1442 *J. Chem. Eng. Data* **2003,** *48,* 1442−1445

Densities and Excess Molar Volumes of Aqueous Solutions of *n*-Methyldiethanolamine (MDEA) at Temperatures from (283.15 to 363.15) K

J. Manuel Bernal-García

Instituto Mexicano del Petróleo, México D.F. C.P. 07330, México

Mariana Ramos-Estrada and Gustavo A. Iglesias-Silva*

Departamento de Ingeniería Química, Instituto Tecnológico de Celaya, Celaya, Guanajuato, CP 38010, Mexico

Kenneth R. Hall

Chemical Engineering Department, Texas A&M University, College Station, Texas 77843

In this paper, we present atmospheric pressure liquid densities for binary mixtures of *n*-methyldiethanolamine + water over the entire composition range at temperatures between 263.15 and 363.15 K. We measure the liquid densities using a vibrating tube densimeter and use them to produce a correlation for excess molar volumes based upon a Redlich−Kister equation. The excess volumes exhibit negative deviations from ideality at all the investigated temperatures and become less negative with increasing temperature.

Introduction

The design of acid gas treatment equipment requires accurate physical property data. Alkanolamine aqueous solutions often are used for the removal of acidic gases such as CO_2 and H_2S, from natural gas and refinery streams. Recently, considerable interest has focused upon the use of sterically hindered amines, especially *n*-methyldiethanolamine (MDEA). One of the advantages of using MDEA solutions in the above applications is their high loading capacity (1 mol of CO_2/mol of MDEA), in the absence of H_2S. Also, MDEA is frequently a secondary solvent in the selective removal of H_2S in the presence of CO_2.

DiGuillo et al.,[1] Li and Shen,[2] and Aguila-Hernández et al.[3] have reported densities for pure MDEA at temperatures between (296.3 and 470.9) K. Al-Ghawas et al.[4] have measured experimental liquid densities of aqueous solutions of MDEA at temperatures between (288.15 and 333.15) K and at concentrations up to 50 mass % MDEA. Rinker et al.[5] have reported densities at the same compositions but at temperatures up to 373.15 K. Li and Lie[6] have measured the densities of two aqueous solutions of (20 and 30) mass % MDEA at temperatures between (303.15 and 333.15) K. Welsh and Davis[7] have published densities for a 50 mass % aqueous solution of MDEA at different temperatures. Using a hydrometer calibrated with distilled water, pure amines, and sodium chloride, Weiland et al.[8] have reported the density of aqueous solutions of MDEA at 298.15 K and concentrations up to 50 mass %. Because of no industrial interest, densities of aqueous solutions with greater than 50 mass % MDEA do not appear in the literature. In this work, we measure the liquid densities of water + MDEA mixtures from 283.15 to 363.15 K over a wide range of compositions from 10 to 95 mass % MDEA. We also correlate the excess molar volumes of these mixtures using a Redlich−Kister equation and present the characteristic constants.

Experimental Section

Apparatus and Procedures. We have used a digital, vibrating densimeter (Anton Paar, DMA 5000) to determine the densities of MDEA, water, and their binary mixtures. The apparatus has a built-in platinum thermometer with an accuracy of ±0.01 K on the ITS-90. The precisions for density and temperature measurements are $\pm 0.002\ \mathrm{kg{\cdot}m^{-3}}$ and 0.001 K, respectively. We perform the density determinations by measuring the periodic oscillation of a vibrating U-tube filled with liquid samples. At each temperature, the relationship between the density of the sample and its period oscillation is

$$\rho(T) = (\tau^2 - B)/A \tag{1}$$

where A and B are instrument constants determined by the manufacturer for a calibration using dried air and ultrapure water at each investigated temperature. To test the calibration, we have measured the density of water before and after all the binary mixture density measurements.

