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Ternary Isobaric Vapor−Liquid Equilibria of Methanol + *N*-Methyldiethanolamine + Water and Methanol + 2-Amino-2-methyl-1-propanol + Water Systems

Alain Barreau,* Pascal Mougin, Catherine Lefebvre, Quinn M. Luu Thi, and Julien Rieu

Institut Français du Pétrole, 1-4 Avenue de Bois Préau 92852, Rueil-Malmaison, Cedex, France

Isobaric vapor−liquid equilibrium (VLE) data for a wide range of temperatures, pressures, and compositions were measured for the methanol + *N*-methyldiethanolamine (MDEA) + water and methanol + 2-amino-2-methyl-1-propanol (AMP) + water ternary systems. The vapor pressure of pure AMP and two binary subsystems, MDEA + water and methanol + AMP, was also studied. For MDEA + methanol, MDEA + water, AMP + methanol, and AMP + water, the nonrandom two-liquid (NRTL) parameters were fitted using all our experimental data and VLE and H^E data taken from the literature.

Introduction

Due to environmental considerations, the removal of acid gases such as CO_2 and H_2S from natural gas is an important operation in the natural gas industry. Chemical solvents belonging to the family of alkanolamines have been almost exclusively used for many decades. Several authors[1−3] have reported the advantage of combining a chemical solvent (aqueous solution of alkanolamine) with a physical solvent (methanol).

The knowledge of acid gas solubilities in these solvents is essential for the design of gas treatment processes and, of course, for the prediction of their thermodynamic properties. The methanol + 2,2′-diethanolamine + water ternary system has already been described in the literature.[4] In this work, accurate phase equilibrium data for a wide range of temperatures, pressures, and compositions were measured for the methanol + *N*-methyldiethanolamine (MDEA) + water and methanol + 2-amino-2-methyl-1-propanol (AMP) + water ternary systems.

The binary subsystems were also studied and compared to the literature data from Voutsas et al.[5] for the *N*-methyldiethanolamine + water binary system.

The nonrandom two-liquid (NRTL) activity coefficient model with temperature-dependent interaction parameters was used for the thermodynamic modeling of the ternary systems.

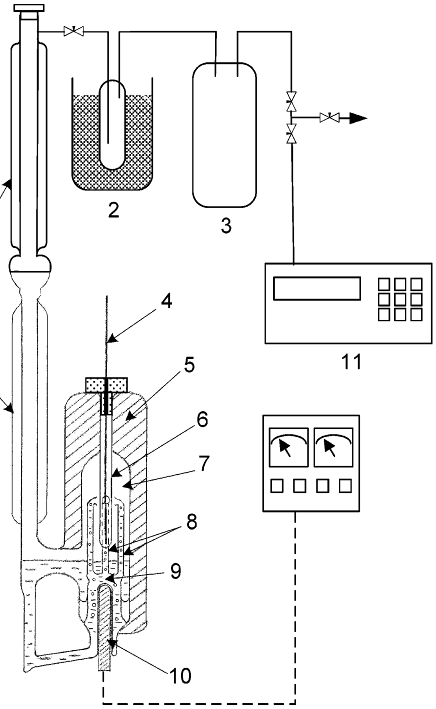

Figure 1. Experimental equipment: 1, condensers; 2, dry ice trap; 3, buffer; 4, Pt100 resistance thermometer; 5, vacuum jacket; 6, thermometer well; 7, equilibrium chamber; 8, Cottrell pumps; 9, reboiler; 10, heater; 11, pressure controller.

Experimental Section

Materials. MDEA (purity 99+ %) and methanol (purity 99.9 %) were purchased from Aldrich. AMP was purchased from Fluka with a purity of 99+ %. They were used without further purification. The water used was bidistilled.

Table 1. Experimental and Calculated Vapor Pressures of Pure AMP with the Antoine Correlation Proposed by Pappa et al.[8]

T/K	P^s/kPa	P^s/kPa from Antoine[8]	100 AD[a]
364.11	5.00	5.11	2.3
377.39	10.00	9.94	0.6
392.71	20.00	19.83	0.9
402.56	30.00	29.76	0.8
415.99	50.00	49.64	0.7
425.48	70.00	69.43	0.8

[a] AD = ($|P^{s,\text{exptl}} - P^{s,\text{calcd}}|/P^{s,\text{exptl}}$).

