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# 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 $CO_2$ and $H_2S$, 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 reference[8] 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.

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

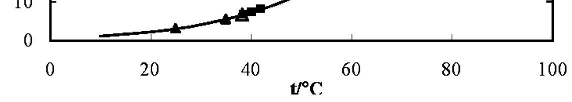

**Figure 1.** Equilibrium vapor pressure of water at different temperatures: −, this work; ▲, ref 2; ●, ref 3; ◆, ref 4; ■, ref 5; △, ref 6.

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 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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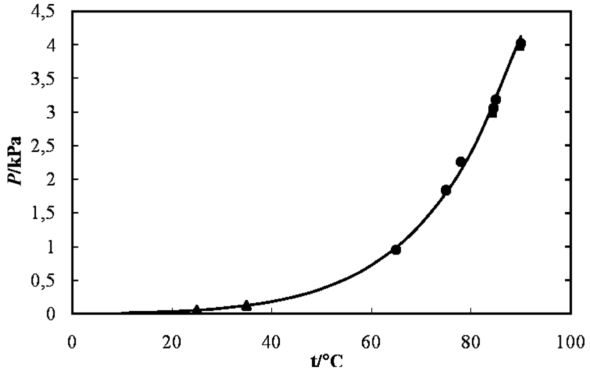

**Figure 2.** Equilibrium vapor pressure of MEA at different temperatures: −, this work; ▲, ref 2; ●, ref 3; ◆, ref 4; ■, ref 5.

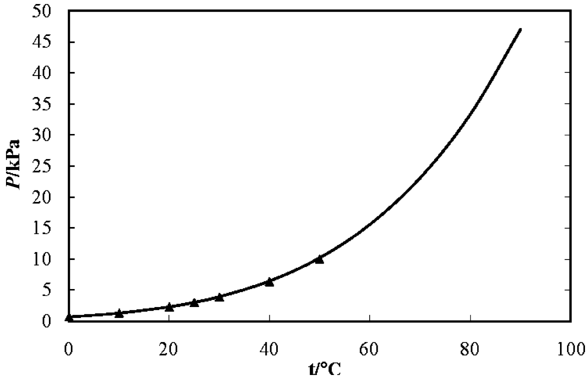

**Figure 3.** Equilibrium vapor pressure of 4-methylmorpholine at different temperatures: −, this work; ▲, ref 8.

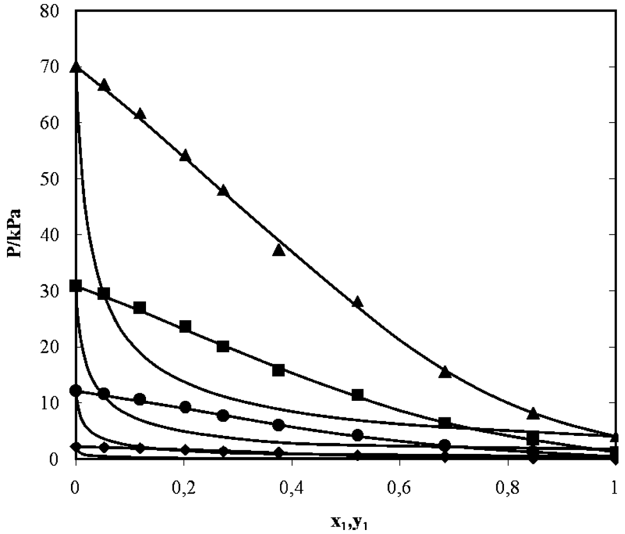

**Figure 4.** Experimental and calculated $P-x(y)$ behavior of the system MEA (1) + water (2) at different temperatures: ◆, 293.15 K; ●, 323.15 K; ■, 343.15; ▲, 363.15 K; −, calculated values using Barker's method.

