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Ebulliometric Determination of Vapor−Liquid Equilibria for Pure Water, Monoethanolamine, *N*-Methyldiethanolamine, 3-(Methylamino)-propylamine, and Their Binary and Ternary Solutions

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Vapor−liquid equilibria (VLE) for binary and ternary aqueous solutions of water, monoethanolamine (MEA), *N*-methyldiethanolamine (MDEA), and 3-(methylamino)propylamine (MAPA) were measured in a modified Swietoslawski ebulliometer at (40, 60, 80, and 100) °C. Experimental temperature (T) and total pressure (P) were measured, and the compositions of both the liquid (x) and vapor (y) phases were analyzed. Boiling temperatures (T_b) of pure water and amines were measured over the pressure range of $P = (2.5 \text{ to } 101.3)$ kPa. Experimental activity coefficients (γ) were calculated from the experimental P, T, x, and y data and were fit to the Wilson and NRTL equations.

Introduction

Vapor−liquid equilibria (VLE) are fundamental properties, and a knowledge of them is essential for the design and operation of separation processes. Many experiments are necessary for obtaining such equilibrium data, at least for binary systems, where nonidealities in both phases must be determined.[1] Ebulliometry enables very fast and accurate determination of the vapor−liquid equilibrium. The accuracy of the results is limited by only the purity of the substances used and the precision of the analytical methods used for the sample analyses. An advantage of the method is that degassing is not required. It also involves a simple apparatus, and straightforward procedures are used.[2]

Aqueous alkanolamine solutions are widely used for the removal of the acid gases (CO_2 and H_2S) from gas mixtures. In addition to the well-established industrial uses of experimental data for these completely miscible (water + alkanolamine) systems, there is a general scientific interest in using such experimental data in combination with theories or mathematical models to improve our understanding of molecular interactions in nonideal liquid systems.[3]

For proper thermodynamic modeling, accurate equilibrium data for the amine + water binary system over a wide range of temperatures, pressures, and amine concentrations are essential. Values of the limiting activity coefficients (γ^∞) are important for the development of new thermodynamic models as well as for the adjustment of reliable model parameters or the choice of selective solvents for the absorption.

Table 1. Equlibrium Vapor Pressures of Pure H_2O with Relative Deviations from Riedel Equation[27]

T °C	P kPa	% dev	T °C	P kPa	% dev	T °C	P kPa	% dev
38.48	6.78	−0.74	75.65	39.83	0.37	89.74	69.83	0.53
40.09	7.38	−0.86	75.69	39.83	0.21	89.78	69.83	0.38
41.84	8.11	−0.71	76.76	41.40	−0.35	94.33	82.79	0.36
49.96	12.28	−0.62	76.79	41.39	−0.51	94.34	82.79	0.32
49.99	12.28	−0.78	76.82	41.40	−0.57	94.52	82.79	−0.35
50.00	12.27	−0.89	79.99	47.18	−0.48	94.54	82.79	−0.40
52.32	13.78	−0.70	80.00	47.18	−0.50	94.54	82.78	−0.44
52.46	13.80	−1.24	83.87	55.17	−0.32	98.52	96.51	0.42
59.61	19.84	1.12	83.92	55.18	−0.49	98.55	96.51	0.31
59.70	19.84	0.70	83.93	55.17	−0.54	98.75	96.47	−0.43
60.02	19.88	−0.58	85.72	59.88	0.64	98.76	96.58	−0.36
60.02	19.88	−0.58	85.77	59.88	0.42	98.76	96.58	−0.38
60.03	19.88	−0.62	89.40	68.92	0.49	99.54	99.28	−0.39
60.04	19.87	−0.72	89.44	68.92	0.36	99.71	100.59	0.31
67.26	27.60	−0.41	89.65	69.00	−0.34	99.74	100.59	0.20
67.29	27.58	−0.60	89.68	69.00	−0.43	100.01	100.98	−0.39
67.32	27.60	−0.69	89.68	68.98	−0.46			

Table 2. Vapor Pressures of Monoethanolamine (MEA)

	P/kPa					P/kPa			
T_b/°C	meas	corr	% dev[a]	% dev[b]	T_b/°C	meas	corr	% dev[a]	% dev[b]
84.31	2.98	2.98	0.13	4.62	130.28	24.97	24.87	0.39	0.96
89.84	3.98	3.98	−0.01	3.91	135.04	29.97	29.98	−0.02	0.32
96.18	5.48	5.48	−0.02	3.25	142.66	39.95	39.99	−0.10	−0.08
101.14	6.98	6.98	0.03	2.82	142.63	39.98	39.95	0.09	0.12
105.26	8.47	8.47	−0.06	2.36	151.46	54.95	54.93	0.03	−0.17
110.92	10.97	10.97	−0.02	1.90	156.29	64.95	64.96	−0.02	−0.28
117.99	14.96	14.96	−0.03	1.34	158.46	69.95	69.94	0.02	−0.27
124.86	19.97	19.98	−0.03	0.87	162.46	79.95	79.95	0.00	−0.30

[a] Deviation from the correlation using Antoine parameters fitted in this work. [b] Deviation from the correlation using Riedel parameters from ref 28.

VLE data for alkanolamine + water systems are rarely available in the literature. Binary VLE data are often reported as the composition of the liquid phase either at constant pressure as a function of temperature or at constant temperature as a function of pressure (P, T, x data). Total pressure over MEA + H_2O solutions was measured by Nath and Bender[4] at (60, 78, and 91.7) °C and by Touhara[5] at (25 and 35) °C. Hilliard[6] measured vapor pressure over (3.5, 7.0, 11.0, and 23.8) molal MEA + H_2O solutions over the temperature range of (39.8 to 72.7) °C. Vapor-phase composition and activity coefficients were then calculated from the total pressure data on the basis of the Gibbs−Duhem equation. However, total vapor pressure data do not allow direct

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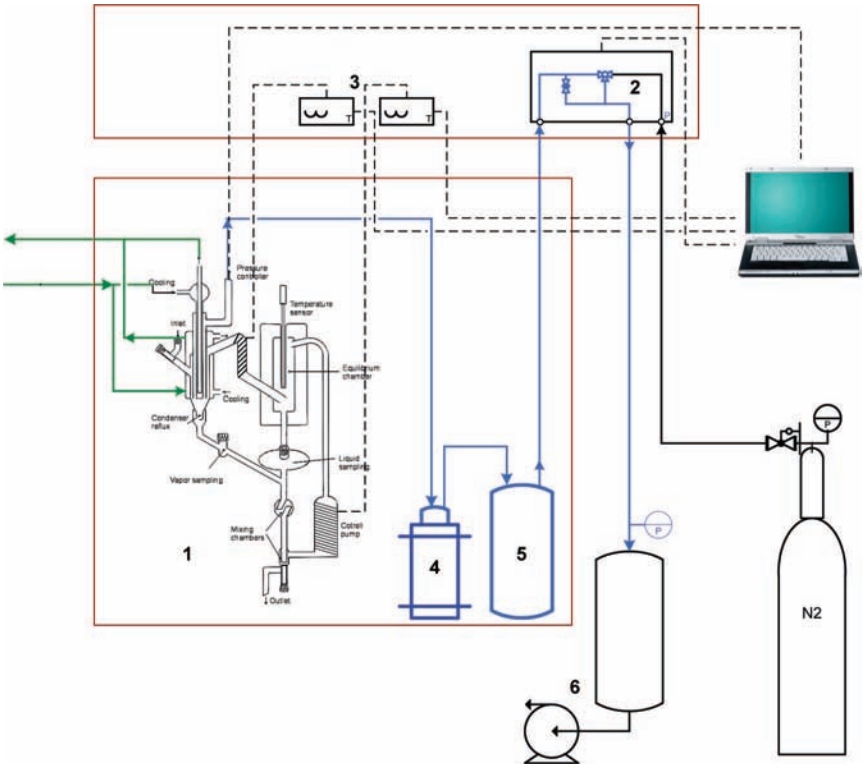

Figure 1. Experimental setup: 1, ebulliometer; 2, pressure controller; 3, temperature controllers; 4, cold trap; 5, buffer vessel; 6, vacuum pump with a buffer vessel.