Experimental Apparatus and Procedure. The measurements were performed in an ebulliometer based on Cottrell's apparatus[6] developed in our laboratory. A schematic diagram is presented in Figure 1. About 50 cm^3 of liquid mixture was loaded into the flask. The pressure was fixed by the pressure controller, and the liquid was heated by electric resistance. The liquid and vapor rose to the equilibrium chamber through three Cottrell pumps. The vapor was condensed and returned to the reboiler by a thermosiphon. The heat power, the condenser temperature, the total amount of liquid in the ebulliometer, and the position

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* To whom correspondence should be addressed. Tel: +33 1 47 52 66 51. Fax: +33 1 47 52 70 25. E-mail: alain.barreau@ifp.fr.

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Table 2. Experimental Isobaric VLE Data for the Methanol(1) + AMP(2) Binary System

	T/K				
x_1	P = 30.00 kPa	P = 50.00 kPa	P = 70.00 kPa	P = 90.00 kPa	P = 101.33 kPa
0.0954	311.89	323.23	331.18	337.43	340.40
0.2377	317.81	329.43	337.66	329.19	347.73
0.5075	330.56	342.84	351.95	359.07	362.76
0.7404	350.90	364.27	373.74	381.19	384.72
0.8919	371.93	388.01	401.30	410.15	411.64

Table 3. Experimental Isobaric VLE Data for the Water(1) + AMP(2) + Methanol(3) Ternary System

		T/K				
x_1	x_2	P = 30.00 kPa	P = 50.00 kPa	P = 70.00 kPa	P = 90.00 kPa	P = 101.33 kPa
0.1951	0.3903	329.94	341.71	350.10	356.93	360.27
0.3003	0.3893	334.35	346.18	355.09	361.72	365.01
0.3926	0.1948	324.34	335.97	344.30	350.79	353.97
0.3958	0.2931	330.37	342.30	350.77	357.40	360.67
0.3860	0.3803	336.70	348.89	357.31	363.97	367.25
0.4991	0.2904	334.99	347.00	355.63	362.39	365.64
0.5932	0.1980	331.66	343.61	352.10	358.73	361.93

Table 4. Experimental Isobaric VLE Data for the Water(1) + MDEA(2) Binary System

	T/K				
x_1	P = 10.00 kPa	P = 30.00 kPa	P = 50.00 kPa	P = 70.00 kPa	P = 90.00 kPa
0.3983	341.62	366.35	380.05	389.75	397.18
0.2035	358.79	388.38	403.03		
0.0573	394.14				

Table 5. Experimental Isobaric VLE Data for the Water(1) + MDEA(2) + Methanol(3) Ternary System

		T/K				
x_1	x_2	P = 30.00 kPa	P = 50.00 kPa	P = 70.00 kPa	P = 90.00 kPa	P = 101.33 kPa
0.1999	0.3975	328.01	340.69	349.78	357.89	361.76
0.2997	0.3937	332.38	345.20	353.68	360.74	364.04
0.3451	0.2205	323.40	335.19	343.73	350.31	353.20
0.4124	0.2943	330.13	342.92	352.05	359.00	361.80
0.3894	0.3868	337.23	348.76	357.61	364.77	368.16
0.5100	0.2904	334.58	346.97	356.52	363.94	367.47
0.6001	0.1991	330.79	342.85	351.46	358.23	361.50

Table 6. DIPPR Parameters

component	A	B	C	D	E
water	73.649	−7258.2	−7.3037	4.1656×10^{-6}	2
methanol	82.718	−6904.5	−8.8622	7.4664×10^{-6}	2
MDEA	253.07	−18378	−33.972	2.3348×10^{-5}	2
AMP	258.658	−17453	−34.804	2.3100×10^{-5}	2

Table 7. NRTL Parameters

binary system	a_{ij}	b_{ij}/K	a_{ji}	b_{ji}/K	$\alpha_{ij} = \alpha_{ji}$
water + MDEA	7.4176	−1630.06	−1.100	−207.98	0.3[a]
MDEA + methanol	15.9252	29422.06	−0.9995	109.03	0.3[a]
water + AMP	3.5860	−327.50	0.3735	−573.30	0.3[a]
AMP + methanol	4.4500	−2025.00	−7.1005	2799.12	0.3[a]
water + methanol	0.5110[b]	199.80[b]	0.7361[b]	−360.70[b]	0.2442[b]

[a] Fixed value. [b] SIMSCI databank.[11]

of the Pt 100Ω probe inside the thermometer will have an influence on the bubble temperature accuracy. These parameters have been studied by Vellut.[7] The pressure of the system was controlled within using a Ruska 7250*i* pressure controller. The bubble temperature was measured using a Hart Scientific Model 1502A digital thermometer with a Pt 100Ω probe calibrated in our metrology laboratory. The global compositions of the mixtures were determined by weighing. Due to the very small volume of the vapor phase, the liquid-phase composition was considered equal to the global composition. The estimated experimental uncertainties in pressure, temperature, and liquid-phase composition are ±0.01 kPa, ±0.05 K, and ±0.0002 mole fraction, respectively.