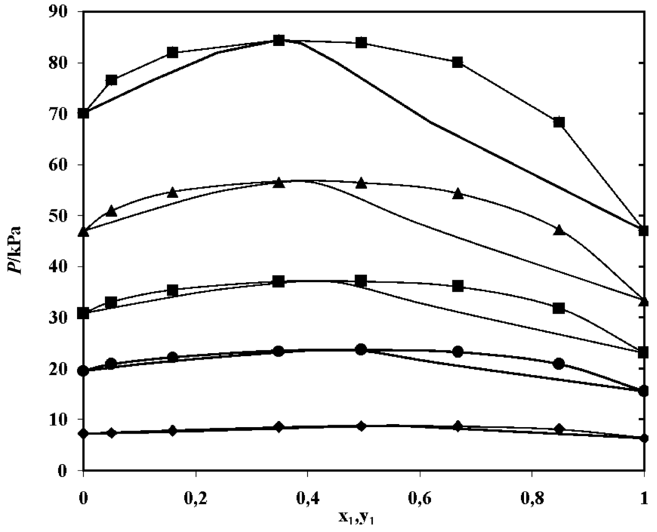

**Figure 5.** Experimental and calculated $P-x(y)$ behavior of the system 4-methylmorpholine (1) + water (2) at different temperatures: ♦, 313.15 K; ■, 333.15 K; ●, 343.15 K; ■, 353.15 K; ▲, 363.15 K; −, calculated values using Barker's method.

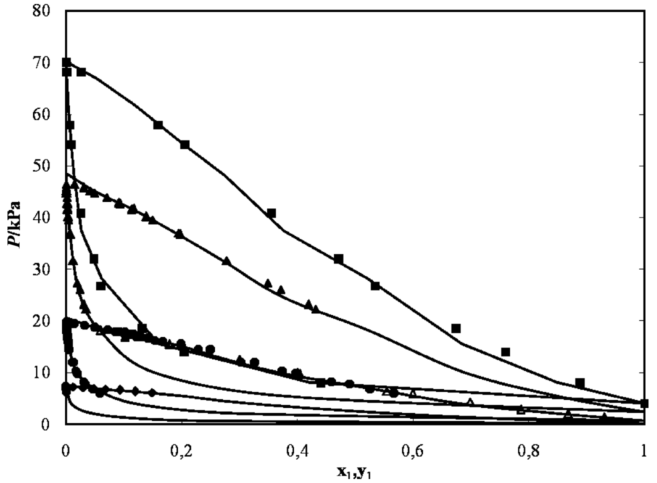

**Figure 6.** Total pressure $P$ versus liquid (vapor) phase compositions ($P-x(y)$): −, this work at (313.15, 333.15, 353.15, and 363.15) K; ◆, ref 5 at 313.15 K; ●, ref 5 at 333.15 K; △, ref 3 at 333.15 K; ▲, ref 5 at 353.15 K; ■, ref 4 at 363.15 K for the system MEA (1) + water (2).

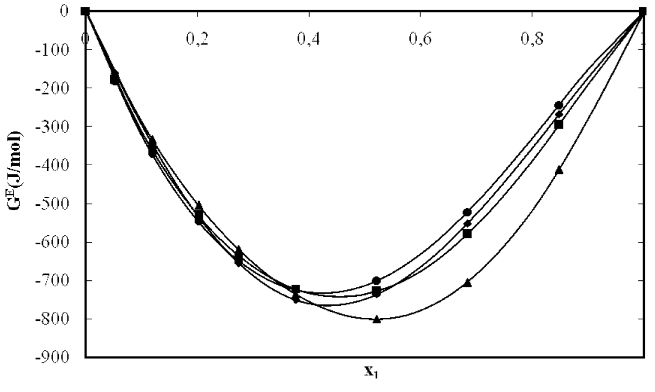

**Figure 7.** $G^E$ against $x_1$ for the MEA (1) + water (2) system: ◆, 293.15 K; ●, 323.15 K; ■, 343.15 K; ▲, 363.15 K; −, calculated values using eq 4.

