

Isothermal Vapor–Liquid Equilibria of (Monoethanolamine + Water) and (4-Methylmorpholine + Water) Binary Systems at Several Temperatures

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The vapor pressures of (monoethanolamine (MEA) + water) and (4-methylmorpholine + water) and of all the pure components were measured by means of two static devices at temperatures between (283 and 363) K. The data were correlated with the Antoine equation. From these data, excess Gibbs functions were calculated for several constant temperatures and fitted to a fourth-order Redlich–Kister equation using Barker's method. The (4-methylmorpholine + water) binary system shows maximum azeotropic behavior over the whole temperature range. The (MEA + water) binary mixture exhibits negative deviations in G^E , whereas for the (4-methylmorpholine + water) system, the excess Gibbs energy is positive for all investigated temperatures over the whole composition range.

Introduction

The purification of the natural gas as well as the sweetening of gas streams in petroleum refining are of major importance for both energy and environmental purposes. The dominant technique for these processes is the absorption of acid gases, primarily CO₂ and H₂S, into aqueous solutions of alkanolamines.¹

Vapor–liquid equilibrium of the acid gas/alkanolamine/water system is a key factor for the design of gas treating processes. The proper thermodynamic modeling of the water/alkanolamine binary system is necessary.

In this work, accurate phase equilibrium data (P , T , x) for a wide range of temperatures, pressures, and alkanolamines concentrations were determined. The experimental VLE of the pure compounds monoethanolamine (MEA, CAS # 141-43-5), 4-methylmorpholine (CAS # 109-02-4) or water, and the aqueous solutions were performed using static devices.

A survey of the literature shows that VLE data are scarce. For (MEA + water), there exist various references which provide isothermal^{2–5} or isobaric^{6,7} VLE data. For (4-methylmorpholine), only one reference⁸ reports thermodynamic study of aqueous dilute solutions.

Experimental Section

The alkanolamines were supplied by Aldrich Chem. (Milwaukee, WI, USA). They were used without further purification. The purities, tested by GLC, were > 99 %. Aqueous solutions were prepared from distilled and deionized water.

For the pure compounds, MEA and 4-methylmorpholine, the vapor pressure measurements were carried out using a static apparatus. The description of the apparatus and the experimental procedure can be found elsewhere,^{9–12} so only the most salient information is given here. The apparatus was equipped with a differential manometer from MKS, type 670, model 616A. The

Table 1. Coefficients A , B , and C and Overall Mean Relative Deviation in Pressure of the Antoine Equation (Equation 1)^a

compound	temperature range (K)	A	B	C	$\delta P/P$ (%)
MEA	283.34 to 363.09	8.940141	2432.111	236.48041	0.674
4-methylmorpholine	273.18 to 353.08	6.994581	1370.409	218.15213	0.052
water	282.87 to 363.80	8.303772	1858.012	242.80147	0.357

$$^a \delta P/P (\%) = (1/N) \sum_{i=1}^n 100((P_{\text{calc}} - P_{\text{exp}})/P_{\text{exp}}).$$

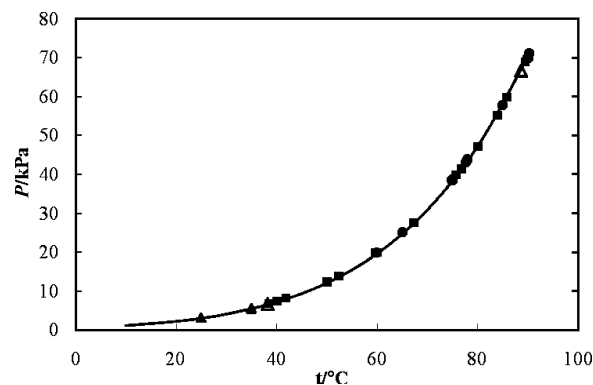


Figure 1. Equilibrium vapor pressure of water at different temperatures: —, this work; ▲, ref 2; ●, ref 3; ◆, ref 4; ■, ref 5; △, ref 6.

pressure measurement consisted of applying the vapor pressure of the sample on the measurement side of the gauge. The reference side was submitted to a permanent-dynamic pumping. The residual pressure was 10^{−4} Pa and therefore can be neglected. Temperature measurements were carried out using a copper–constantan thermocouple calibrated against a 25 Ω platinum resistance standard thermometer (± 0.001 K, IPTS 90) and a Leeds & Northrup bridge (± 10^{−4} Ω). During measurements, the stability of the temperature is ± 0.02 K. The differential pressure gauge was calibrated against a U-manometer filled with mercury or apiezon oil depending on pressure range. The levels in both arms of the U-shaped manometer were read by a cathetometer (reference 70298, from Bouty France) to the nearest 0.001 mm. The calibration was then checked by