Table 8. Average Absolute Deviations between Experimental Data and Calculated Value with the NRTL Model

system			100 AAD[a]
water + MDEA	VLE	our data	1.07
		Xu[9]	0.64
		Voutsas[5]	0.97
	H^E	Maham[13,14]	5.85
water + MDEA + methanol	VLE	our data	0.87
methanol + AMP	VLE	our data	0.71
water + AMP	VLE	Pappa[8]	0.44
	H^E	Mathonnat[15]	5.43
water + AMP + methanol	VLE	our data	0.45

[a] $$\mathrm{AAD} = \frac{1}{NP}\sum_i^{\mathrm{NP}} \frac{|T_i^{\mathrm{exptl}} - T_i^{\mathrm{calcd}}|}{T_i^{\mathrm{exptl}}} \text{ or } \frac{1}{\mathrm{NP}}\sum_i^{\mathrm{NP}} \frac{|H_i^{E,\mathrm{exptl}} - H_i^{E,\mathrm{calcd}}|}{H_i^{E,\mathrm{exptl}}}$$
(NP, number of data points).

Experimental Results

Vapor Pressure of Pure AMP. AMP vapor pressures were measured in the temperature range from (364.1 to 425.5) K and compared to the Antoine correlation proposed by Pappa et al.[8] The results are presented in Table 1. Except for the first point, which is out of the range of the correlation, the deviations are less than 1 %.

Methanol + AMP Mixtures. Bubble temperaturea for the methanol + AMP binary system were measured along five isobars: (30.00, 50.00, 70.00, 90.00, and 101.33) kPa. The results are presented in Table 2.