Chemicals. Fischer supplied the water, and Huntsman produced the MDEA. The stated purity for MDEA is 99 mass %. The water is HPLC grade with purity greater than 99.95 mass %. We used these samples as received. We prepared the mixtures gravimetrically using an analytical balance (Ohaus model AS120S) with a precision of ±0.1 mg. The overall uncertainty in the compositions is 0.2 mol %.

---

* Corresponding author. Phone: 01152 (461) 6115108. Fax: 01152 (461) 6117474. E-mail: gais@iqcelaya.itc.mx.

10.1021/je030120x CCC: $25.00

Table 1. Experimental Densities (ρ) and Excess Molar Volumes (V^E) for the MDEA (1) + Water (2) Mixture

	T	ρ	V^E		T	ρ	V^E		T	ρ	V^E
x_1	K	kg·m^{-3}	cm^3·mol^{-1}	x_1	K	kg·m^{-3}	cm^3·mol^{-1}	x_1	K	kg·m^{-3}	cm^3·mol^{-1}
1.0000	283.152	1047.527	0.000 00	0.3715	283.150	1062.292	−1.254 77	0.0902	283.152	1041.808	−0.606 34
0.7430	283.155	1051.628	−0.558 31	0.2571	283.153	1062.935	−1.220 42	0.0604	283.152	1030.906	−0.401 77
0.7175	283.153	1052.252	−0.620 78	0.1823	283.152	1058.881	−1.045 95	0.0168	283.152	1009.779	−0.105 42
0.5828	283.151	1056.201	−0.946 68	0.1293	283.153	1051.611	−0.831 67	0.0000	283.150	999.699	0.000 00
0.4849	283.153	1059.632	−1.155 19								
1.0000	288.148	1044.5	0.000 00	0.3715	288.148	1058.500	−1.196 57	0.0902	288.147	1039.369	−0.584 80
0.7430	288.148	1047.903	−0.491 11	0.2571	288.144	1059.433	−1.176 32	0.0604	288.148	1028.999	−0.388 48
0.7175	288.149	1048.493	−0.551 72	0.1823	288.148	1055.609	−1.008 19	0.0168	288.148	1008.826	−0.103 15
0.5828	288.148	1052.493	−0.886 60	0.1293	288.148	1048.699	−0.801 62	0.0000	288.150	999.099	0.000 00
0.4849	288.148	1056.011	−1.103 61								
1.0000	293.147	1041.604	0.000 00	0.3715	293.148	1055.044	−1.152 54	0.0902	293.145	1036.821	−0.563 97
0.7430	293.148	1044.219	−0.417 27	0.2571	293.145	1055.870	−1.129 68	0.0604	293.146	1026.937	−0.375 78
0.7175	293.149	1044.814	−0.479 65	0.1823	293.146	1052.266	−0.969 53	0.0168	293.147	1007.623	−0.101 07
0.5828	293.151	1048.826	−0.822 55	0.1293	293.145	1045.700	−0.771 69	0.0000	293.15	998.203	0.000 00
0.4849	293.150	1052.347	−1.044 65								
1.0000	298.147	1037.863	0.000 00	0.3715	298.146	1051.328	−1.132 69	0.0902	298.146	1034.162	−0.552 97
0.7430	298.148	1040.510	−0.411 02	0.2571	298.145	1052.255	−1.108 07	0.0604	298.145	1024.734	−0.369 91
0.7175	298.148	1041.100	−0.472 16	0.1823	298.145	1048.867	−0.949 61	0.0168	298.147	1006.190	−0.100 77
0.5828	298.150	1045.112	−0.810 86	0.1293	298.145	1042.627	−0.755 65	0.0000	298.150	997.043	0.000 00
0.4849	298.148	1048.636	−1.029 90								
1.0000	303.145	1034.100	0.000 00	0.3715	303.146	1047.576	−1.114 47	0.0902	303.145	1031.401	−0.543 49
0.7430	303.148	1036.780	−0.405 83	0.2571	303.145	1048.589	−1.088 08	0.0604	303.145	1022.387	−0.364 94
0.7175	303.149	1037.373	−0.466 49	0.1823	303.145	1045.403	−0.931 36	0.0168	303.144	1004.547	−0.100 69
0.5828	303.148	1041.361	−0.799 69	0.1293	303.144	1039.471	−0.741 22	0.0000	303.150	995.645	0.000 00
0.4849	303.148	1044.884	−1.015 93								
1.0000	308.145	1030.322	0.000 00	0.3715	308.146	1043.997	−1.108 01	0.0902	308.146	1028.535	−0.535 04
0.7430	308.148	1033.033	−0.401 39	0.2571	308.146	1044.866	−1.068 99	0.0604	308.145	1019.905	−0.360 68
0.7175	308.148	1033.629	−0.461 66	0.1823	308.148	1041.876	−0.914 39	0.0168	308.145	1002.707	−0.100 70
0.5828	308.149	1037.595	−0.789 97	0.1293	308.147	1036.227	−0.727 82	0.0000	308.150	994.029	0.000 00
0.4849	308.150	1041.095	−1.002 38								
1.0000	313.146	1026.523	0.000 00	0.3715	313.145	1039.983	−1.082 35	0.0902	313.146	1025.563	−0.527 38