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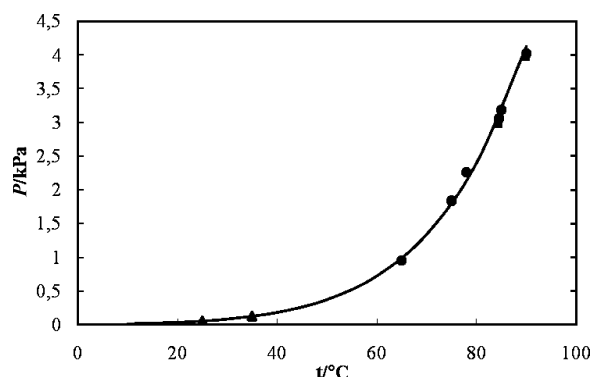


Figure 2. Equilibrium vapor pressure of MEA at different temperatures: —, this work; ▲, ref 2; ●, ref 3; ◆, ref 4; ■, ref 5.

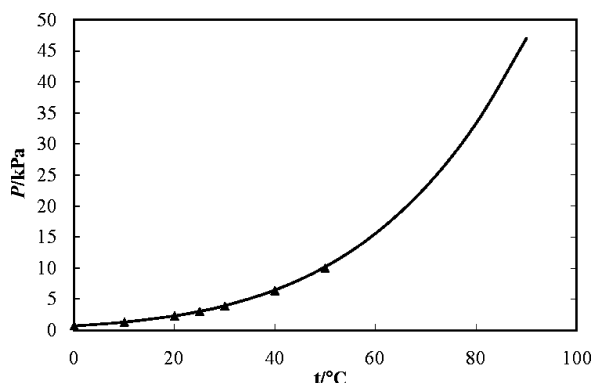


Figure 3. Equilibrium vapor pressure of 4-methylmorpholine at different temperatures: —, this work; ▲, ref 8.

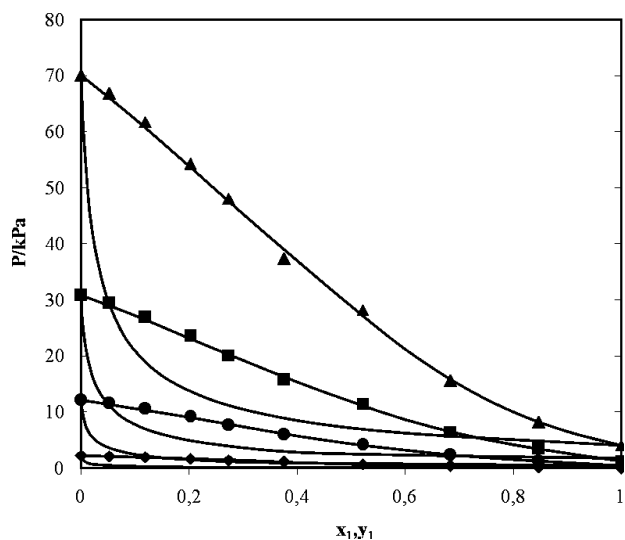


Figure 4. Experimental and calculated P - $x(y)$ behavior of the system MEA (1) + water (2) at different temperatures: ◆, 293.15 K; ●, 323.15 K; ■, 343.15 K; ▲, 363.15 K; —, calculated values using Barker's method.

measuring the vapor and the sublimation pressures of water and naphthalene.¹⁰ The uncertainty of the measurements is estimated to be: $\sigma(P) = 0.03(P/\text{Pa})$ for $P < 600$ Pa; $\sigma(P) = 0.01(P/\text{Pa})$ for P in the range (600 to 1300) Pa, $\sigma(P) = 0.03(P/\text{Pa})$ for P over 1300 Pa, and $\sigma(T) = 0.02$ K for the temperature range $203 \leq T/\text{K} \leq 463$.

