
								0.103	6.5221	0.419	8.0683	0.839	7.3512				
										0.453	7.5117	0.833	6.7266				
										0.436	6.9399						
										0.424	6.3566						

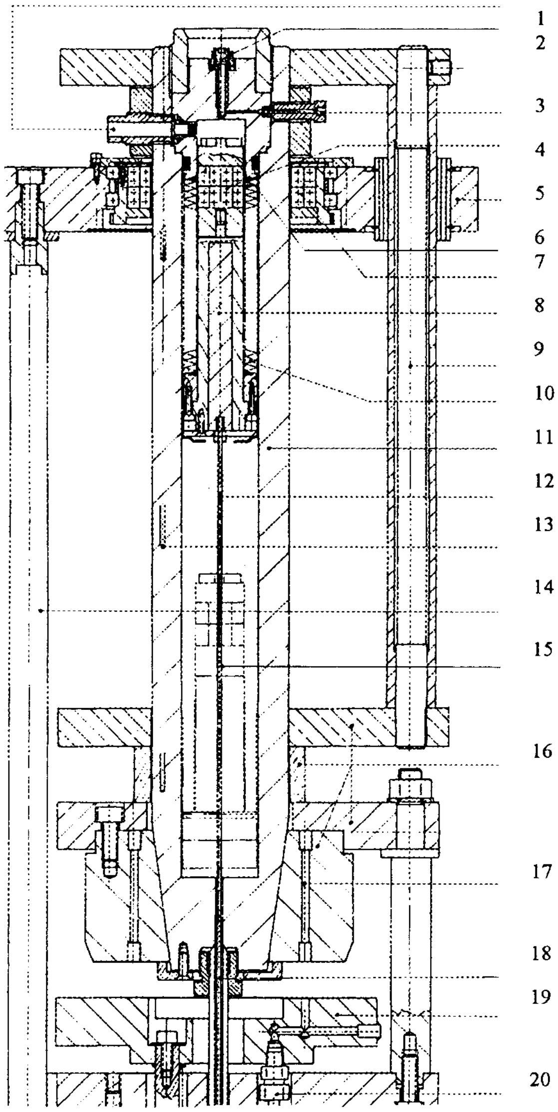

Figure 2. Schematic diagram of the measurement cell: (1) saphir windows; (2) stainless steel valve; (3) fluid introduction; (4) internal iron kernel for the stirrer; (5) stirrer support; (6) stirrer; (7) external iron kernel for the stirrer; (8) copper cylinder; (9) copper column; (10) bellow; (11) chamber; (12) copper rod; (13) thermocouple; (14) column connecting the support of the external stirrer with the micrometric table; (15) low position of the stirrer; (16) cooper mass for transferring the heating or cooling fluid to the bottom of the bellow; (17) cooling circuit; (18) entrance tube of the compression fluid; (19) cooling platform; (20) entrance of liquid nitrogen.

tion defined by

$$\Delta P/P(\%) = \frac{100}{N_P}\sum_{i=1}^{N_P}\left|\frac{P_{\mathrm{exp},i} - P_{\mathrm{cal},i}}{P_{\mathrm{exp},i}}\right| \tag{7}$$

$$\Delta y = \frac{1}{N_y}\sum_{i=1}^{N_y}|y_{\mathrm{exp},i} - y_{\mathrm{cal},i}| \tag{8}$$

are given in Table 5 where N_P and N_y are respectively the numbers of determinations of bubble-point pressures and of vapor-phase compositions.

The vapor−liquid equilibrium of methanol + water has been measured by Griswold and Wong (1952) between 373.15 K and 523.15 K, by Schroder (1958) at 413.15 K, and by Hirata and Suda (1967) and Hirata et al. (1975) at pressures of 0.3 MPa and 0.5 MPa. The results obtained from these authors and our data are summarized in Table 6. The agreement is satisfactory. Moreover, we can remark in Figure 4 that our own measurements at 424.15 K agree with those of Griswold and Wong (1952) at 423.15 K, the only reference temperature.