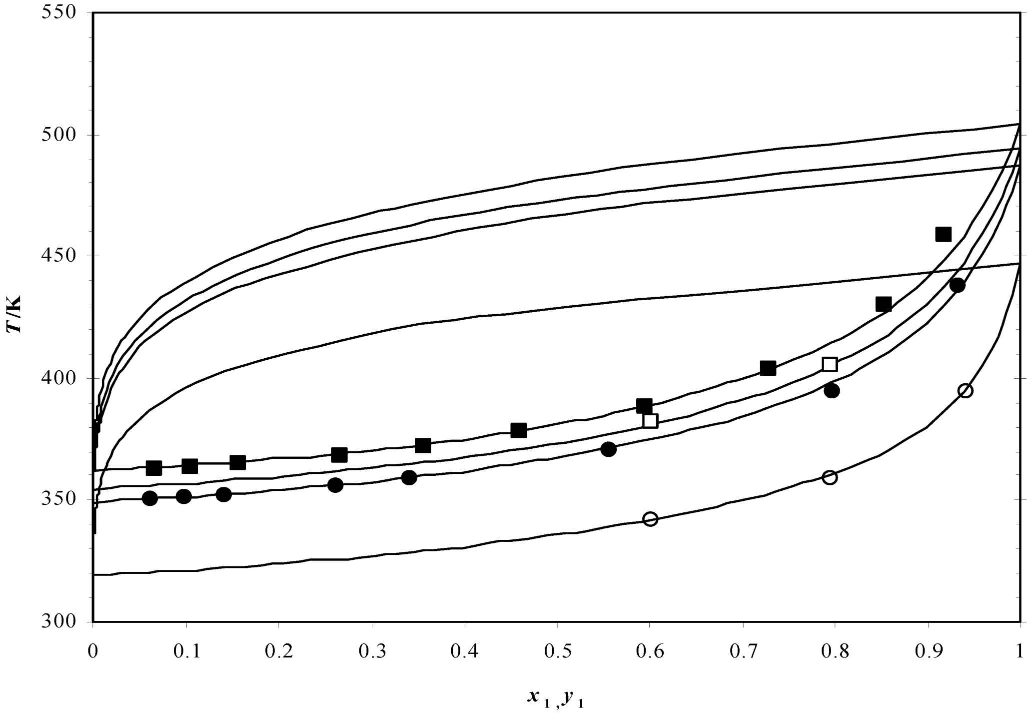

Figure 2. VLE behavior of the binary system MDEA(1) + water(2): ○, □, our experimental data at 10.0 kPa and 50.0 kPa; ●, ■, experimental data of Voutsas[5] at 40.0 kPa and 66.7 kPa; —, calculated using the NRTL model with the parameters given in Table 7 at 10.0 kPa, 40.0 kPa, 50.0 kPa, and 66.7 kPa.

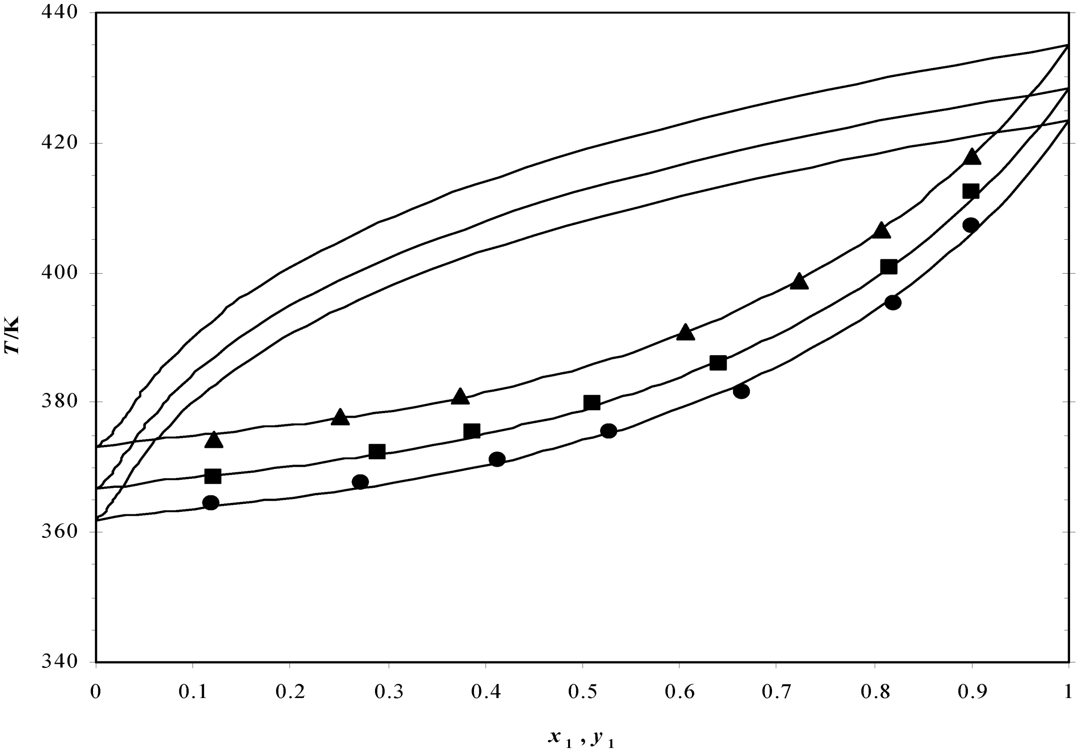

Figure 3. VLE behavior of the binary system AMP(1) + water(2): ●, ■, ▲, experimental data of Pappa[8] at 66.7 kPa, 80.0 kPa, and 101.3 kPa; —, calculated using the NRTL model with the parameters given in Table 7 at 66.7 kPa, 80.0 kPa, and 101.3 kPa.

Water + AMP + Methanol Mixtures. Bubble temperatures for the ternary system were measured along five isobars: (30.00, 50.00, 70.00, 90.00, and 101.33) kPa for seven different mole ratios of water + AMP + methanol approximately equal to 20:40:40, 30:40:30, 40:20:40, 40:30:30, 40:40:20, 50:30:20, and 60:20:20. The results are presented in Table 3.

Water + MDEA Mixtures. The water + MDEA binary system has been studied previously.[5,9] Bubble temperatures for the water + MDEA binary system were measured only at three compositions. The results are presented in Table 4.

Water + MDEA + Methanol Mixtures. Bubble temperatures for the ternary system were measured along five isobars: (30.00, 50.00, 70.00, 90.00, and 101.33) kPa for the same mole ratios as the water + AMP + methanol system. The results are presented in Table 5.