For the pure water and the two binary systems, the experimental vapor pressure, P , data were obtained with an apparatus described in detail by Blondel-Telouk et al.,^{13,14} as a function of the temperature, T , for constant mole fraction composition, x_i . The apparatus allows measurements at pressures from (27

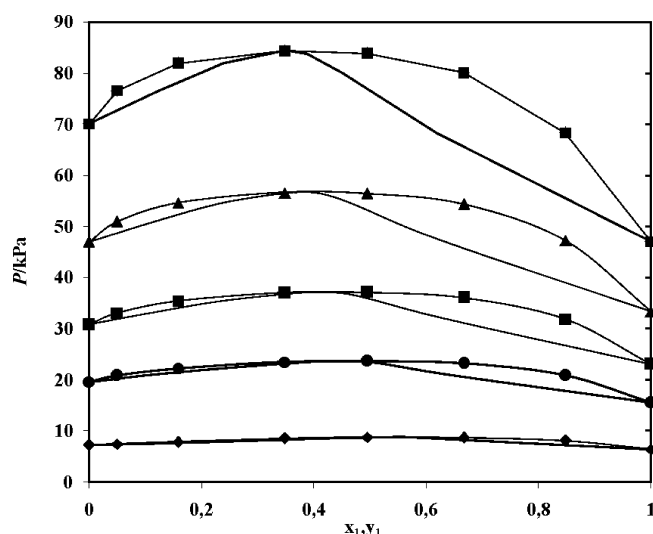


Figure 5. Experimental and calculated P - $x(y)$ behavior of the system 4-methylmorpholine (1) + water (2) at different temperatures: ◆, 313.15 K; ■, 333.15 K; ●, 343.15 K; ■, 353.15 K; ▲, 363.15 K; —, calculated values using Barker's method.

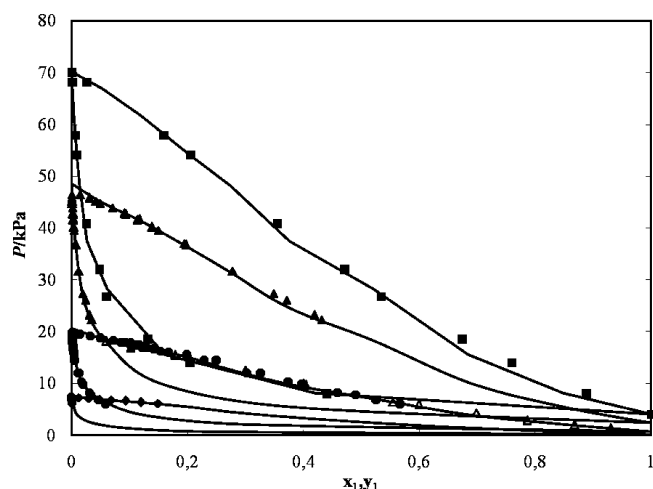


Figure 6. Total pressure P versus liquid (vapor) phase compositions (P - $x(y)$): —, this work at (313.15, 333.15, 353.15, and 363.15) K; ◆, ref 5 at 313.15 K; ●, ref 5 at 333.15 K; △, ref 3 at 333.15 K; ▲, ref 5 at 353.15 K; ■, ref 4 at 363.15 K for the system MEA (1) + water (2).

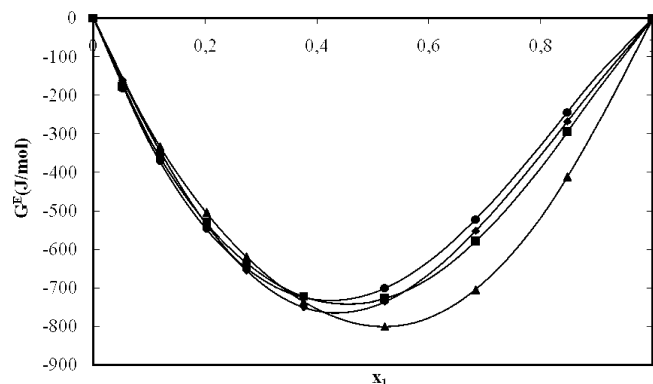


Figure 7. G^E against x_1 for the MEA (1) + water (2) system: ◆, 293.15 K; ●, 323.15 K; ■, 343.15 K; ▲, 363.15 K; —, calculated values using eq 4.

to $200 \cdot 10^3$) Pa and at temperatures from (258.15 to 468.15) K. The pressure was measured with a pressure gauge (Rosemount, model 1151 DPE 22S2, Minneapolis, Minn., USA), separated from the working fluid by a differential pressure indicator (MKS,