Table 3. Vapor Pressure of *N*-Methyldiethanolamine (MDEA)

	P/kPa			
T_b/°C	meas	corr	% dev[a]	% dev[b]
136.54	2.48	2.48	0.13	11.20
140.28	2.98	2.98	−0.02	12.38
143.57	3.48	3.49	−0.37	13.07
148.81	4.48	4.46	0.53	15.13
153.50	5.48	5.49	−0.20	15.38
157.33	6.48	6.48	0.05	16.14
162.35	7.98	7.98	0.00	16.62

[a] Deviation from the correlation using Antoine parameters fitted in this work. [b] Deviation from the correlation using Riedel parameters from ref 19.

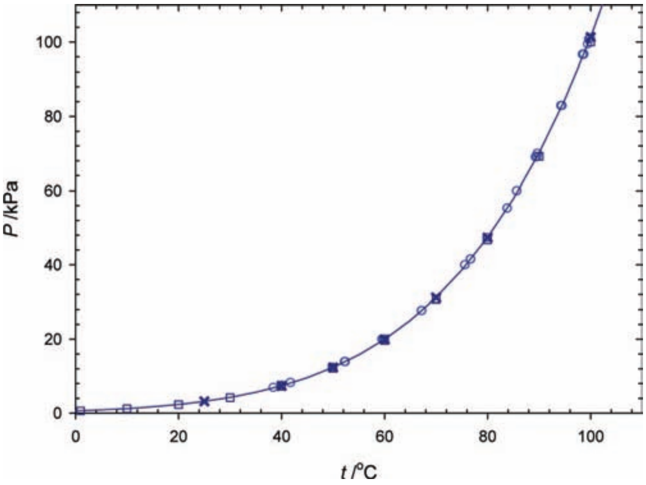

Figure 2. Equilibrium vapor pressure of water at different temperatures: ○, this work; ×, ref 25; □, ref 26; —, ref 27.

calculation of individual component activity coefficients or extrapolation to infinite dilution. Therefore, activity coefficients regressed from total pressure data cannot be accurately determined.[6] Experimental activity coefficients for MEA and water can be calculated from the *P*, *T*, *x*, and *y* data from Tochigi[7] at (70 and 90) °C and from isobaric measurements done by Park and Lee[8] at atmospheric pressure and by Cai et al.[9] at (66.66 and 101.33) kPa. Isobaric *T* and *x* measurements for the MDEA + H_2O solutions were performed by Voutsas et al.[10] at (40.0, 53.3, and 66.7) kPa and by Barreau et al.[11] at (30, 50, 70, 90, and 101.33) kPa. Xu et al.[12] reported total pressure data depending on temperature for aqueous MDEA solutions of different concentrations, $w = (0.10 \text{ to } 0.70)$. The authors calculated vapor-phase composition on the basis of the Gibbs−Duhem equation. No VLE data on MAPA and its aqueous solutions were found in the open literature.

Table 4. Vapor Pressure of 3-(Methylamino)propylamine (MAPA)

	P/kPa			
T_b/°C	meas	corr	% dev[a]	% dev[b]
53.66	3.46	3.46	0.00	4.37
58.47	4.47	4.45	0.53	4.87
64.21	5.97	5.92	0.78	5.04
70.76	7.97	8.09	−1.56	2.67
80.63	12.48	12.60	−0.94	3.01
92.61	20.47	20.67	−0.96	2.66
99.62	27.96	27.10	3.07	6.38
110.38	39.97	40.09	−0.30	2.92
124.84	64.98	65.05	−0.10	3.00
131.55	79.98	80.26	−0.35	2.79
139.35	101.27	101.37	−0.10	3.12

[a] Deviation from the correlation using Antoine parameters fitted in this work. [b] Deviation from the correlation using Riedel parameters from ref 29.

In this work VLE measurements provide experimental data on pressure, temperature, and the composition of both phases (*P*, *T*, *x*, *y*) for binary and ternary aqueous solutions of monoethanolamine (MEA), *N*-methyldiethanolamine (MDEA), and 3-(methylamino)propylamine (MAPA) in a commercially

Table 5. Parameters for the Antoine and Riedel Equations for Pure Water and Amines

	A	*B*	*C*	*D*	*E*	eq	ref
H_2O	72.55	−7206.7	−7.1385	$4.05 \cdot 10^{-6}$	2	Riedel[a]	27
MEA	92.624	−10367	−9.4699	$1.90 \cdot 10^{-18}$	6	Riedel[a]	28
MEA	8.0178 ± 0.03	1910.3 ± 17.2	202.18 ± 1.45			Antoine[b]	this work
MDEA	82.8943	−11011.8	−8.03383	$1.68146 \cdot 10^{-18}$	6	Riedel[a]	19
MDEA	10.182 ± 0.22	3578.6 ± 159.4	264.24 ± 7.80		2	Antoine[b]	this work
MAPA	102.2308	−9048.927	−11.71686	0.00427	1	Riedel[a]	29
MAPA	7.0850 ± 0.22	1392.2 ± 127.9	191.88 ± 12.96		2	Antoine[b]	this work

[a] $\ln(P_{vap}/\mathrm{Pa}) = A + B(T/\mathrm{K}) + C \cdot \ln(T/\mathrm{K}) + D(T/\mathrm{K})^E$. [b] $\log_{10}(P_{vap}/\mathrm{mm\ Hg}) = A - B/((T/°\mathrm{C}) + C)$

Table 6. VLE Data for MEA (1) + H_2O (2) System Depending on Composition at (40 and 60) °C

T/°C	P/kPa	x_1	y_1
MEA (1) + H_2O (2), 40 °C			
40.02	7.28	0.0121	0.0001
40.08	7.18	0.0297	0.0002
39.93	6.98	0.0477	0.0003
40.10	6.88	0.0678	0.0005
40.09	6.67	0.0928	0.0007
39.88	6.38	0.1192	0.0009
40.04	6.18	0.1486	0.0016
MEA (1) + H_2O (2), 60 °C (1)			
60.02	19.57	0.0136	0.0003
60.01	19.19	0.0315	0.0007
60.00	18.76	0.0491	0.0008
59.11	17.98	0.0922	0.0013
60.06	17.46	0.1167	0.0017
60.10	18.37	0.0718	0.0010
MEA (1) + H_2O (2), 60 °C (2)			
60.00	6.07	0.5663	0.0576
59.94	7.87	0.4899	0.0324
60.08	9.88	0.3966	0.0192
60.06	12.08	0.3015	0.0109
59.99	14.58	0.2281	0.0053
59.96	16.06	0.1672	0.0032
60.02	17.28	0.1033	0.0020
MEA (1) + H_2O (2), 60 °C (3)			
60.00	6.88	0.5249	0.0463
60.02	8.27	0.4584	0.0304
60.04	10.37	0.3730	0.0168
60.00	15.18	0.1995	0.0042
60.05	16.77	0.1412	0.0024
59.94	17.68	0.1000	0.0016
MEA (1) + H_2O (2), 60 °C (4)			
60.03	19.88	0.0000	0.0000
59.98	19.57	0.0131	0.0001
60.03	18.85	0.0489	0.0007
60.05	17.98	0.0850	0.0011
60.02	16.98	0.1293	0.0021
60.11	12.08	0.3256	0.0124
MEA (1) + H_2O (2), 60 °C (5)			
60.12	14.48	0.2493	0.0049
60.13	15.67	0.1986	0.0044
60.12	16.97	0.1212	0.0021
60.02	17.88	0.1016	0.0013
MEA (1) + H_2O (2), 60 °C (6)			
60.02	19.58	0.0137	0.0001
59.97	18.78	0.0500	0.0005
60.05	17.48	0.1119	0.0015
59.98	16.26	0.1533	0.0025

Table 7. VLE Data for MEA (1) + H_2O (2) System Depending on Composition at (80 and 100) °C