Table 9. Water(1) + AMP(2) + Methanol(3) Ternary System Calculated with the NRTL Model[a]

		T/K									
		$P = 30.00$ kPa		$P = 50.00$ kPa		$P = 70.00$ kPa		$P = 90.00$ kPa		$P = 101.33$ kPa	
x_1	x_2	NRTL	100 AD[b]	NRTL	100 AD[b]	NRTL	100 AD[b]	NRTL	100 AD[b]	NRTL	100 AD[b]
0.1951	0.3903	330.50	0.99	342.21	0.73	350.57	0.61	357.18	0.30	360.41	0.16
0.3003	0.3893	333.85	0.82	345.71	0.64	354.18	1.11	360.88	0.94	364.15	0.93
0.3926	0.1948	324.66	0.63	336.14	0.27	344.27	0.04	350.67	0.15	353.79	0.23
0.3958	0.2931	330.75	0.66	342.45	0.22	350.79	0.02	357.36	0.05	360.57	0.12
0.3860	0.3803	336.50	0.33	348.49	0.53	357.04	0.32	363.81	0.17	367.12	0.14
0.4991	0.2904	334.60	0.63	346.50	0.68	354.96	0.81	361.65	0.83	364.91	0.79
0.5932	0.1980	331.90	0.41	343.70	0.13	352.08	0.03	358.68	0.06	361.89	0.04

[a] Comparison with experimental data. [b] $\mathrm{AD} = \dfrac{|T_i^{\mathrm{exptl}} - T_i^{\mathrm{calcd}}|}{T_i^{\mathrm{exptl}}}$.

Table 10. Water(1) + MDEA(2) + Methanol(3) Ternary System Calculated with the NRTL Model.

		T/K									
		$P = 30.00$ kPa		$P = 50.00$ kPa		$P = 70.00$ kPa		$P = 90.00$ kPa		$P = 101.33$ kPa	
x_1	x_2	NRTL	100 AD[b]	NRTL	100 AD[b]	NRTL	100 AD[b]	NRTL	100 AD[b]	NRTL	100 AD[b]
0.1999	0.3975	329.12	2.03	341.71	1.52	350.61	1.08	357.59	0.35	360.99	0.87
0.2997	0.3937	332.62	0.40	345.41	0.29	354.44	0.94	361.52	0.89	364.96	1.01
0.3451	0.2205	323.02	0.76	334.96	0.37	343.38	0.50	349.97	0.43	353.18	0.03
0.4124	0.2943	329.75	0.67	342.21	1.02	350.99	1.34	357.88	1.31	361.22	0.65
0.3894	0.3868	336.19	1.62	349.17	0.55	358.32	0.84	365.49	0.79	368.98	0.86
0.5100	0.2904	334.01	0.93	346.71	0.35	355.64	1.05	362.64	1.43	366.04	1.52
0.6001	0.1991	331.03	0.42	343.43	0.83	352.15	0.88	358.98	0.88	362.29	0.90

[a] Comparison with experimental data. [a] $\mathrm{AD} = \dfrac{|T_i^{\mathrm{exptl}} - T_i^{\mathrm{calcd}}|}{T_i^{\mathrm{exptl}}}$.