Table 2. Values of the Vapor Pressure P , Standard Deviations $\delta P/P$ (%), Activity Coefficients γ_1 and γ_2 , and Excess Molar Gibbs Functions G^E , for the Binary System MEA (1) + Water (2)

x_1	y_1	P/kPa	$\delta P/P$ (%)	γ_1	γ_2	$G^E/\text{J}\cdot\text{mol}^{-1}$	x_1	y_1	P/kPa	$\delta P/P$ (%)	γ_1	γ_2	$G^E/\text{J}\cdot\text{mol}^{-1}$
$T = 283.15\text{ K}$							$T = 333.15\text{ K}$						
0.0000	0.0000	1.1995	0.00	0.3220	1.0000	0.0	0.0000	0.0000	19.6156	0.00	0.2557	1.0000	0.0
0.0527	0.0002	1.1363	-0.05	0.3130	1.0004	-143.2	0.0527	0.0007	18.7262	1.30	0.3189	0.9942	-182.2
0.1190	0.0006	1.0671	1.50	0.3322	0.9942	-320.8	0.1190	0.0021	17.1441	1.73	0.4002	0.9734	-367.6
0.2023	0.0014	0.9290	0.77	0.3922	0.9623	-518.0	0.2023	0.0051	14.9731	2.16	0.5018	0.9325	-540.9
0.2740	0.0026	0.7888	-0.63	0.4695	0.9094	-650.1	0.2740	0.0092	12.6144	-1.02	0.5871	0.8879	-643.2
0.3759	0.0060	0.5974	-1.26	0.6067	0.8036	-763.6	0.3759	0.0190	9.8436	-3.01	0.7034	0.8142	-721.6
0.5214	0.0178	0.3779	1.36	0.8076	0.6380	-768.8	0.5214	0.0473	7.0760	3.16	0.8519	0.6973	-709.4
0.6840	0.0515	0.1986	-0.55	0.9531	0.5000	-593.0	0.6840	0.1195	3.9889	-1.29	0.9686	0.5760	-543.4
0.8480	0.1436	0.0930	0.10	0.9974	0.4365	-301.9	0.8480	0.2898	2.1527	0.27	1.0076	0.5134	-263.0
1.0000	1.0000	0.0158	0.00	1.0000	0.4282	0.0	1.0000	1.0000	0.7274	0.00	1.0000	0.6008	0.0
$T = 293.15\text{ K}$							$T = 343.15\text{ K}$						
0.0000	0.0000	2.2838	0.00	0.2776	1.0000	0.0	0.0000	0.0000	30.8153	0.00	0.2727	1.0000	0.0
0.0527	0.0003	2.1697	0.48	0.2984	0.9979	-160.3	0.0527	0.0008	29.4211	1.28	0.3379	0.9944	-178.4
0.1190	0.0008	2.0146	1.57	0.3417	0.9849	-344.1	0.1190	0.0026	26.9824	1.73	0.4182	0.9749	-359.8
0.2023	0.0019	1.7528	1.51	0.4208	0.9460	-534.7	0.2023	0.0061	23.6113	1.91	0.5134	0.9377	-531.2
0.2740	0.0036	1.4658	-1.25	0.5072	0.8922	-655.1	0.2740	0.0108	20.1650	-0.49	0.5903	0.8978	-635.4
0.3759	0.0082	1.1224	-1.50	0.6477	0.7932	-750.4	0.3759	0.0217	15.7391	-3.46	0.6940	0.8307	-722.1
0.5214	0.0233	0.7327	1.79	0.8398	0.6435	-736.2	0.5214	0.0527	11.5226	3.42	0.8312	0.7174	-728.5
0.6840	0.0636	0.3969	-0.74	0.9720	0.5192	-552.1	0.6840	0.1338	6.4709	-1.39	0.9507	0.5863	-580.0
0.8480	0.1658	0.1968	0.14	1.0048	0.4726	-267.7	0.8480	0.3298	3.4854	0.30	1.0019	0.4999	-296.1
1.0000	1.0000	0.0382	0.00	1.0000	0.5170	0.0	1.0000	1.0000	1.3472	0.00	1.0000	0.5454	0.0
$T = 303.15\text{ K}$							$T = 353.15\text{ K}$						
0.0000	0.0000	4.1478	0.00	0.2544	1.0000	0.0	0.0000	0.0000	47.0737	0.00	0.2972	1.0000	0.0
