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Surface Tension of Binary Mixtures of Water + *N*-Methyldiethanolamine and Ternary Mixtures of This Amine and Water with Monoethanolamine, Diethanolamine, and 2-Amino-2-methyl-1-propanol from 25 to 50 °C

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The surface tension of aqueous solutions of *N*-methyldiethanolamine and diethanolamine + *N*-methyldiethanolamine, monoethanolamine + *N*-methyldiethanolamine and 2-amino-2-methyl-1-propanol + *N*-methyldiethanolamine was measured at temperatures from 25 °C to 50 °C. For binary mixtures the concentration range was 0−50 mass % *N*-methyldiethanolamine, and for the tertiary mixtures the concentration range for each amine was 0−50 mass %. The experimental values were correlated with temperature and mole fraction. The maximum deviation in both cases was always less than 0.5%.

Introduction

The absorption of CO_2 by aqueous solutions of alkanolamines has been extensively studied because of their industrial importance in gas purification plants. They are especially useful in the removal of acidic components such as CO_2 and H_2S from gas streams (Fathi and Baheri, 1995; Tontiwatchwuthikul et al., 1992; Xu et al., 1996). Industrially important alkanolamines are monoethanolamine (MEA), diethanolamine (DEA), *N*-methyldiethanolamine (MDEA), Diiso-propanolamine (DIPA), and 2-amino-2-methyl-1-propanol (AMP). In general these amines are used in aqueous solutions, and the absorption in mixed amines has specific advantages over the use of single amines (Rangwala et al. 1992).

On the other hand, the surface tension of the liquid phase affects the hydrodynamics and mass transfer rates of processes where a gas−liquid interface exists, like gas absorption (Vázquez et al., 1996a, 1997a). Therefore to know the surface tension of these amine solutions is very important for the design of absorption equipment.

In continuation of our previous papers on the surface tension of binary aqueous solutions of alkanolamines (Vázquez et al., 1996b, 1997b), in this work we have determined the surface tension of the binary aqueous solutions of MDEA (over the entire concentration range) and ternary aqueous mixtures of MDEA + MEA, MDEA + DEA, and MDEA + AMP, at temperatures of 25 °C to 50 °C. The total amine concentration for the ternary mixtures was held constant at 50 mass %, and MEA/DEA or MEA or AMP mass % ratio was varied from 0/50 to 50/0, in 10 mass % steps.

Experimental Section

Aqueous solutions were prepared with distilled deionized water. Alkanolamines were Merck products of nominal purity >99% for the MEA and >98% for MDEA, AMP, and DEA. All the solutions were prepared by mass with deviations of less than 0.3% from the desired nominal concentration. For the binary mixture, the values of the mole fraction, x_A, correspond to 0−100 mass %, at 10% mass % intervals, of MDEA.

Surface tension was determined at 5 °C intervals, between 25 °C and 50 °C, using a Traube stalagmometer and a Prolabo tensiometer, which employs the Wilhelmy plate principle (Lin et al., 1990; Van der Bogaert and Joos, 1980). The detailed experimental procedure has been described elsewhere (Vázquez et al., 1995a,b). In general, each surface tension value reported was an average of 5−10 measurements, where the maximum deviations from the average value were always less than 0.4%. The precision of the temperature control in all these measurements was ±0.05 °C, and the precision of the measurements was ±0.02 mN m^{-1}.

Results and Discussion

The surface tension data for *N*-methyldiethanolamine, *N*-methyldiethanolamine + monoethanolamine, *N*-methyldiethanolamine + diethanolamine, and *N*-methyldiethanolamine + 2-amino-2-methyl-1-propanol aqueous solutions are tabulated in Tables 1, 2, 3, and 4, respectively. In all systems studied the surface tension decreased linearly with increasing temperature for any given concentration or mass percent ratio of amine.

The experimental surface tensions of ternary mixtures of MDEA + DEA + water, at 40 °C s, were compared with those obtained by Rinker et al. (1994). The deviations are always less than 1−2% (Figure 1).

The surface tensions of binary mixtures were correlated with temperature by the expression proposed by Jasper (1972) for the pure components:

$$\sigma/\text{mN}\cdot\text{m}^{-1} = K_1 - K_2\cdot t/°\text{C} \tag{1}$$

This equation also fitted the data of Table 1 for each concentration with deviations less than 0.5%. The fitted values of K_1 and K_2 are listed in Table 5.