0.7430	313.148	1029.270	−0.398 21	0.2571	313.145	1041.088	−1.050 80	0.0604	313.148	1017.291	−0.356 94
0.7175	313.148	1029.869	−0.458 17	0.1823	313.146	1038.284	−0.898 51	0.0168	313.145	1000.686	−0.100 81
0.5828	313.148	1033.797	−0.780 76	0.1293	313.145	1032.899	−0.715 38	0.0000	313.150	992.212	0.000 00
0.4849	313.148	1037.267	−0.989 31								
1.0000	318.150	1022.700	0.000 00	0.3715	318.148	1036.135	−1.068 14	0.0902	318.145	1022.489	−0.520 40
0.7430	318.149	1025.488	−0.396 24	0.2571	318.145	1037.253	−1.033 34	0.0604	318.145	1014.547	−0.353 53
0.7175	318.148	1026.090	−0.455 95	0.1823	318.145	1034.626	−0.883 53	0.0168	318.145	998.493	−0.100 96
0.5828	318.150	1029.974	−0.772 65	0.1293	318.145	1029.474	−0.703 34	0.0000	318.150	990.208	0.000 00
0.4849	318.150	1033.397	−0.976 54								
1.0000	323.145	1018.877	0.000 00	0.3715	323.145	1032.233	−1.052 95	0.0902	323.144	1019.309	−0.513 52
0.7430	323.149	1021.686	−0.393 29	0.2571	323.145	1033.364	−1.015 82	0.0604	323.145	1011.677	−0.350 17
0.7175	323.149	1022.300	−0.453 66	0.1823	323.145	1030.901	−0.868 71	0.0168	323.144	996.136	−0.101 02
0.5828	323.149	1026.125	−0.763 89	0.1293	323.145	1025.957	−0.691 25	0.0000	323.150	988.030	0.000 00
0.4849	323.149	1029.491	−0.962 97								
1.0000	328.143	1015.022	0.000 00	0.3715	328.145	1028.284	−1.038 37	0.0902	328.145	1016.031	−0.507 10
0.7430	328.149	1017.874	−0.392 95	0.2571	328.149	1029.414	−0.998 75	0.0604	328.149	1008.688	−0.347 04
0.7175	328.149	1018.491	−0.453 21	0.1823	328.149	1027.105	−0.854 42	0.0168	328.147	993.628	−0.101 12
0.5828	328.149	1022.244	−0.756 08	0.1293	328.146	1022.352	−0.679 54	0.0000	328.150	985.688	0.000 00
0.4849	328.145	1025.543	−0.949 91								
1.0000	333.145	1011.430	0.000 00	0.3715	333.144	1024.272	−1.010 67	0.0902	333.144	1012.651	−0.497 79
0.7430	333.148	1014.039	−0.368 49	0.2571	333.143	1025.407	−0.973 32	0.0604	333.145	1005.577	−0.341 84
0.7175	333.148	1014.649	−0.428 68	0.1823	333.144	1023.242	−0.834 39	0.0168	333.145	990.972	−0.100 59
0.5828	333.148	1018.330	−0.729 06	0.1293	333.144	1018.640	−0.663 03	0.0	333.150	983.191	0.000 00
0.4849	333.148	1021.558	−0.920 90								
1.0000	338.145	1007.246	0.000 00	0.3715	338.149	1020.189	−1.006 33	0.0902	338.148	1009.172	−0.494 51
0.7430	338.149	1010.158	−0.391 82	0.2571	338.148	1021.340	−0.964 92	0.0604	338.144	1002.348	−0.340 56
0.7175	338.149	1010.765	−0.450 72	0.1823	338.145	1019.307	−0.826 49	0.0168	338.144	988.168	−0.100 96
0.5828	338.148	1014.373	−0.740 07	0.1293	338.144	1014.883	−0.656 35	0.0000	338.150	980.546	0.000 00
0.4849	338.149	1017.528	−0.923 67								
1.0000	343.148	1003.321	0.000 00	0.3715	343.145	1016.154	−0.994 80	0.0902	343.145	1005.595	−0.488 24
0.7430	343.149	1006.225	−0.388 65	0.2571	343.145	1017.215	−0.948 03	0.0604	343.148	999.025	−0.337 67
0.7175	343.149	1006.825	−0.446 86	0.1823	343.149	1015.304	−0.812 68	0.0168	343.149	985.251	−0.101 15
0.5828	343.148	1010.371	−0.731 12	0.1293	343.147	1011.201	−0.650 23	0.0000	343.150	977.759	0.000 00
0.4849	343.149	1013.461	−0.910 58								
1.0000	348.146	999.377	0.000 00	0.3715	348.144	1011.871	−0.972 06	0.0902	348.148	1001.926	−0.481 92
0.7430	348.149	1002.258	−0.384 61	0.2571	348.150	1013.029	−0.930 73	0.0604	348.145	995.582	−0.334 34
0.7175	348.150	1002.842	−0.441 40	0.1823	348.145	1011.228	−0.798 55	0.0168	348.145	982.189	−0.100 93
0.5828	348.148	1006.319	−0.720 60	0.1293	348.144	1007.252	−0.638 35	0.0000	348.150	974.838	0.000 00
0.4849	348.149	1009.348	−0.896 66								