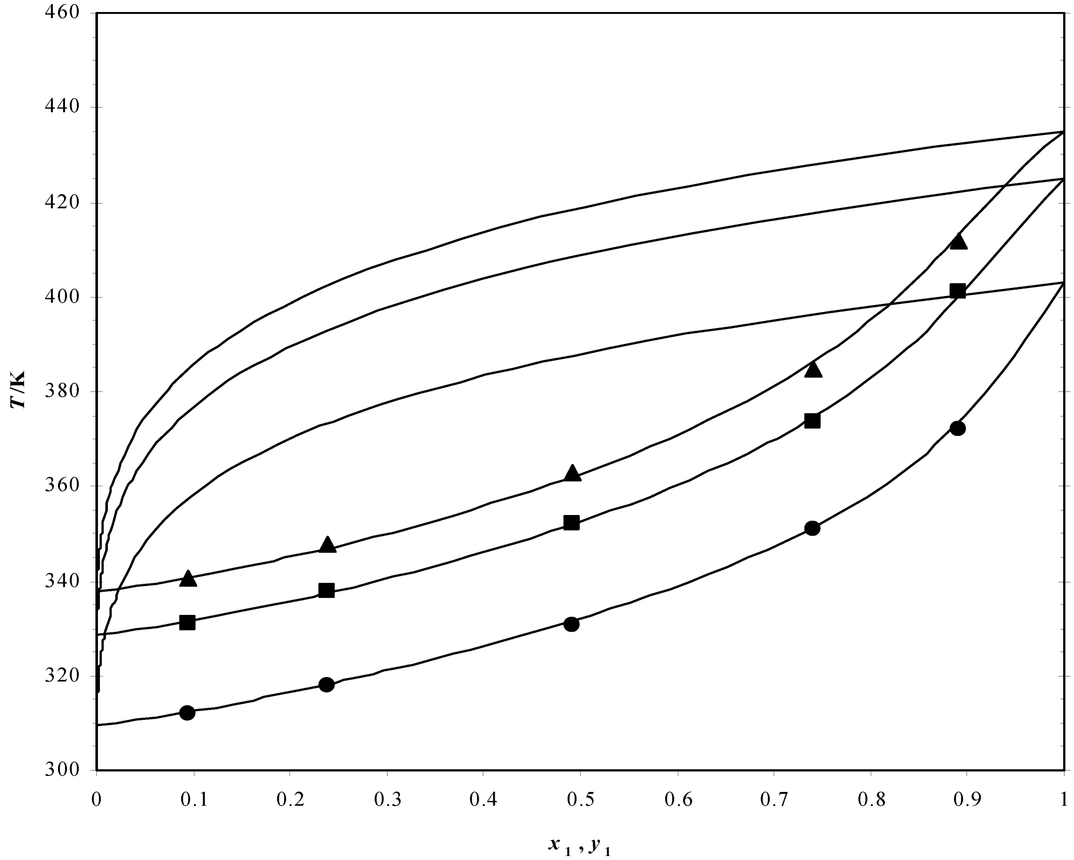

Figure 4. VLE behavior of the binary system AMP(1) + methanol(2): ●, ■, ▲, our experimental data at 30.0 kPa, 70.0 kPa, and 101.3 kPa; —, calculated using the NRTL model with the parameters given in Table 7 at 30.0 kPa, 70.0 kPa, and 101.3 kPa.

Thermodynamic Modeling

The NRTL model developed by Renon and Prausnitz[10] was used to correlate the water + MDEA + methanol and water + AMP + methanol systems. The expression for the activity coefficients is

$$\ln \gamma_1 = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_k x_k \tau_{kj} G_{kj}}{\sum_k G_{kj} x_k} \right) \quad (1)$$

where

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}), \quad \alpha_{ji} = \alpha_{ij} \quad (2)$$

The MDEA + methanol, MDEA + water, AMP + methanol, and AMP + water τ_{ij} parameters were fitted with a temperature dependence as follows:

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T/\mathrm{K}} \quad (3)$$

α is taken to be equal to 0.3. The water + methanol binary NRTL parameters were taken from the SIMSCI database.[11]

Vapor pressures for water, methanol, and MDEA were taken from the correlation proposed by the DIPPR database.[12] For AMP, our experimental data and data from Pappa et al.[8] have been correlated using a DIPPR equation:

$$\ln(P^s/\mathrm{Pa}) = A + B/(T/\mathrm{K}) + C \ln(T/\mathrm{K}) + D(T/\mathrm{K})^E \quad (4)$$

The average percentage deviation in vapor pressure is about 0.6 %. The DIPPR parameters are given in Table 6.

The database used to fit the NRTL parameters consists of: (a) for the system containing MDEA, our binary and ternary experimental data, water + MDEA vapor−liquid equilibrium (VLE) data from Xu et al.[9] and Voutsas et al.,[5] and water + MDEA H^E data from Maham et al.[13,14]; (b) for the system containing AMP, our binary and ternary experimental data, water + AMP VLE data from Pappa et al.,[8] and water + AMP H^E data from Mathonat et al.[15] The NRTL parameters were obtained by minimizing the following objective function (OF)

$$\mathrm{OF} = \sum_{i=1}^{N_1} \left| \frac{T_i^{\mathrm{exptl}} - T_i^{\mathrm{calcd}}}{T_i^{\mathrm{exptl}}} \right| + \sum_{j=1}^{N_2} \left| \frac{H_j^{E,\mathrm{exptl}} - H_j^{E,\mathrm{calcd}}}{H_j^{E,\mathrm{exptl}}} \right| \quad (5)$$

and are reported in Table 7.