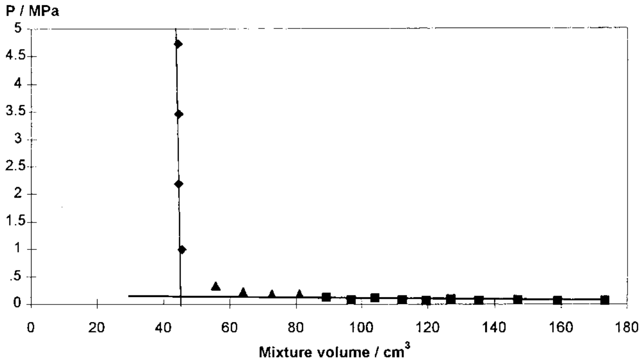

Figure 3. Determination of bubble pressure of methanol (1) + water (2) at 363.15 K for x_1 = 0.4980: ◆, data in single-phase region (liquid); ■, data in two-phase region; ▲, data in two-phase region not taken into account in linear regression.

Table 2. Bubble Pressures for the Methanol (1) + Water (2) System at Five Different Temperatures

	P/MPa				
x_1	363.15 K	383.15 K	403.15 K	424.15 K	442.15 K
0.1061	0.117	0.227	0.403	0.665	1.157
0.2872	0.153	0.293	0.567	0.937	1.477
0.4980	0.181	0.369	0.647	1.073	1.704
0.6876	0.219	0.401	0.715	1.218	1.906
0.9061	0.238	0.458	0.844	1.296	2.093

Table 3. Comparison of Experimental and Calculated Liquid-Phase Density Data at Selected Temperatures and Pressures

T/K	pressure range (MPa)	no. of data	$\Delta\rho/\rho$ (%)	$\beta_r(\rho)$
332.55	13.751−1.150	44	2.63	−0.30
363.17	13.052−1.062	46	2.62	−1.17
383.57	13.039−0.995	46	2.89	−1.75
403.52	12.896−0.942	45	2.97	−1.96
424.05	12.937−2.126	40	2.85	−1.81
443.50	12.763−2.411	37	3.18	−1.76

Table 4. Pure Component Parameters Used in This Study

compd	T_c/K	P_c/MPa	T_b/K	$\tilde{b}$/cm³mol⁻¹	m_1	m_2
methanol	512.58	8.094	337.70	23.995	1.080 64	−0.170 98
water	647.37	22.120	373.15	11.089	1.358 60	0.165 64

Table 5. Vapor−Liquid Equilibrium Results for Methanol + Water

type	ref	temp range (K)	pressure range (MPa)	N_P	$\Delta P/P$ (%)	N_y	Δy
isothermal	1 to 13	243−474	0.00005−3.950	449	1.86	262	0.018
isobaric	14 to 39	307−421	0.026−0.507	422	2.13	387	0.011
global				871	1.99	649	0.014

Conclusion

We have described a high-pressure apparatus designed to obtain pressure−density−temperature data of a pure-component or a mixture over the temperature range 210 K−470 K and at pressures up to 70 MPa. The densities of

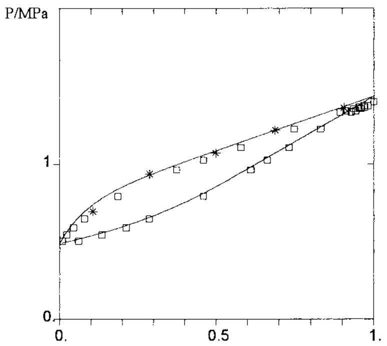

Figure 4. Vapor−liquid equilibria of the methanol−water binary system at 424.15 K. Calculated curve: full line. Data: *, our work; □, Griswold and Wong at 423.15 K.

Table 6. Relative Mean Deviations in the Bubble-Point Pressure for Our Data and Those Reported in the Literature

T/K	*P*/MPa	N_P	Δ*P*/*P* (%)	ref
363.15		5	1.76	our work
383.15		5	1.33	our work
403.15		5	2.79	our work
424.15		5	2.67	our work
442.15		5	1.10	our work
373.15		18	1.54	Griswold and Wong
423.15		16	0.81	Griswold and Wong
473.15		17	3.82	Griswold and Wong
413.15		6	1.29	Schroeder
	0.304	10	2.96	Hirata and Suda
	0.507	11	2.14	Hirata. and Suda
	0.304	26	1.78	Hirata et al.
	0.507	26	2.21	Hirata et al.

the methanol + water have been measured in the single-phase and two-phase region. The VLE pressure−composition data obtained from densities are in good agreement with literature values that have been fitted to the excess function-equation of state model by adjusting an interaction parameter.

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