Table 1 (Continued)

x_1	T/K	ρ/kg·m^{-3}	V^E/cm^3·mol^{-1}	x_1	T/K	ρ/kg·m^{-3}	V^E/cm^3·mol^{-1}	x_1	T/K	ρ/kg·m^{-3}	V^E/cm^3·mol^{-1}
1.0000	353.145	995.408	0.000 00	0.3715	353.147	1007.635	−0.954 22	0.0902	353.146	998.157	−0.475 35
0.7430	353.150	998.262	−0.380 67	0.2571	353.145	1008.784	−0.913 24	0.0604	353.149	992.036	−0.330 99
0.7175	353.149	998.834	−0.436 45	0.1823	353.144	1007.085	−0.784 39	0.0168	353.146	979.011	−0.100 84
0.5828	353.149	1002.236	−0.710 33	0.1293	353.148	1003.386	−0.631 43	0.0000	353.150	971.785	0.000 00
0.4849	353.149	1005.191	−0.882 34								
1.0000	358.148	991.411	0.000 00	0.3715	358.144	1003.346	−0.935 92	0.0902	358.149	994.302	−0.468 83
0.7430	358.148	994.238	−0.377 17	0.2571	358.145	1004.483	−0.895 68	0.0604	358.146	988.382	−0.327 41
0.7175	358.149	994.796	−0.431 79	0.1823	358.144	1002.870	−0.769 99	0.0168	358.144	975.732	−0.101 10
0.5828	358.149	998.114	−0.699 86	0.1293	358.146	999.335	−0.621 20	0.0000	358.150	968.606	0.000 00
0.4849	358.148	1000.995	−0.868 05								
1.0000	363.146	987.391	0.000 00	0.3715	363.150	999.011	−0.917 26	0.0902	363.145	989.819	−0.447 21
0.7430	363.149	990.181	−0.373 17	0.2571	363.146	1000.118	−0.877 47	0.0604	363.148	984.560	−0.321 98
0.7175	363.148	990.730	−0.427 15	0.1823	363.149	998.583	−0.755 15	0.0168	363.148	972.319	−0.100 93
0.5828	363.149	993.956	−0.689 02	0.1293	363.149	995.203	−0.610 67	0.0000	363.150	965.305	0.000 00
0.4849	363.148	996.751	−0.852 84								