T/°C	P/kPa	x_1	y_1
MEA (1) + H_2O (2), 80 °C (1)			
79.97	46.45	0.0146	0.0003
80.01	45.80	0.0305	0.0006
79.98	44.77	0.0495	0.0010
79.99	43.89	0.0703	0.0014
79.98	42.86	0.0907	0.0020
80.03	41.69	0.1167	0.0025
MEA (1) + H_2O (2), 80 °C (2)			
79.99	45.18	0.0424	0.0009
80.04	42.68	0.0932	0.0020
80.01	40.18	0.1387	0.0036
80.01	36.98	0.1952	0.0064
79.99	31.67	0.2778	0.0122
79.99	26.07	0.3713	0.0242
MEA (1) + H_2O (2), 80 °C (3)			
80.02	22.27	0.4315	0.0348
79.96	23.18	0.4190	0.0301
79.99	27.37	0.3489	0.0191
80.07	36.78	0.1974	0.0071
80.00	39.58	0.1492	0.0037
80.01	41.58	0.1129	0.0023
MEA (1) + H_2O (2), 100 °C (1)			
100.01	99.57	0.0143	0.0005
99.99	97.68	0.0321	0.0012
100.00	95.69	0.0534	0.0019
99.98	93.68	0.0727	0.0027
100.00	91.51	0.0955	0.0040
100.00	89.30	0.1173	0.0045
MEA (1) + H_2O (2), 100 °C (2)			
100.03	96.58	0.0447	0.0018
99.99	91.08	0.0962	0.0038
100.03	86.16	0.1412	0.0064
100.02	79.88	0.1963	0.0099
99.99	68.78	0.2833	0.0183
99.99	57.28	0.3810	0.0356
99.99	45.97	0.4773	0.0555
MEA (1) + H_2O (2), 100 °C (3)			
99.98	50.98	0.4310	0.0490
99.99	53.68	0.4066	0.0389
100.01	62.19	0.3395	0.0265
100.03	70.69	0.2685	0.0180
100.00	79.98	0.1938	0.0096
100.02	86.38	0.1395	0.0065
100.00	90.28	0.1039	0.0044
100.02	93.47	0.0749	0.0025
MEA (1) + H_2O (2), 100 °C (4)			
99.99	58.78	0.3630	0.0284
100.01	66.17	0.3059	0.0205
100.00	75.06	0.2351	0.0128
100.03	79.78	0.1957	0.0103
100.02	84.68	0.1554	0.0068
99.97	89.57	0.1106	0.0043
100.02	92.88	0.0826	0.0033
100.03	95.26	0.0606	0.0020

important range of temperatures and compositions. In practice, the mole fraction of alkanolamine in an acid-gas−alkanolamine−water system generally varies from near 0 to less than 0.2. Therefore, an accurate representation of amine activity coefficients in this region is important, especially for determining the composition of the liquid phase at chemical equilibrium.[13]

Aqueous solutions of MEA and MDEA are the most widely used solvents for acid gas removal. The use of amine blends is becoming increasingly attractive to operators of alkanolamine-based gas sweetening units for reducing operating costs,

Table 8. VLE Data for MDEA (1) + H_2O (2) System Depending on Composition and Temperature

T/°C	P/kPa	x_1	y_1
MDEA (1) + H_2O (2), 40 °C			
39.87	7.27	0.0076	0.00001
40.09	7.27	0.0188	0.00000
40.03	7.17	0.0292	0.00001
40.00	7.08	0.0403	0.00002
40.05	6.98	0.0540	0.00001
39.84	6.78	0.0693	0.00002
39.95	6.67	0.0850	0.00002
39.95	6.47	0.1074	0.00003
MDEA (1) + H_2O (2), 60 °C (1)			
60.02	19.88	0	0
60.02	19.77	0.0047	0.00004
59.98	19.58	0	0
59.96	19.47	0.0169	0.00003
60.05	18.10	0.0878	0.00008
59.98	17.07	0.1329	0.00012
59.95	15.37	0.2045	0.00020
60.04	13.38	0.2902	0.00030
MDEA (1) + H_2O (2), 60 °C (2)			
60.05	12.87	0.3045	0.00041
59.99	13.98	0.2622	0.00033
60.05	14.87	0.2262	0.00018
59.97	14.66	0.2333	0.00019
60.03	15.67	0.1947	0.00017
60.01	16.67	0.1537	0.00015
60.01	17.77	0.1047	0.00009
59.99	18.48	0.0699	0.00008
MDEA (1) + H_2O (2), 80 °C (1)			
79.96	31.97	0.3063	0.00074
79.99	40.47	0.1480	0.00018
79.97	42.57	0.1040	0.00009
80.00	43.88	0.0757	0.00008
79.99	44.77	0.0547	0.00008
80.00	45.48	0.0390	0.00007
MDEA (1) + H_2O (2), 80 °C (2)			
79.99	47.19	0	0
80.00	46.98	0.0056	0.00001
80.01	46.59	0.0142	0.00003
80.02	46.29	0.0217	0.00004
80.02	45.09	0.0475	0.00008
80.02	43.89	0.0742	0.00015
80.02	42.58	0.0973	0.00014
80.03	40.68	0.1391	0.00021
80.01	38.68	0.1743	0.00029
80.00	36.20	0.2196	0.00054
MDEA (1) + H_2O (2), 100 °C (1)			
100.10	68.97	0.3194	0.00111
100.05	74.68	0.2600	0.00095
99.90	78.77	0.2277	0.00069
100.03	83.08	0.1882	0.00052
99.98	91.97	0.0989	0.00030
100.01	94.48	0.0723	0.00027
100.08	96.18	0.0533	0.00023
MDEA (1) + H_2O (2), 100 °C (2)			
100.01	99.88	0.0113	0.00007
100.00	98.67	0.0239	0.00013
100.01	96.96	0.0461	0.00017
99.99	92.77	0.0903	0.00044
100.00	88.38	0.1391	0.00054
100.10	83.68	0.1867	0.00069
99.98	71.67	0.2900	0.00098
100.00	64.18	0.3573	0.00140
MDEA (1) + H_2O (2), 100 °C (3)			
100.00	100.40	0.0059	0.00003
100.00	99.80	0.0120	0.00007
100.01	98.80	0.0232	0.00013
100.00	96.21	0.0537	0.00022
100.01	94.00	0.0753	0.00031
100.00	91.66	0.0991	0.00046

Table 9. VLE Data for MAPA (1) + H_2O (2) System Depending on Composition and Temperature

T/°C	P/kPa	x_1	y_1
MAPA (1) + H_2O (2), 40 °C			
39.91	7.28	0.0099	0.00008
39.87	7.18	0.0203	0.00016
40.11	7.17	0.0320	0.00026
39.95	6.98	0.0460	0.00052
39.87	6.78	0.0623	0.00068
39.94	6.58	0.0810	0.00133
39.88	6.28	0.1006	0.00192
39.95	5.98	0.1228	0.00301
MAPA (1) + H_2O (2), 60 °C (1)			
60.09	9.27	0.4506	0.16230
60.05	9.78	0.4167	0.12090
60.05	10.37	0.3647	0.08830
59.50	10.78	0.3199	0.06720
60.01	11.87	0.2635	0.04070
60.03	13.58	0.2113	0.02480
60.02	15.28	0.1577	0.01090
59.98	16.77	0.1115	0.00453
59.94	17.97	0.0741	0.00220
MAPA (1) + H_2O (2), 60 °C (2)			
60.02	19.88	0	0
60.00	19.77	0.0025	0.00009
59.99	19.68	0.0095	0.00017
59.99	19.57	0.0138	0.00026
60.00	19.47	0.0191	0.00043
60.01	18.87	0.0459	0.00112
59.97	17.57	0.0908	0.00303
59.99	15.98	0.1393	0.01060
59.97	14.38	0.1872	0.01940
60.03	12.87	0.2430	0.03460
MAPA (1) + H_2O (2), 80 °C (1)			
79.99	47.18	0	0
80.00	49.66	0.0053	0.00018
80.02	46.78	0.0099	0.00045
79.98	46.47	0.0149	0.00061
80.00	46.27	0.0200	0.00079
79.98	44.68	0.0510	0.00243
80.03	41.87	0.0997	0.00663
80.02	35.28	0.1967	0.02790
79.99	31.97	0.2535	0.04740
MAPA (1) + H_2O (2), 80 °C (2)			
79.99	27.08	0.3891	0.12640
80.04	28.28	0.3458	0.09430
80.03	29.37	0.3165	0.07460
79.97	30.97	0.2756	0.05690
80.02	32.88	0.2412	0.04110
80.00	35.37	0.1973	0.02490
80.01	38.27	0.1495	0.01450
80.04	41.47	0.1051	0.00720
80.00	43.28	0.0750	0.00399
80.00	49.66	0.0053	0.00018
MAPA (1) + H_2O (2), 100 °C (1)			
100.01	100.98	0	0
99.99	100.38	0.0059	0.00080
100.00	99.87	0.0116	0.00140
100.00	99.27	0.0180	0.00210
100.01	98.88	0.0224	0.00160
99.99	95.58	0.0557	0.00570
100.01	89.34	0.1111	0.01400
99.98	82.48	0.1671	0.02690
100.00	75.29	0.2320	0.04950
99.97	69.28	0.3044	0.07570
MAPA (1) + H_2O (2), 100 °C (1)			
99.99	61.58	0.4262	0.14010
100.00	64.48	0.3746	0.10830
100.03	67.28	0.3280	0.08250
99.99	70.28	0.2822	0.06650
100.01	74.67	0.2380	0.04860
99.98	79.38	0.1932	0.03180
100.01	85.06	0.1437	0.01980
99.99	90.7	0.0979	0.01070
99.99	93.17	0.0758	0.00820