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 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 $\gamma_1$ and $\gamma_2$, and Excess Molar Gibbs Functions $G^E$, for the Binary System MEA (1) + Water (2)**

| $x_1$ | $y_1$ | $P$/kPa | $\delta P/P$ (%) | $\gamma_1$ | $\gamma_2$ | $G^E$/J·mol$^{-1}$ | $x_1$ | $y_1$ | $P$/kPa | $\delta P/P$ (%) | $\gamma_1$ | $\gamma_2$ | $G^E$/J·mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $T = 283.15$ K | | | | | | | $T = 333.15$ 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 |
| | | | $T = 293.15$ K | | | | | | | $T = 343.15$ 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 |
| | | | $T = 303.15$ K | | | | | | | $T = 353.15$ 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 |
| | | | $T = 313.15$ K | | | | | | | $T = 363.15$ 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 |
| | | | $T = 323.15$ 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 ± 0.01 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 $10^{-4}$ Ω). 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 $P < 13.3$ 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, $\sigma(T) = 0.01$ 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 $\gamma_1$ and $\gamma_2$, and Excess Molar Gibbs Functions $G^E$ for the Binary System 4-Methylmorpholine (1) + Water (2)**

| $x_1$ | $y_1$ | $P$/kPa | $\delta P/P$ (%) | $\gamma_1$ | $\gamma_2$ | $G^E$/J·mol$^{-1}$ |
|---|---|---|---|---|---|---|
| | | | $T = 313.15$ 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 |
| | | | $T = 323.15$ 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 |
| | | | $T = 333.15$ 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 |
| | | | $T = 343.15$ 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 |
| | | | $T = 353.15$ 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 |
| | | | $T = 363.15$ 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 |

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

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

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

The overall mean relative deviation in pressure is

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

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 literature[2−5] 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 literature[2−6] (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's[15] method

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

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 Tsonopoulos,[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 $\sigma$ (kPa) for Least-Squares Representations by Equation 4**

| $T$/K | $G_1$ | $\sigma$ | $G_2$ | $\sigma$ | $G_3$ | $\sigma$ | $G_4$ | $\sigma$ |
|---|---|---|---|---|---|---|---|---|
| | | | | 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-methymorpholine + 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) |

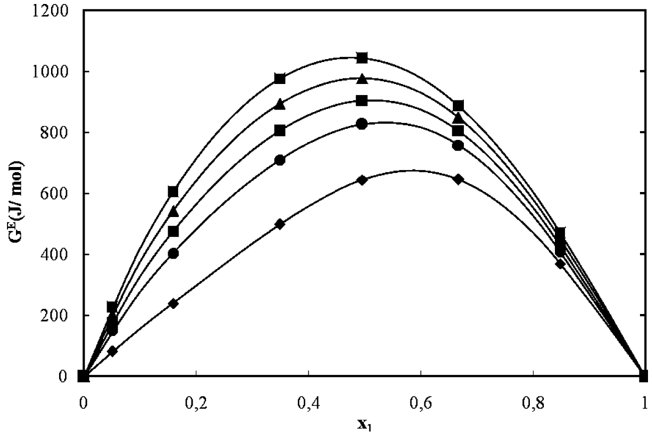

**Figure 8.** $G^E$ against $x_1$ for the 4-methylmorpholine (1) + water (2) system: ◆, 313.15 K; ●, 333.15 K; ■, 343.15 K; ▲, 353.15K; ■, 363.15 K; —, calculated values using eq 4.

the liquid and vapor phases, the activity coefficients $\gamma_1$ and $\gamma_2$, 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 $\sigma$ 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 Nath[3] (at 333.15 K), Tochigi[4] (at 363.15 K), and Kim[5] (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 $-779\ \mathrm{J \cdot mol^{-1}}$ at $T$ = 283.15 K to $-720\ \mathrm{J \cdot mol^{-1}}$ at $T$ = 33.15 K, then decreases with increasing temperature to $-799\ \mathrm{J \cdot mol^{-1}}$ (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 $646\ \mathrm{J \cdot mol^{-1}}$ at $T$ = 313.15 K to $1045\ \mathrm{J \cdot mol^{-1}}$ 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.

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## Literature Cited

(1) Kohl, A.; Nielsen, R. *Gas Purification*, 5th ed.; Gulf Publishing Co.: Houston, 1997.