The average absolute deviations between experimental data and calculated values with the NRTL model are shown in Table 8. All the binary systems, the ternary systems, and the excess enthalpy data are well correlated. Tables 9 and 10 compare the calculated values of the NRTL model with our experimental data for both ternary systems.

Figure 2 compares our experimental data and experimental data from Voutsas et al.[5] with correlated VLE behavior of the MDEA + water binary system. Figure 3 compares experimental data from Pappa et al.[8] with correlated VLE behavior of the AMP + water binary system, and Figure 4 compares our experimental data with the correlated VLE behavior of the AMP + methanol binary system.

Conclusion

In this work, isobaric VLE data have been measured for a wide range of temperatures, pressures, and compositions for the methanol + MDEA + water and methanol + AMP + water ternary systems using an ebulliometric method. The vapor pressures of pure AMP and two binary subsystems, MDEA + water and methanol + AMP, have also been studied.

The MDEA + methanol, MDEA + water, AMP + methanol, and AMP + water NRTL parameters have been fitted using all our experimental data and additional VLE and H^E data taken from the literature. All the binary systems, the ternary systems, and the excess enthalpy data are very well correlated.

Literature Cited

(1) Banasiak, J. Solubility of Carbon Dioxide in Methanol−Monoethanolamine Mixtures. *Gaz. woda Tech. Sanit.* **1981**, *55*, 196−199.
(2) Henni, A.; Mather, A. E. Solubility of Carbon Dioxide in Methyldiethanolamine + Methanol + Water. *J. Chem. Eng. Data* **1995**, *40*, 493−495.
(3) Habchi Tounsi, K. N.; Barreau, A.; Le Corre, E.; Mougin, P.; Neau, E. Measurement of Carbon Dioxide Solubility in a Solution of Diethanolamine Mixed with Methanol. *Ind. Eng. Chem. Res.* **2005**, *44*, 9239−9243.
(4) Horstmann, S.; Mougin, P.; Lecomte, F.; Fischer, K.; Gmehling, J. Phase Equilibrium and Excess Enthalpy Data for the System Methanol + 2,2′-Diethanolamine + Water. *J. Chem. Eng. Data* **2002**, *47*, 1496−1501.
(5) Voutsas, E.; Vrachnos, A.; Magoulas, K. Measurement and Thermodynamic Modeling of the Phase Equilibrium of Aqueous *N*-Methyldiethanolamine Solutions. *Fluid Phase Equilib.* **2004**, *224*, 193−197.
(6) Cottrell, G. *J. Am. Chem. Soc.* **1919**, *41*, 721.
(7) Vellut, D., Ph.D. Thesis, Université Claude Bernard, Lyon, France, 2000.
(8) Pappa, G.; Anastasi, C.; Voutsas, E. Measurement and Thermodynamic Modeling of the Phase Equilibrium of Aqueous 2-Amino-2-methylpropanol Solutions. *Fluid Phase Equilib.* **2006**, *243*, 193−197.
(9) Xu, S.; Qig, S.; Zhen, Z.; Zhang, C.; Carroll, J. J. Vapor Pressure Measurements of Aqueous *N*-Methyldiethanolamine Solutions. *Fluid Phase Equilib.* **1991**, *67*, 197−201.
(10) Renon, H.; Prausnitz, J. M. Local Composition in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135−144.
(11) Simulation Sciences Inc., PRO/II 5.61, 1994−2002.
(12) Design Institute for Physical Properties, DIADEM Professional 1.0.0, BYU DIPPR Lab.
(13) Maham, Y.; Mather, A. E.; Helper, L. G. Excess Molar Enthalpies of (Water + Alkanolamine) Systems and Some Thermodynamic Calculations. *J. Chem. Eng. Data* **1997**, *42*, 988−992.
(14) Maham, Y.; Mather, A. E.; Mathonat, C. Excess Properties of (Alkyldiethanolamine + H_2O) Mixtures at Temperatures from (298.15 to 338.15) K. *J. Chem. Thermodyn.* **2000**, *32*, 229−236.
(15) Mathonat, C.; Maham, Y.; Mather, A. E.; Helper, L. G. Excess Molar Enthalpies of (Water + Monoalkanolamine) Mixtures at 298.15 K and 308.15 K. *J. Chem. Eng. Data* **1997**, *42*, 993−995.

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