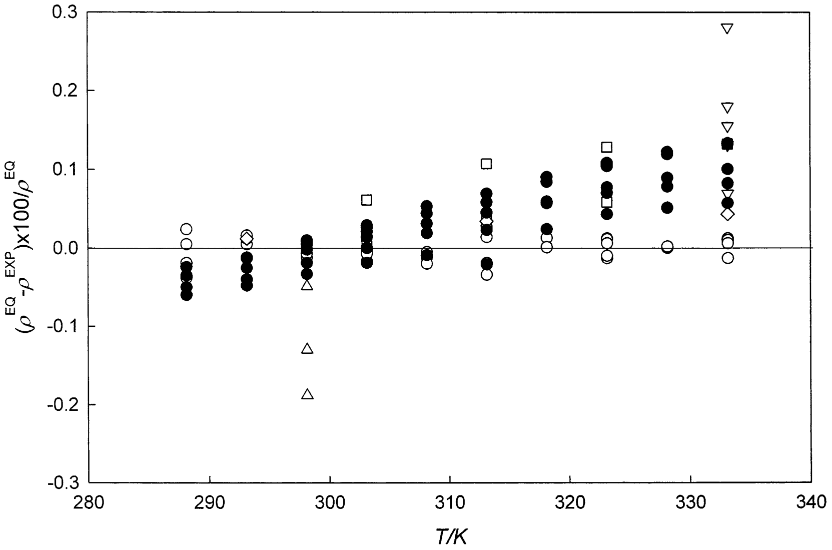

Figure 1. Percentage deviations of experimental densities of MDEA + water mixtures from the correlation of Al-Ghawas et al.:[4] ●, this work; ○, Al-Ghawas et al.;[4] ▽, Rinker et al.;[5] □, Li and Shen;[2] ◇, Welsh and Davis;[7] △, Weiland et al.[8]

Results and Discussion

We measured the densities of pure water to check the calibration of the equipment and compare our experimental results with those obtained from the standard equation of state for water developed by Wagner and Pruss.[9] The agreement with the equation of state is within 0.005%.

We have measured experimental densities (ρ) at atmospheric pressure from 283.15 K to 323.15 K. Table 1 shows the results for eleven binary mixtures of MDEA + water. Also, we have compared our results with a correlation given by Al-Ghawas et al.[4] Figure 1 shows that our density measurements agree within ±0.15% compared to calculations with the Al-Ghawas correlation. The highest deviations occur at temperatures between (323 and 333) K. The absolute average percentage deviation of the present work from this correlation is 0.021%.