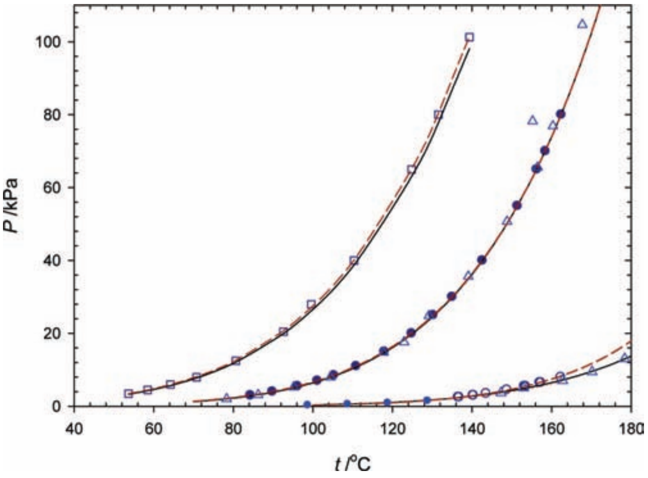

Figure 3. Equilibrium vapor pressure of pure amines at different temperatures. MDEA: ○, this work; Δ, ref 17; light blue ●, ref 18. MEA: dark blue ●, this work; Δ, ref 16. MAPA: □, this work; ---. Antoine equation; —, Riedel equation with parameters given in Table 5.

improving product quality, or both.[14] MAPA was selected as a promising additive to MDEA to improve the process of CO_2 removal.

Experimental values of the activity coefficient of species *i* in the liquid may then be calculated by using measured variables as follows[15]

$$\gamma_i = \frac{y_i P}{x_i P_i^{\text{sat}}} \Phi_i \; (i = 1, 2) \tag{1}$$

Table 10. VLE Data for MEA (1) − MDEA (2) − H_2O (3) Mixtures

T/°C	P/kPa	x_1	x_2	y_1	y_2
		0.10 MEA (1) + 0.30 MDEA (2) + 0.60 H_2O (3)			
39.97	6.48	0.04038	0.06438	0.000360	0.000025
60.04	17.47	0.04487	0.07322	0.000645	0.000047
79.98	41.79	0.04425	0.07308	0.000982	0.000127
100.00	90.30	0.04163	0.06792	0.001634	0.000473
		0.20 MEA (1) + 0.20 MDEA (2) + 0.60 H_2O (3)			
39.97	6.18	0.08607	0.04688	0.000877	0.000019
60.09	16.97	0.08696	0.04691	0.001402	0.000035
80.01	40.78	0.08038	0.04798	0.002499	0.000198
100.01	87.98	0.08286	0.04581	0.003547	0.000397
		0.30 MEA (1) + 0.10 MDEA (2) + 0.60 H_2O (3)			
39.94	5.98	0.12581	0.02522	0.001394	0.000013
59.99	16.37	0.12906	0.02454	0.002203	0.000020
80.00	39.68	0.11616	0.02037	0.003308	0.000062
100.02	85.58	0.11809	0.02231	0.004833	0.000094

where

$$\Phi_i \equiv \frac{\hat{\phi}_i}{\phi_i^{\text{sat}}} \exp\left\{\frac{-V_i^{\text{l}}(P - P_i^{\text{sat}})}{RT}\right\} \tag{2}$$

At low to moderate pressures, the factor Φ_i is of relatively minor importance and may be neglected.

Accurate data for the vapor pressures of the pure components are very important for the calculation of the activity coefficients. Daubert et al.[16,17] reported vapor pressures of pure MEA and MDEA. The vapor pressure of pure MDEA was also measured by Noll et al.[18] in the temperature range below that of the present work and by Von Niederhausern et al.[19] at much higher temperatures. The measurements are very sensitive to the experimental conditions and to the purity of the materials used.

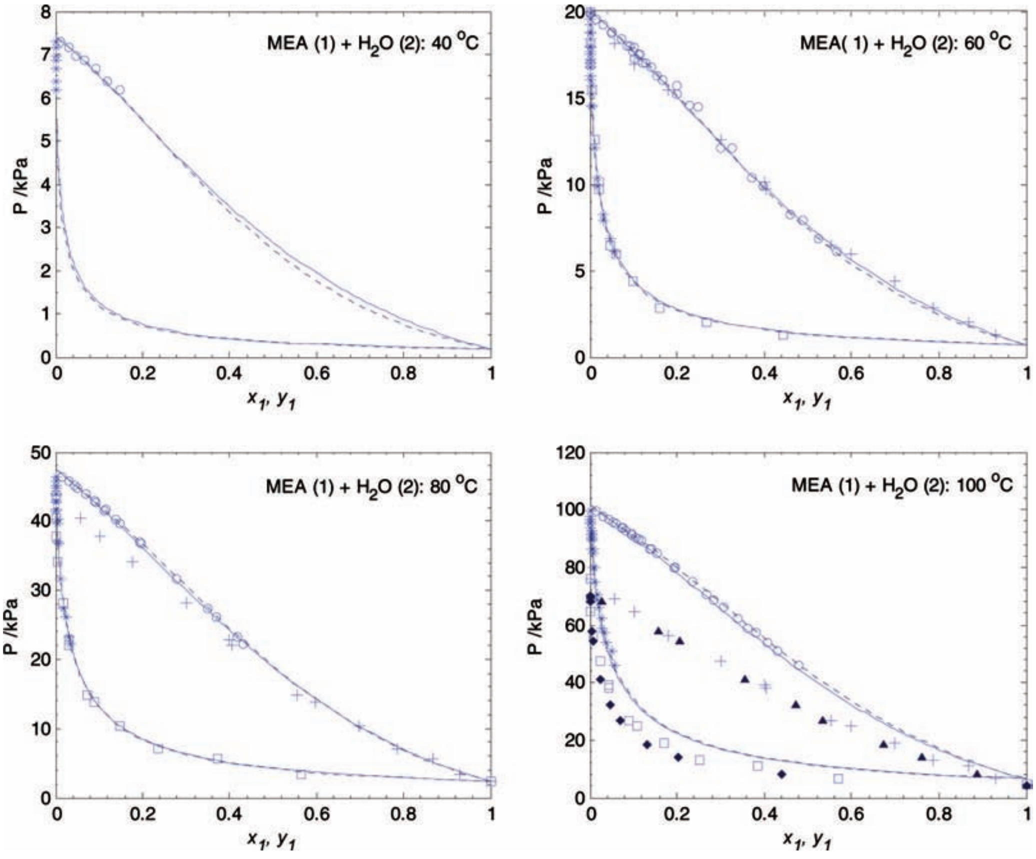

Figure 4. Total pressure *P* versus liquid/vapor-phase compositions *x*, *y*: ○/*, this work at (40, 60, 80, and 100) °C; +/□, ref 4 at (60, 78, and 92) °C; ▲/♦, ref 7 at 90 °C; —, calculated using Wilson model; ---, calculated using NRTL model with parameters given in Table 12.