0.0527	0.0003	3.9488	0.86	0.2934	0.9961	-172.3	0.0527	0.0010	44.9353	1.20	0.3614	0.9949	-171.7
0.1190	0.0010	3.6387	1.64	0.3537	0.9786	-359.7	0.1190	0.0031	41.3398	1.71	0.4367	0.9776	-348.0
0.2023	0.0025	3.1664	1.98	0.4462	0.9360	-544.6	0.2023	0.0072	36.2541	1.55	0.5214	0.9453	-518.5
0.2740	0.0048	2.6291	-1.55	0.5379	0.8828	-656.3	0.2740	0.0124	31.4879	0.17	0.5877	0.9107	-627.0
0.3759	0.0107	2.0295	-1.81	0.6774	0.7902	-739.3	0.3759	0.0241	24.5504	-3.92	0.6773	0.8506	-726.6
0.5214	0.0292	1.3628	2.18	0.8593	0.6525	-714.2	0.5214	0.0574	18.2721	3.64	0.8030	0.7402	-758.6
0.6840	0.0767	0.7535	-0.91	0.9823	0.5363	-527.1	0.6840	0.1476	10.1845	-1.46	0.9267	0.5958	-633.4
0.8480	0.1914	0.3887	0.18	1.0094	0.4983	-246.9	0.8480	0.3733	5.4430	0.33	0.9936	0.4786	-344.9
1.0000	1.0000	0.0867	0.00	1.0000	0.5842	0.0	1.0000	1.0000	2.3998	0.00	1.0000	0.4685	0.0
$T = 313.15\text{ K}$							$T = 363.15\text{ K}$						
0.0000	0.0000	7.2219	0.00	0.2452	1.0000	0.0	0.0000	0.0000	70.1021	0.00	0.3295	1.0000	0.0
0.0527	0.0004	6.8852	1.11	0.2960	0.9949	-179.6	0.0527	0.0013	66.8887	1.07	0.3891	0.9957	-162.6
0.1190	0.0013	6.3158	1.68	0.3677	0.9749	-368.3	0.1190	0.0037	61.7997	1.68	0.4552	0.9813	-332.9
0.2023	0.0033	5.5003	2.22	0.4682	0.9309	-548.4	0.2023	0.0083	54.3261	1.11	0.5257	0.9550	-503.8
0.2740	0.0062	4.5650	-1.58	0.5613	0.8797	-654.3	0.2740	0.0139	48.1112	0.95	0.5797	0.9263	-618.9
0.3759	0.0134	3.5436	-2.17	0.6961	0.7934	-730.7	0.3759	0.0262	37.4297	-4.37	0.6544	0.8737	-735.7
0.5214	0.0353	2.4403	2.54	0.8671	0.6647	-702.5	0.5214	0.0613	28.2757	3.81	0.7685	0.7656	-800.5
0.6840	0.0906	1.3664	-1.05	0.9848	0.5512	-517.4	0.6840	0.1605	15.5943	-1.51	0.8966	0.6049	-705.0
0.8480	0.2206	0.7231	0.21	1.0113	0.5134	-239.1	0.8480	0.4200	8.2313	0.37	0.9823	0.4508	-411.4
1.0000	1.0000	0.1855	0.00	1.0000	0.6223	0.0	1.0000	1.0000	4.1263	0.00	1.0000	0.3791	0.0
$T = 323.15\text{ K}$													
0.0000	0.0000	12.1070	0.00	0.2462	1.0000	0.0							
0.0527	0.0005	11.5528	1.25	0.3048	0.9943	-182.7							
0.1190	0.0017	10.5762	1.71	0.3833	0.9733	-370.7							
0.2023	0.0041	9.2219	2.27	0.4868	0.9300	-546.9							
0.2740	0.0077	7.6934	-1.40	0.5776	0.8817	-649.7							
0.3759	0.0162	5.9931	-2.57	0.7044	0.8016	-724.6							
0.5214	0.0414	4.2215	2.87	0.8643	0.6797	-700.9							
0.6840	0.1049	2.3782	-1.18	0.9800	0.5644	-522.8							
0.8480	0.2533	1.2767	0.24	1.0106	0.5182	-244.3							
1.0000	1.0000	0.3762	0.00	1.0000	0.6278	0.0							