We have calculated the excess molar volume from our experimental density data using

$$V^E = V_m - \sum_{i=1}^{2} x_i V_i^\circ \qquad (2)$$

with

$$V_m = [\sum_{i=1}^{2} x_i(\mathrm{MW}_i)]/\rho_m$$

where V_m is the molar volume of the liquid mixture, V_i° is the molar volume of pure component i, MW$_i$ is the molar mass of pure component i, ρ_m is the experimental liquid density, and x_i is the mole fraction of component i. Experimental density measurements of pure MDEA are correlated by

$$\rho_{\mathrm{MDEA}} = 1175.29556 - (2.0613 \times 10^{-1})T - (0.85863 \times 10^{-3})T^2 \qquad (3)$$

and our density measurements of water together with those of Bettin and Spieweck[10] are

$$\rho_{\mathrm{water}} = 755.85532 + 1.86609T - (3.5506 \times 10^{-3})T^2 \qquad (4)$$

where ρ is in kilograms per cubic meter and T is in kelvin.

Table 1 contains the excess molar volumes for the mixtures of MDEA + water and shows that the system exhibits negative deviations from ideality at all the investigated temperatures. Figure 2 shows that the excess volume becomes less negative with increasing temperature. We correlated the excess volumes to a Redlich−Kister type equation by least-squares fitting with

$$V^E = x_1 x_2 \sum_{i=0}^{3} a_i (x_1 - x_2)^i \qquad (5)$$

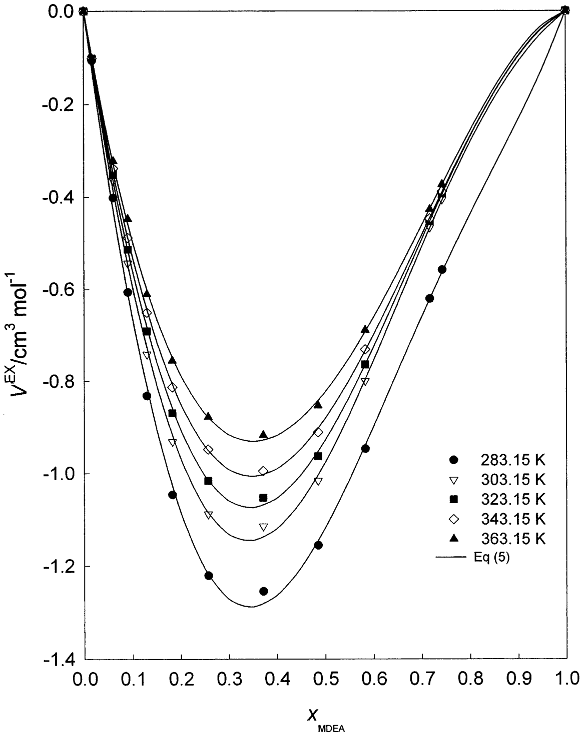

Figure 2. Excess molar volume for the MDEA (1) + water (2) mixture as a function of the mole fraction at different temperatures.

Table 2. Coefficients a_i Used in Eq 5

T/K	a_0	a_1	a_2	a_3	std dev
283.15	−4.470 338	3.847 654	−0.815 55	−1.347 225	0.0201
288.15	−4.246 842	3.894 348	−0.476 176	−1.052 793	0.0210
293.15	−4.018 118	4.020 048	−0.141 412	−0.897 907	0.0180
298.15	−3.959 761	3.915 092	−0.069 608	−0.791 312	0.0169
303.15	−3.904 517	3.814 82	−0.020 603	−0.696 864	0.0159
308.15	−3.862 584	3.759 35	0.025 579	−0.699 986	0.0126
313.15	−3.804 836	3.616 303	0.051 942	−0.504 632	0.0134
318.15	−3.759 228	3.517 94	0.068 015	−0.423 849	0.0120
323.15	−3.710 528	3.419 707	0.080 119	−0.339 185	0.0108
328.15	−3.664 04	3.315 832	0.069 118	−0.271 139	0.0095
333.15	−3.551 296	3.281 975	0.143 492	−0.147 699	0.0095
338.15	−3.567 457	3.104 566	0.047 951	−0.113 122	0.0079
343.15	−3.521 613	3.025 362	0.054 974	−0.030 504	0.0068
348.15	−3.462 366	2.911 385	0.066 706	0.118 351	0.0073
353.15	−3.406 672	2.813 514	0.067 59	0.241 015	0.0073
358.15	−3.350 55	2.714 955	0.068 604	0.344 891	0.0071
363.15	−3.292 079	2.655 086	0.059 497	0.266 146	0.0086

where a_i are the adjusted coefficients. Table 2 contains the values of these coefficients and their standard deviations for V^E at each temperature, defined as

$$\sigma = \left[\frac{\sum(V^E_{exp} - V^E_{cal})^2}{n - m}\right]^{1/2} \tag{6}$$

where n is the number of experimental points and m is the number of parameters.