(2) Touhara, H.; Okazaki, S.; Okino, F.; Tanaka, H.; Ikari, K.; Nakanishi, K. Thermodynamic Properties of Aqueous Mixtures of Hydrophilic Compounds 2. Aminoethanol and Its Methyl Derivatives. *J. Chem. Thermodyn.* **1982**, *14* (2), 145–156.

(3) Nath, A.; Eberhard, A. Isothermal vapor-liquid equilibriums of binary and ternary mixtures containing alcohol, alkanolamine, and water with a new static device. *J. Chem. Eng. Data* **1983**, *28* (4), 370–375.

(4) Tochigi, K.; Akimoto, K.; Ochi, K.; Liu, F.; Kawase, Y. Isothermal vapor-liquid equilibria for water + 2-aminoethanol + dimethyl sulfoxide and its constituent three binary systems. *J. Chem. Eng. Data* **1999**, *44* (3), 588–590.

(5) Kim, I.; Svendsen, H. F.; Borrensen, E. Ebulliometric Determination of vapor-liquid equilibria for pure water, monoethanolamine, n-methyldiethanoalmine, 3-(methylamino)-propylamine, and their binary and ternary solutions. *J. Chem. Eng. Data* **2008**, *53*, 2421–2531.

(6) Cai, Z.; Xie, R.; Wu, Z. Binary isobaric vapor-liquid equilibria of ethanolamines + water. *J. Chem. Eng. Data* **1996**, *41* (5), 1101–1103.

(7) Park, S. B.; Lee, H. Vapour-liquid equilibria for the binary monoethanolamine + water and monoethanolamine + ethanol systems. *Korean J. Chem. Eng.* **1997**, *14*, 146–148.

(8) Cabani, S.; Conti, A.; Giannessi, D.; Lepori, L. Thermodynamic study of aqueous dilute solutions of organic compounds. Part 3.-Morpholines and Piperazines. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 1154–1160.

(9) Sawaya, T.; Mokbel, I.; Rauzy, E.; Saab, J.; Berro, C.; Jose, J. Experimental vapour pressures of alkyl and aryl sulfides. Prediction by a group contribution method. *Fluid Phase Equilib.* **2004**, *226*, 283–288.

(10) Sarraute, S.; Mokbel, I.; Costa Gomes, M. F.; Majer, V.; Delepine, H.; Jose, J. Vapour pressures, aqueous solubility, Henry's law constants and air/water partition coefficients of 1,8-dichlorooctane and 1,8-dibromooctane. *Chemosphere* **2006**, *64*, 1829–1836.

(11) Sawaya, T.; Mokbel, I.; Ainous, N.; Rauzy, E.; Berro, C.; Jose, J. Experimental vapor pressures of six*n*-Alkanes (C21, C23, C25, C27, C29, C30) in the temperature range between 350 and 460 K. *J. Chem. Eng. Data* **2006**, *51*, 854–858.

(12) Sarraute, S.; Mokbel, I.; Costa Gomes, M. F.; Majer, V; Jose, J. Atmosphere/water partition of halocyclohexanes from vapour pressure and solubility data. *Atmos. Environ.* **2008**, *42*, 4724–4734.

(13) Blondel-Telouk, A. Conception et mise au point d'un dispositif statique pour ladétermination de la masse molaire moyenne des coupes pétrolières par tonométrie. Etude d'équilibres liquide-vapeur de quatre systèmes binaires. Thèse de Doctorat (Université Lyon I, France), 1994; pp 1−272.

(14) Blondel-Telouk, A.; Loiseleur, H.; Barreau, A.; Behar, E.; Jose, J. Determination of the average molecular weight of petroleum cuts by vapor pressure depression. *Fluid Phase Equilib.* **1995**, *110*, 315–339.

(15) Barker, J. A. Determination of Activity Coefficients from total pressure measurements. *Aust. J. Chem.* **1953**, *6* (3), 207–210.

(16) Tsonopoulos, C. An empirical correlation of second virial coefficients. *AIChE J.* **1974**, *20*, 263–272.

(17) Tsonopoulos, C. Second virial coefficients of polar haloalkanes. *AIChE J.* **1975**, *21*, 827–829.

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