model 615D, MKS Instruments, USA). The pressure gauges were periodically checked against a Hg or oil manometer and a Bouty (Paris, France) type 70298 cathetometer, which when combined provide pressures with an uncertainty of 1 Pa. The temperature of the oil-filled thermostat was maintained constant to $\pm 0.01\text{ K}$. The temperature was measured by means of a copper–constantan thermocouple calibrated against a Leeds and Northrup standard platinum resistance thermometer 8163-B, calibrated by the National Bureau of Standards (Washington D.C., USA) and connected to a Mueller type G2 bridge (with a precision of $10^{-4}\ \Omega$). All temperatures are reported on ITS-90. The estimated uncertainties in pressure, temperature, and mole fraction are: $\sigma(P) = 0.15(P/\text{Pa})$ for $P < 13.3\text{ Pa}$, $\sigma(P) = 0.05(P/\text{Pa})$ at pressure between (13.3 and 200) Pa, $\sigma(P) =$

$0.005(P/\text{Pa})$ in the range (200 to 1000) Pa, $\sigma(P) = 0.002(P/\text{Pa})$ for the range (1000 to $200 \cdot 10^3$) Pa, $\sigma(T) = 0.01\text{ K}$, and $\sigma(x_i) = 0.0002$.

Mixtures were prepared by mass and thoroughly degassed by distillation as described by Blondel-Tellouk et al.^{13,14} The final composition of the liquid was determined after each pressure measurement by gas liquid chromatography with a column filled with a stationary phase of Carbowax and a thermal conductivity detector.

Results and Discussion

The experimental vapor pressure data were fitted to the Antoine equation

Table 3. Values of the Vapor Pressure P , Standard Deviations $\delta P/P$ (%), Activity Coefficients γ_1 and γ_2 , and Excess Molar Gibbs Functions G^E for the Binary System 4-Methylmorpholine (1) + Water (2)

x_1	y_1	P/kPa	$\delta P/P$ (%)	γ_1	γ_2	$G^E/\text{J}\cdot\text{mol}^{-1}$
$T = 313.15 \text{ K}$						
0.0000	0.0000	7.2219	0.00	1.9699	1.0000	0.0
0.0500	0.0786	7.4594	-0.01	1.8194	1.0018	82.4
0.1585	0.2240	7.8856	0.01	1.7257	1.0069	240.2
0.3486	0.4371	8.5495	-0.02	1.6572	1.0240	498.7
0.4955	0.5302	8.7841	0.04	1.4510	1.1336	645.0
0.6669	0.5768	8.7493	-0.01	1.1684	1.5420	645.9
0.8478	0.6807	8.6173	-0.00	1.0124	2.3787	370.6
1.0000	1.0000	6.4707	0.00	1.0000	2.4630	0.0
$T = 323.15 \text{ K}$						
0.0000	0.0000	12.1070	0.00	2.6256	1.0000	0.0
0.0500	0.0905	12.6941	0.01	2.2610	1.0036	118.7
0.1585	0.2303	13.5099	-0.01	1.9274	1.0208	325.9
0.3486	0.4168	14.4246	-0.08	1.6901	1.0686	607.7
0.4955	0.4987	14.6771	0.17	1.4427	1.2044	740.0
0.6669	0.5423	14.5043	-0.07	1.1545	1.6504	705.8
0.8478	0.6566	13.2915	-0.01	1.0070	2.4849	388.1
1.0000	1.0000	10.2075	-0.00	1.0000	2.3863	0.0
$T = 333.15 \text{ K}$						
0.0000	0.0000	19.6156	0.00	3.2562	1.0000	0.0
0.0500	0.1007	20.8320	0.07	2.7030	1.0045	149.6
0.1585	0.2365	22.2643	-0.08	2.1376	1.0307	404.0
0.3486	0.3969	23.4765	-0.12	2.7151	1.1107	710.3
0.4955	0.4674	23.7023	0.30	1.4272	1.2740	826.7
0.6669	0.5123	23.2288	-0.12	1.1433	1.7401	758.6
0.8478	0.6374	20.8995	-0.01	1.0060	2.5492	408.6
1.0000	1.0000	15.5830	0.00	1.0000	2.4425	0.0
$T = 343.15 \text{ K}$						
0.0000	0.0000	30.8153	0.00	3.8690	1.0000	0.0
0.0500	0.1093	33.0868	0.13	3.1429	1.0051	177.2
0.1585	0.2415	35.4381	-0.18	2.3443	1.0385	476.0
0.3486	0.3776	36.9904	-0.13	1.7325	1.1497	805.9
0.4955	0.4378	37.1169	0.38	1.4091	1.3396	905.7
0.6669	0.4859	36.0621	-0.14	1.1345	1.8139	806.0
0.8478	0.6212	31.8634	-0.01	1.0072	2.5873	430.2
1.0000	1.0000	23.1011	0.00	1.0000	2.5611	0.0
$T = 353.15 \text{ K}$						
0.0000	0.0000	47.0737	0.00	4.4785	1.0000	0.0
0.0500	0.1166	51.0198	0.19	3.5787	1.0056	202.7
0.1585	0.2448	54.6709	-0.28	2.5391	1.0452	542.9
0.3486	0.3592	56.6018	-0.11	1.7433	1.1855	894.4
0.4955	0.4106	56.5241	0.43	1.3907	1.3995	977.8
0.6669	0.4625	54.4334	-0.16	1.1270	1.8749	848.9
0.8478	0.6069	47.2466	-0.01	1.0091	2.6093	451.2
1.0000	1.0000	33.3536	0.00	1.0000	2.6959	0.0
$T = 363.15 \text{ K}$						
0.0000	0.0000	70.1021	0.00	5.0933	1.0000	0.0
0.0500	0.1227	76.5902	0.23	4.0072	1.0060	226.8
0.1585	0.2465	81.9961	-0.39	2.7170	1.0513	605.6
0.3486	0.3418	84.3427	-0.07	1.7487	1.2180	976.1
0.4955	0.3860	83.9213	0.45	1.3730	1.4533	1043.7
0.6669	0.4416	80.0946	-0.16	1.1204	1.9255	887.9
0.8478	0.5941	68.3167	0.00	1.0110	2.6207	470.8
1.0000	1.0000	47.0220	0.00	1.0000	2.8215	0.0