Table 11. VLE Data for MDEA (1) − MAPA (2) − H_2O (3) Mixtures

T/°C	P/kPa	x_1	x_2	y_1	y_2
	0.25 MDEA (1) + 0.10 MAPA (2) + 0.65 H_2O (3)				
59.91	18.37	0.04535	0.02691	0.00029	0.00057
80.03	43.58	0.04456	0.02853	0.00035	0.00118
100.00	93.48	0.05480	0.03008	0.00082	0.00234
	0.25 MDEA (1) + 0.15 MAPA (2) + 0.60 H_2O (3)				
59.97	17.98	0.04678	0.03950	0.00000	0.00091
59.96	17.87	0.04714	0.03914	0.00000	0.00092
80.03	42.58	0.05102	0.04456	0.00035	0.00231
100.00	91.6	0.05108	0.04514	0.00152	0.00420
	0.25 MDEA (1) + 0.20 MAPA (2) + 0.55 H_2O (3)				
60.01	17.48	0.05548	0.05696	0.00024	0.00167
80.00	41.98	0.05702	0.06290	0.00023	0.00295
80.04	41.49	0.06211	0.06460	0.00022	0.00322
80.02	42.19	0.05571	0.05662	0.00033	0.00271
100.00	90.83	0.05483	0.05662	0.00105	0.00557
99.99	88.89	0.06502	0.06711	0.00066	0.00646
100.00	90.5	0.05602	0.05855	0.00030	0.00469

In any proper experimental determination of VLE, it is essential that the vapor pressures of the pure components be measured with the same apparatus and for the same lots of materials as those used for the other measurements so that they are an integral part of the data set.[20] In this work, the vapor pressures of the pure alkanolamines were measured, fit to the Antoine equation, and used for the calculation of the experimental activity coefficients.

Experimental Section

Materials. The alkanolamines studied in this work were MEA (Sigma Aldrich, ≥ 99 %), MDEA (Aldrich, 99 + %), and MAPA (Acros Organics, 99 %). The chemicals were used as received without further purification. Aqueous solutions were prepared from distilled and deionized water.

Experimental Procedure. The measurements were performed in a modified Swietoslawski ebulliometer that is described in detail by Hala et al.[21] and Rogalski and Malanowski.[22] The scheme of the experimental setup is shown in Figure 1. The equilibrium still, which is made of glass, has a volume of 200 mL. It is designed for operation at temperatures of below 200 °C and pressures of a maximum of 1 bar. The temperatures were measured with calibrated Pt-100 resistance thermosensors with an uncertainty of ± 0.05 K. These were logged online via a Chub-E4 thermometer readout (Hart Scientific, Fluke). The pressure was measured and controlled with a calibrated DPI520 rack mounted pressure controller (Druck, Germany). The uncertainty of the pressure controller was ± 0.3 kPa.

To measure the boiling temperatures, we charged about 80 mL of the solution to the ebulliometer, which was purged with nitrogen in advance. The pressure was set to the desired value, and the liquid was heated by an electric heater and was partially evaporated. The stream of overhead liquid and vapor was pumped by a Cottrell pump to the equilibrium chamber where the temperature sensor was placed. The measured temperature corresponds to the equilibrium conditions established at the given total pressure and the compositions of the liquid and vapor phases. The system was considered to be in equilibrium when no change in pressure and temperature was observed for a minimum of 10 min.

The apparatus enables the withdrawal of samples of both vapor condensate and liquid phase. A gradual change of the composition of the solution in the apparatus was achieved by

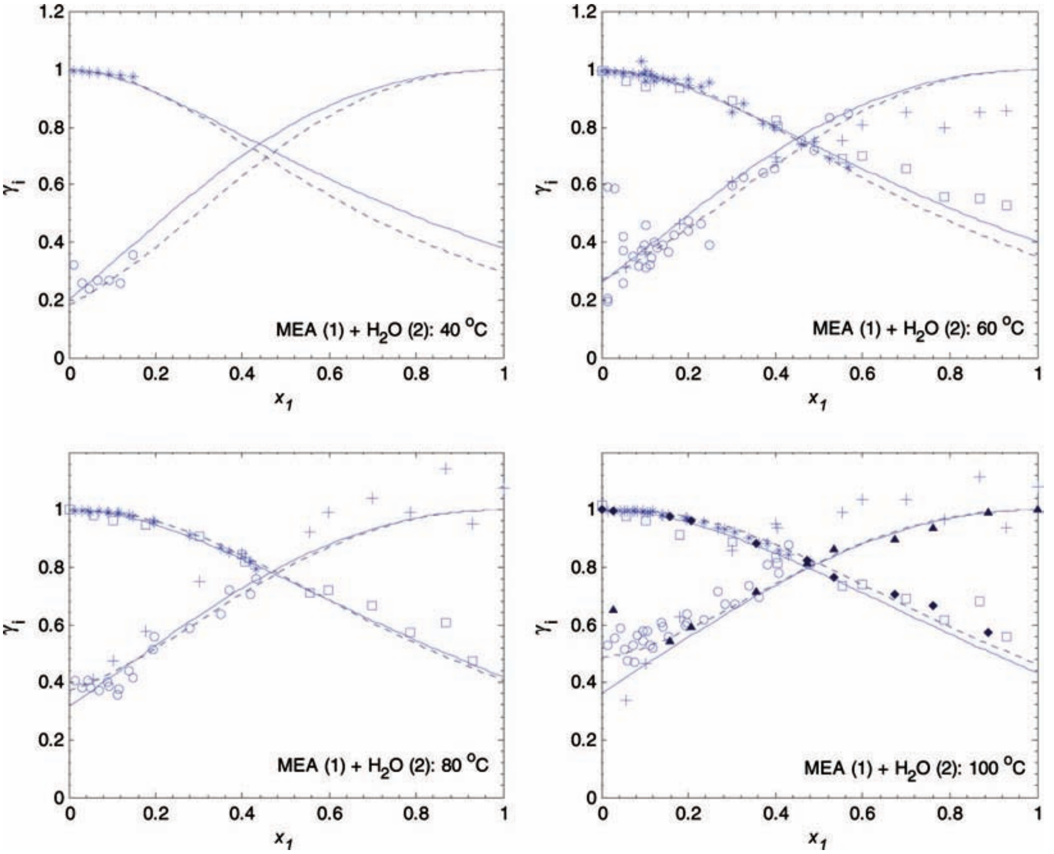

Figure 5. Activity coefficients of MEA, γ_1, and water, γ_2, depending on composition at different temperatures: ○/*, MEA/H_2O from this work at (40, 60, 80, and 100) °C; +/□, MEA/H_2O from ref 4 at (60, 78, and 92) °C; ▲/♦, MEA/H_2O from ref 7 at 90 °C; —, calculated using Wilson model; ---, calculated using NRTL model with parameters given in Table 12.