Conclusions

We have measured the densities of eleven mixtures of MDEA + water at temperatures between (283.15 and 363.15) K and at concentrations from 10 to 95 mass % MDEA. Our density measurements agree within 0.15% compared to values reported in the literature. We present the excess volume using a Redlich−Kister type equation. The excess volumes of these binary mixtures exhibit negative deviations from ideality and become less negative with increasing temperature.

Literature Cited

(1) DiGuillo, R. M.; Lee, R.-J.; Schaeffer, S. T.; Brasher, L. L.; Teja, A. S. Densities and Viscosities of the Ethanolamines. *J. Chem. Eng. Data* **1992**, *37*, 239−242.

(2) Li, M. H.; Shen, K. P. Densities and Solubilities of Solutions of Carbon Dioxide in Water + Monoethanolamine + *N*-Methyldiethanolamine. *J. Chem. Eng. Data* **1992**, *37*, 288−290.

(3) Aguila-Hernández, J.; Gómez-Quintana, R.; Murrieta-Guevara, F.; Romero-Martínez, A.; Trejo, A. Liquid Density of Aqueous Blended Alkanolamines and *N*-methylpyrrolidone as a Function of Concentration and Temperature. *J. Chem. Eng. Data* **2001**, *46*, 861−867.

(4) Al-Ghawas, H. A.; Hagewiesche, D. P.; Ruiz-Ibañez, G.; Sandall, O. C. Physicochemical Properties Important for Carbon Dioxide Absorption in Aqueous Methyldiethanolamine. *J. Chem. Eng. Data* **1989**, *34*, 385−391.

(5) Rinker, E. B.; Oelschlager, D. W.; Tomas, A.; Henry, K. R.; Sandall, O. C. Viscosity, Density and Surface Tension of Binary Mixtures of Water and *N*-Methyldiethanolamine and Water and Diethanolamine and Tertiary Mixtures of these Amines with Water over the Temperature Range 20−100 °C. *J. Chem. Eng. Data* **1994**, *39*, 392−395.

(6) Li, M.-H.; Lie, Y.-C. Densities and Viscosities of Solutions of MEA + N-MDEA + Water and Monoethanolamine + 2-Amino-2-methyl-1-Propanol + Water. *J. Chem. Eng. Data* **1994**, *39*, 444−447.

(7) Welsh, L. M.; Davis, R. A. Density and Viscosity of Aqueous Blends of *N*-Methyldiethanolamine and 2-Amino-2-methyl-1-propanol. *J. Chem. Eng. Data* **1995**, *40*, 257−259.

(8) Weiland, R. H.; Dingman, J. C.; Cronin, D. B.; Browning, G. J. Density and Viscosity of Some Partially Carbonated Aqueous Alkanolamine Solutions and Their Blends. *J. Chem. Eng. Data* **1998**, *43*, 378−382.

(9) Wagner, W.; Pruss, A. The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use. *J. Phys. Chem. Ref. Data* **2002**, *31*, 387−535.

(10) Bettin, H.; Spieweck, F. Die Dichte des Wassers als Funktion der Temperatur nach Einführung der Internationlen Temperaturskala von 1990. *PTB-Mitt.* **1990**, *100*, 195−196.

Received for review January 20, 2003. Accepted July 28, 2003. The Texas Engineering Experiment Station, Texas A&M University, and the Instituto Tecnológico de Celaya have provided financial support for this work.

JE030120X