$$\log_{10} P (\text{mm Hg}) = A - \frac{B}{C + t (^\circ\text{C})} \quad (1)$$

The objective function Q was the sum of the squared relative deviations in pressure

$$Q = \sum \left(\frac{P_{\text{calc}} - P_{\text{exp}}}{P_{\text{exp}}} \right)^2 \quad (2)$$

The overall mean relative deviation in pressure is

$$\frac{\delta P}{P} \% = \frac{100}{N} \sum \left(\frac{P_{\text{calc}} - P_{\text{exp}}}{P_{\text{exp}}} \right) \quad (3)$$

where N , the total number of experimental values, is less than 0.1 %.

Table 1 lists, for the pure components MEA, 4-methylmorpholine, and water, the temperature range, the coefficients A , B , and C of the Antoine equation, and the overall mean relative deviation in pressure.

For pure MEA, our vapor pressure data agree to within 0.10 % with those reported in the literature²⁻⁵ in the temperature range (313 to 363) K as shown in Figure 1. For pure water, our vapor pressure data agree to within 0.02 % with those reported in the literature²⁻⁶ (Figure 2) in the temperature range (298 to 363) K. For pure 4-methylmorpholine, our vapor pressures agree with those reported by Cabani et al.⁸ to within 1 % in the temperature range (273 to 313) K (Figure 3).

For the two binary mixtures, the vapor pressures were measured at temperatures between (283.15 (or 313.15 K) and 363.15) K, and the results fitted to the Antoine equation. The molar excess Gibbs functions G^E were estimated from the Redlich-Kister equation using Barker's¹⁵ method

$$G^E = x_1(1 - x_1) \sum_{j=1}^m RTG_j(2x_1 - 1)^{j-1} \quad (4)$$

where x_1 is the molar fraction for the alkanolamine. The coefficients G_j were determined by regression through minimization of the sum of deviations in pressure. Vapor-phase imperfection and variation of Gibbs function of the pure liquid components with pressure were accounted for in terms of the second molar virial coefficients, estimated by the method of Tsionopoulos,^{16,17} and the molar volumes under saturation pressure.

The vapor pressures as a function of the mole fraction for each binary are listed in Table 2 and Table 3 and shown in Figures 4 and 5.

Tables 2 and 3 also list for ((MEA) + water) or (4-methylmorpholine + water) the corresponding compositions of

Table 4. Coefficients G_j and Standard Deviations σ (kPa) for Least-Squares Representations by Equation 4

T/K	G_1	σ	G_2	σ	G_3	σ	G_4	σ
MEA + water								
283.15	-1.32339	(0.024)	0.33259	(0.032)	0.33267	(0.063)	-0.19006	(0.133)
293.15	-1.22828	(0.032)	0.40829	(0.044)	0.25771	(0.086)	-0.09742	(0.181)
303.15	-1.15456	(0.039)	0.43702	(0.054)	0.20145	(0.106)	-0.02141	(0.223)
313.15	-1.09971	(0.045)	0.42589	(0.063)	0.15972	(0.122)	0.03980	(0.254)
323.15	-1.06182	(0.049)	0.38022	(0.069)	0.12830	(0.134)	0.08772	(0.278)
333.15	-1.03953	(0.052)	0.30385	(0.075)	0.10292	(0.143)	0.12334	(0.297)
343.15	-1.03191	(0.054)	0.19952	(0.081)	0.07922	(0.152)	0.14703	(0.313)
353.15	-1.03842	(0.057)	0.06909	(0.087)	0.05267	(0.162)	0.15840	(0.331)
363.15	-1.05882	(0.061)	-0.08622	(0.095)	0.01862	(0.173)	0.15635	(0.351)
4-methylmorpholine + water								
313.15	0.99532	(<10 ⁻³)	0.47224	(0.003)	-0.20564	(0.006)	-0.36053	(0.012)
323.15	1.10486	(0.003)	0.33800	(0.013)	-0.18734	(0.022)	-0.38578	(0.047)
333.15	1.19568	(0.005)	0.20280	(0.020)	-0.15889	(0.036)	-0.34655	(0.075)
343.15	1.12705	(0.007)	0.07614	(0.024)	-0.12378	(0.045)	-0.28242	(0.091)
353.15	1.33177	(0.008)	-0.03817	(0.027)	-0.08626	(0.050)	-0.21561	(0.101)
363.15	1.38156	(0.009)	-0.13952	(0.028)	-0.04896	(0.054)	-0.15581	(0.108)