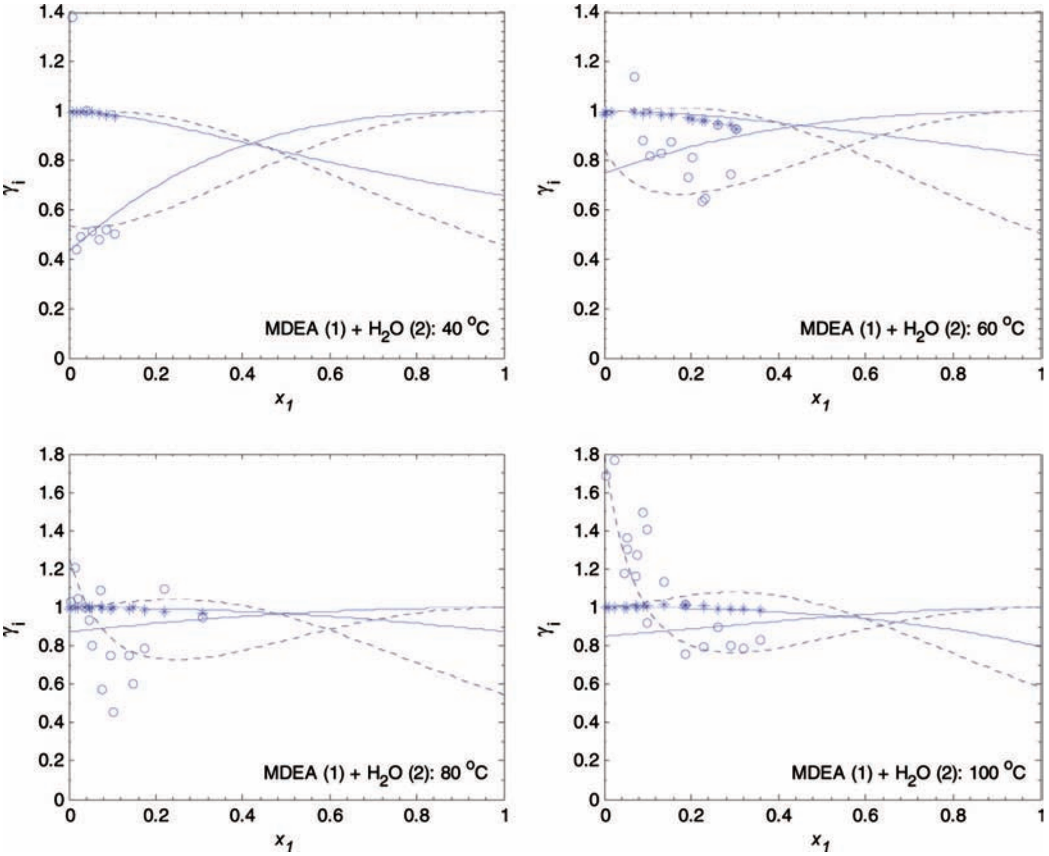

Figure 6. Activity coefficients of MDEA, γ_1, and water, γ_2, depending on composition at different temperatures: ○/*, MDEA/H_2O from this work at (40, 60, 80, and 100) °C; —, calculated using Wilson model; ---, calculated using NRTL model with parameters given in Table 12.

Table 12. Binary Interaction Parameters for Wilson and NRTL Models[a]

	MEA (1) + H_2O (2)	MDEA (1) + H_2O (2)	MAPA (1) + H_2O (2)
		Wilson	
λ_{12}	3099 ± 379	19 917 ± 444	16 253 ± 659
λ_{21}	−5584 ± 218	−20 307 ± 294	−10 316 ± 46
		NRTL	
a_{12}	−0.153 ± 1.40	−1.496 ± 2.17	−2.971 ± 1.76
b_{12}	−868.72 ± 484	−324.42 ± 772	161.67 ± 624
a_{21}	2.087 ± 4.35	8.570 ± 6.29	16.499 ± 4.15
b_{21}	470.19 ± 1509	−1565.15 ± 2234	−5043.81 ± 1448

[a] Temperature dependent parameters:[13] $\tau_{12} = a_{12} + (b_{12}/(T/K))$; $\tau_{21} = a_{21} + (b_{21}/(T/K))$; $\alpha_{12} = \alpha_{21} = 0.2$.

removing some of the solution from the ebulliometer and introducing known quantities of one of the pure components through the sampling ports. The sampling ports are sealed with silicone septa.

The ebulliometer may be operated either in isothermal or in isobaric mode. For the system to run in isothermal mode, the pressure is adjusted after the change in the composition of the solution. In isobaric mode, the temperature is adjusted using the electric heaters.

Analyses of the Samples. The samples of the liquid phase and vapor-phase condensate were taken using disposable plastic syringes and were immediately placed in sealed vials with PTFE septum. The vials were stored in a refrigerator until they were analyzed.

Liquid-phase samples for the binary amine−water solutions were analyzed by titration with aqueous 0.1 M H_2SO_4 using a standard procedure[23] with a potentiometric titrator Titrando-809 (Metrohm AG, Switzerland). Liquid-phase samples of the mixtures of amines were analyzed by gas chromatography (GC). Vapor-phase samples were analyzed both by titration with 0.01 M H_2SO_4 and by GC. The uncertainty of the results was determined from parallel titrations and GC analyses of standard solutions.

Analysis of the amine solutions by GC is not a simple task. First, the amines are very reactive, and they have a strong adsorption affinity for the GC column. Second, the formation of thermal degradation products at high column temperatures is possible. Third, the boiling temperatures of the amines are very high and vary within a large range.[24] A GC method was developed for the amines studied after testing different operating conditions.

The GC was an HP 6850 with an autoinjector and FID detector. The carrier gas was helium at a flow rate of 5.4 mL·min^{-1}. The column Rtx−5 amine (Fused Silica, (30 m)·(0.53 mm)·(1 μm)) was used with an inlet glass liner CIS4/PTV for Agilent GCs with deactivated wool (Restek). A temperature program was used as follows: initial column temperature, t = 50 °C; rate of temperature program, 5 °C·min^{-1} for t = (50 to 100) °C and 10 °C·min^{-1} for t = (100 to 200) °C (hold 10 min at 200 °C); injector/detector temperature, t = 250 °C; injection volume, V = 1 μL (splitless); injector temperature, t = 150 °C; detector temperature, t = 250 °C.

Each sample was injected three times. The analysis time of each injection was about 30 min. The first injection was used for conditioning the column and was not used for calculations. The result of the two next injections was used for the determination of the amine concentration in the solution.

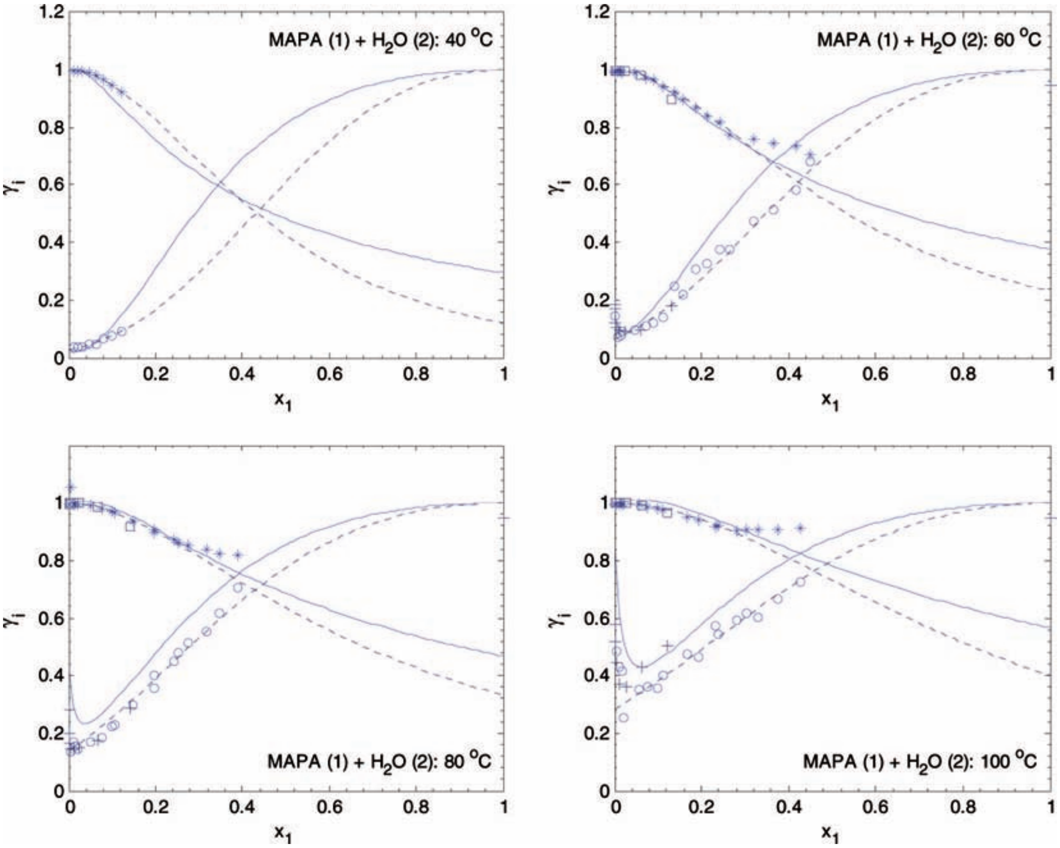

Figure 7. Activity coefficients for MAPA, γ_1, and water, γ_2, depending on composition at different temperatures: ○/*, MAPA/H_2O from this work at (40, 60, 80, and 100) °C; +/□, MAPA/H_2O from ref 29 at (50, 70, and 100) °C; —, calculated using Wilson model; ---, calculated using NRTL model with parameters given in Table 12.

Standard solutions were analyzed after each third or fourth experimental sample to ensure stable conditions throughout the analysis.

Sources of Uncertainties. Inconsistencies in the results may stem from several sources. There are uncertainties in temperature and pressure readings, but they play a negligible role in the total uncertainty. The main source of error is the analysis of the liquid and vapor-phase samples.

The titration of the standard solutions of different amines gave a relative uncertainty of less than 1 % between three parallel titrations. The advantage of this method is that samples are used as they are without any additional processing. However, it is not possible to analyze the samples in the very low concentration range with titration.

GC analysis of the samples was based on calibration experiments. Calibration included analysis of standard solutions of known compositions prepared by mass. Real sample analysis was then made by a comparison of the peak area corresponding to the sample with that of the standard solution by using calibration curves. Integration of the peak area is another source of uncertainty because the result of integration depends on the stability of the baseline and on the selected integration boundaries. Results from the standard solutions showed that the reproducibility of the analyses may vary slightly from amine to amine. Three injections were done for each sample. An average uncertainty for the GC analysis was estimated to be ± 2 %. We note that in a very dilute range (i.e., amine mole fraction in the liquid phase < 0.01), experimental uncertainty in the mole fraction of amine in the vapor phase of ± 0.001 gives an uncertainty in the activity coefficient of ± 50 %.

In the case of GC, some of the samples had to be diluted. Dilution is an additional source of uncertainty. Dilution was done both by using capillary glass tubes of (5 to 50) μL volume and by weighing. The error from dilution was estimated to be ± 2 %.

Results and Discussion

To validate the experimental setup and procedure, we measured the boiling point of water. It is an advantage of the equipment that there is no need for degassing the solution. With the pressure controller turned on, the solution vapor substitutes gradually all gas in the space above the solution. A basic assumption is that at equilibrium there is no inert gas present in the vapor phase and that all vapor is condensed in the condenser. Experiments on the boiling point of pure water confirmed the validity of this assumption. Equilibrium vapor pressures of pure water at different temperatures are given in Table 1, and the results are also compared with data of Stimson[25] and Osborne and Meyers[26] in Figure 2. The data show excellent agreement with the Riedel correlation for pure water with the coefficients given in Perry's Engineering Handbook.[27]

Equilibrium vapor pressures of pure amines are given in Tables 2, 3, and 4. The results were fit with the Antoine equation and compared with the correlations given in the DIPPR database[28] for MEA, in ref 19 for MDEA, and from BASF[29] for MAPA and with experimental data from refs 16 17, 18, and 19 in Figure 3. When fitting vapor pressure of pure MDEA to the Antoine equation, data from ref 18 were used together with the experimental data from this work to widen the

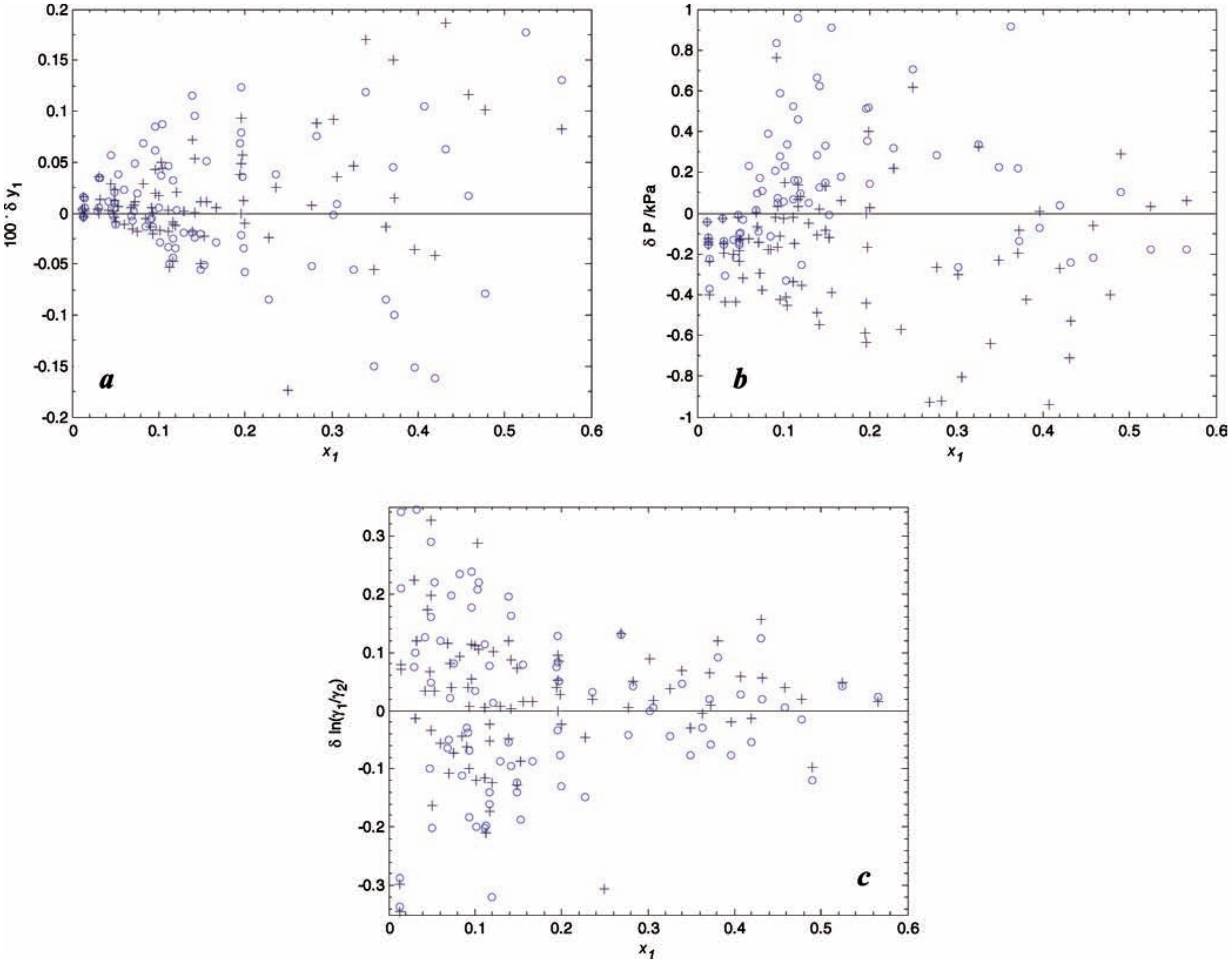

Figure 8. Thermodynamic consistency test for MEA + H_2O system. Residuals (a) $\delta\ y_1$, (b) $\delta\ P$/kPa, and (c) $\delta\ \ln(\gamma_1/\gamma_2)$ depending on composition: ○, calculated using NRTL model; +, calculated using Wilson model with parameters given in Table 12
.

temperature range. Parameters for pure water and amines that were fit in this work are given in Table 5 together with the parameters from literature.

Tables 6, 7, 8, and 9 present VLE data for MEA + H_2O, MDEA + H_2O, and MAPA + H_2O systems. Data for the ternary solutions, MEA + MDEA + H_2O and MDEA + MAPA + H_2O are given in Tables 10 and 11. Correlations for pure amine vapor pressure from both literature and this work gave similar activity coefficients for the components in the mixtures.

Parameter Fitting. Experimental activity coefficients for all systems were calculated using eq 1 and were fit to the Wilson and NRTL models using Modfit,[30] a MatLab program for the estimation of parameters in a general nonlinear multiresponse model. A relative least-squares criteria for the fit was used with an objective function

$$\mathrm{OF} = \sum_{i=1}^{n}\left(\frac{\gamma_i^{\mathrm{exp}} - \gamma_i^{\mathrm{calc}}}{\gamma_i^{\mathrm{exp}}}\right)^2 \tag{3}$$

Regressed binary interaction parameters and root-mean-square (rms) deviations $\delta\ P$, $\delta\ y$, $\delta\ (\ln\ \gamma_1/\gamma_2)$ of the fits are given in the Tables 10 and 11.