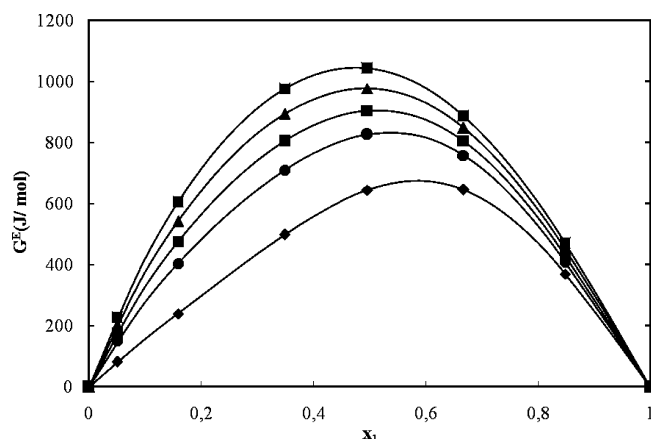


Figure 8. G^E against x_1 for the 4-methylmorpholine (1) + water (2) system: $\blacklozenge$, 313.15 K; $\bullet$, 333.15 K; $\blacksquare$, 343.15 K; $\blacktriangle$, 353.15 K; $\blacktriangledown$, 363.15 K; —, calculated values using eq 4.

the liquid and vapor phases, the activity coefficients γ_1 and γ_2 , and the values of the excess molar Gibbs functions G^E calculated by Barker's method, using the Redlich–Kister equation.

Table 4 lists for the two investigated binary mixtures the coefficients G_j and standard deviations σ for least-squares representations by eq 4.

The (4-methylmorpholine + water) system shows maximum azeotropic behavior over the whole temperature range. The azeotropic compositions vary from 0.6500 at ($T = 313.15$ K) to 0.3500 at ($T = 363.15$ K).

For (MEA + water), as shown in Figure 6, our P – x – y data are in good agreement with those reported by Nath³ (at 333.15 K), Tochigi⁴ (at 363.15 K), and Kim⁵ (at (313.15, 333.15, and 353.15 K)). For (4-methylmorpholine + water), no comparisons were possible for the investigated temperature–pressure–composition (P – x – y) range.

For each system, the molar excess Gibbs functions G^E at different temperatures, calculated from our vapor pressure data, are plotted in Figure 7 and Figure 8 against the mole fraction x_1 of alkanolamine.

The (MEA + water) binary mixture exhibits negative deviations in G^E values calculated from the vapor pressure data. The equimolar G^E of (MEA + water) increases with increasing temperature from $-779 \text{ J}\cdot\text{mol}^{-1}$ at $T = 283.15$ K to $-720 \text{ J}\cdot\text{mol}^{-1}$ at $T = 33.15$ K, then decreases with increasing temperature to $-799 \text{ J}\cdot\text{mol}^{-1}$ (at $T = 363.15$ K).

The (4-methylmorpholine + water) binary mixture exhibits positive deviations in G^E values calculated from the vapor pressure data. The equimolar G^E of (4-methylmorpholine + water) increases with increasing temperature from $646 \text{ J}\cdot\text{mol}^{-1}$ at $T = 313.15$ K to $1045 \text{ J}\cdot\text{mol}^{-1}$ at $T = 363.15$ K.

Summary

Vapor–liquid equilibrium data for the two binary mixtures of (MEA + water) or (4-methylmorpholine + water) were measured at several temperatures using two static devices. Deviations from Raoult's law are negative for the (MEA +

water) and positive for the (4-methylmorpholine + water) binary mixtures and relatively large.

Acknowledgment

This paper is dedicated to the memory of Professor Aïcha Yacouta Nour.

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Received for review July 8, 2008. Accepted May 7, 2009. One of the authors (A. B.) gratefully acknowledges a grant from the Algerian Ministry of High Education and Scientific Research (MESRS).

JE800530U