Total pressure data and activity coefficients for water and MEA are compared with published data from Nath and Bender[4] and Tochigi et al.[5] in Figures 3 and 4. Figures 5 and 6 show experimental and modeled activity coefficients for the MDEA + H_2O and MAPA + H_2O systems.

We calculated excess enthalpies for the binary mixtures by using the NTRL equation with the parameters fitted in this work. The results are compared in Figure 9 with experimental excess enthalpy data from Posey[31] and Touhara et al.[5] for MEA and from Posey[31] and Maham et al.[3] for MDEA.

For MEA, modeling results of Hilliard[6] and Posey[31] show infinite dilution activity coefficients that are higher than those measured in this work. In fact, Austgen's[13] predictions are closer to our experimental values. Both the work of Hilliard[6] and this work seem to underpredict the excess enthalpy of mixing (ΔH^{E}) for aqueous MEA solution. However, compared with Touhara[5] and Posey,[31] better temperature dependency may be seen from our work. We note that binary interaction parameters in this work were derived using only our own VLE data. Model parameters that are fit using published experimental excess enthalpy and other data may improve the model prediction of the present work, as was shown by Posey.[31]

For MDEA, similar activity coefficients' behavior, as shown by the experimental data in Figure 6, was predicted by Posey.[31] However, our data show a somewhat stronger temperature dependency. Model results from our work excellently fit

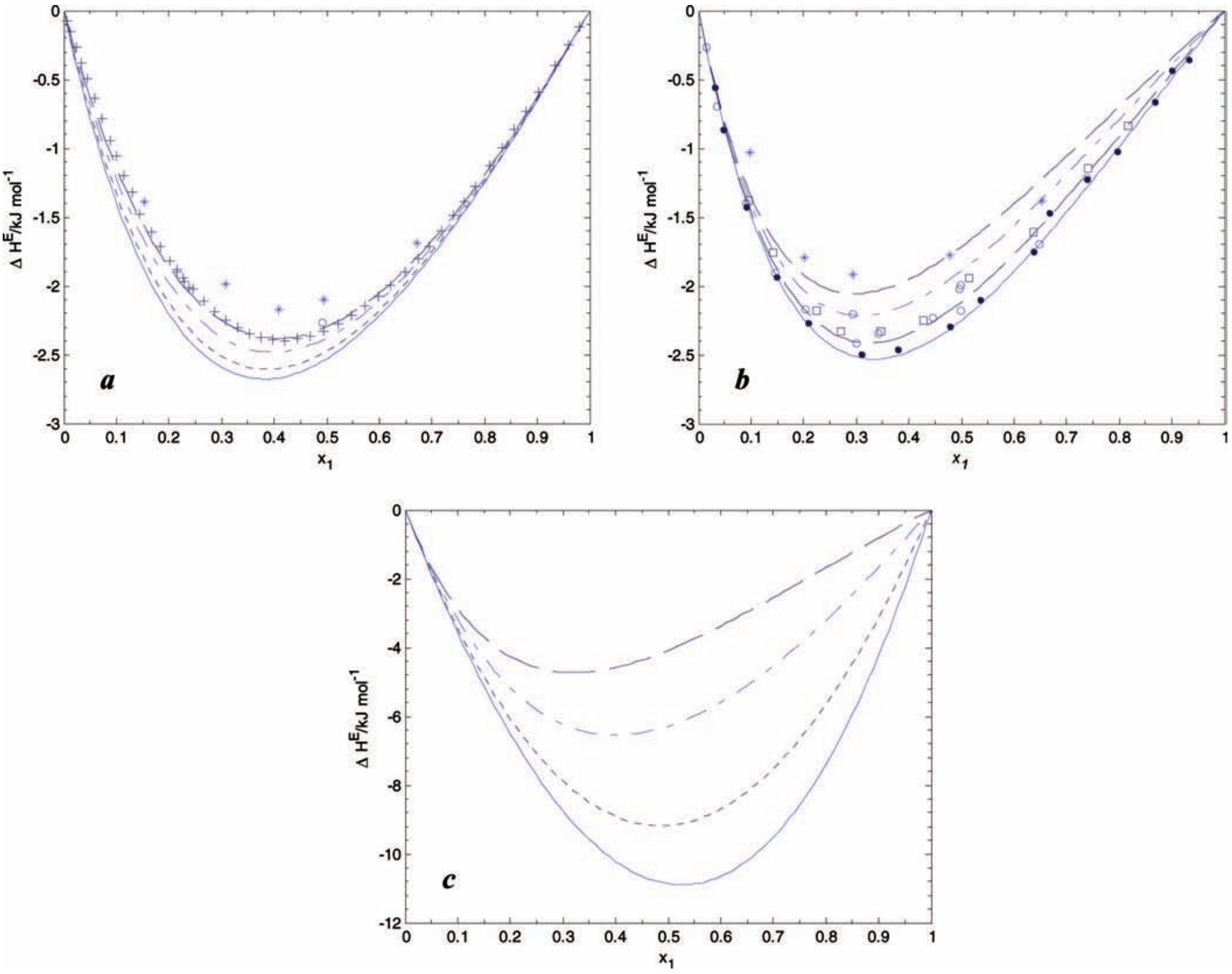

Figure 9. Excess enthalpies, ΔH^{E}, for (a) MEA, (b) MDEA, and (c) MAPA: ○, ref 31; +, ref 5 at 25 °C; *, ref 31 at 70 °C; ●, ref 32 at 25 °C; □, ref 32 at 40 °C. NRTL model: —, 25 °C; ---, 40 °C; —•—, 70 °C; — — —, 100 °C.

Table 13. RMS Error for Model Fitting[a]

	MEA (1) − H_2O (2)		MDEA (1) − H_2O (2)		MAPA (1) − H_2O (2)	
	Wilson	NRTL	Wilson	NRTL	Wilson	NRTL
rms (δ P/kPa)	0.507	0.355	0.447	2.062	1.245	1.358
rms (δ y_1)	0.001	0.001	$6.88 \cdot 10^{-5}$	$7.45 \cdot 10^{-5}$	0.011	0.005
rms (δ $\ln(\gamma_1/\gamma_2)$)	0.190	0.169	0.507	0.426	0.331	0.169

[a] Calculated using the equation

$$\mathrm{RMS}\ \delta\ Y = \sqrt{\sum_{i=1}^{n} \frac{(Y_i - Y_i^{\mathrm{calc}})^2}{n}}$$

experimental data on ΔH^{E} for MDEA from Maham,[3] but there is some discrepancy compared with the experimental data of Posey.[31]

Thermodynamic Consistencies. According to the phase rule, information on P, T, and x is enough to characterize the system. If the experimental data consist of pressure, temperature, and composition of both phases, then the extra experimental information may be used to test the data for thermodynamic consistency. The Gibbs−Duhem equation interrelates activity coefficients of all components in a mixture. Therefore, if data are available for all activity coefficients, then these data should obey the Gibbs−Duhem equation;[32] if they do not, then the data would be deemed inconsistent

$$\frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \qquad (4)$$

Thermodynamic consistency tests of the experimental data were done in this work according to Van Ness.[14] The NRTL and Wilson equations used for fitting are inherently thermodynamically consistent. Therefore, the difference between these two model predictions and the experimental data will tell us about the thermodynamic consistency of the experimental data. Whereas rms deviations are useful for assessing thermodynamic consistency, their absolute values cannot be used as a measure of the thermodynamic consistency of the data sets unless they are normalized. Otherwise, the values of the rms deviations for pressure will be much higher than the rms error for vapor-phase composition. A more useful procedure is therefore to plot residuals versus liquid-phase composition to determine if the deviations scatter uniformly about zero[32] or to plot the experimental data versus model results to see how the data points lie around a diagonal. If the deviations show a clear trend, then systematic errors may be suspected. Plots of residuals for the example of MEA, presented in Figures 7 and 8, show that the experimental data presented in this work are thermodynamically consistent. The other data set showed similar consistencies.

Conclusions

VLE data have been measured for pure water and amines and the binary and ternary mixtures at temperatures of (40, 60, 80, and 100) °C. Antoine parameters for the vapor pressure of pure amines derived in this work were used for the calculation of the experimental activity coefficients. Activity coefficients of the amines and water were fit to the Wilson and NRTL equations. The thermodynamic consistency test shows that data are consistent.

Acknowledgment

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