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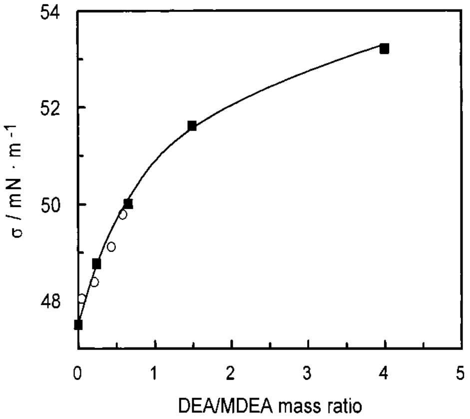

Figure 1. Comparison of the experimental surface tensions of aqueous solutions of *N*-methyldiethanolamine + diethanolamine with published values, at 40 °C: (■) experimental; (○) Rinker et al. (1994).

Table 1. Surface Tension (σ/mN m^{-1}) of *N*-Methyldiethanolamine (A) + Water (B)

	t/°C					
x_A	25	30	35	40	45	50
0.000	72.01	71.21	70.42	69.52	68.84	67.92
0.008	63.72	63.11	62.87	62.17	61.80	61.14
0.017	60.60	59.88	59.71	59.33	59.24	57.96
0.026	58.53	57.68	56.94	56.56	55.50	54.30
0.036	57.28	56.68	56.00	55.55	54.50	53.10
0.048	55.61	54.74	54.24	53.71	52.89	51.30
0.061	53.50	52.30	51.56	51.30	50.70	49.54
0.091	51.35	50.51	50.33	49.70	48.99	47.70
0.131	49.59	49.06	48.24	47.67	46.50	45.34
0.185	48.23	47.30	46.60	45.58	44.80	43.80
0.261	46.00	45.00	44.40	43.52	42.40	41.60
0.377	44.20	43.29	42.70	41.97	41.11	40.39
0.576	41.80	41.10	40.55	40.11	39.68	38.50
1.000	38.90	38.10	37.62	37.31	37.16	36.88

Table 2. Surface Tension (σ/mN m^{-1}) of *N*-Methyldiethanolamine + Monoethanolamine + Water

	% mass MDEA/% mass MEA					
t/°C	0/50	10/40	20/30	30/20	40/10	50/0
25	57.31	55.30	53.60	52.40	50.83	49.59
30	56.52	54.70	52.81	51.60	50.25	49.06
35	55.74	54.00	52.19	50.80	49.51	48.24
40	54.84	53.20	51.60	49.99	48.75	47.50
45	54.16	52.80	51.30	49.54	48.28	46.70
50	53.54	52.34	50.70	49.00	47.20	45.80

Table 3. Surface Tension (σ/mN m^{-1}) of *N*-Methyldiethanolamine + Diethanolamine + Water

	% mass MDEA/% mass DEA					
t/°C	0/50	10/40	20/30	30/20	40/10	50/0
25	57.20	55.65	53.90	52.54	51.32	49.59
30	56.42	54.36	53.14	51.46	50.40	49.06
35	55.62	54.00	52.15	50.81	49.72	48.24
40	54.71	53.25	51.43	49.84	48.85	47.50
45	54.01	52.60	50.93	49.34	48.28	46.70
50	53.07	51.80	50.43	48.42	47.66	45.80

For a given temperature, the surface tension of binary mixtures decreased as the alkanolamine concentration increased. This trend is nonlinear, the change in surface tension caused by a given change in alkanolamine concentration being larger at low concentrations than at high concentrations. We fit the equation

$$\frac{\sigma_W - \sigma}{\sigma_W - \sigma_A} = \left(1 + \frac{a x_W}{1 - b x_W}\right) x_A \qquad (2)$$

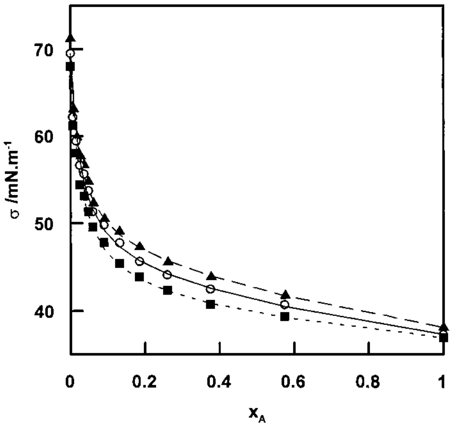

Figure 2. Surface tension of *N*-methyldiethanolamine (A) + water (B) plotted against the mole fraction of MDEA, x_A: (■) experimental, 30 °C; (- - -) calculated, 30 °C; (○) experimental, 40 °C; (—) calculated 40 °C; (▲) experimental 50 °C; (— —) calculated 50 °C.

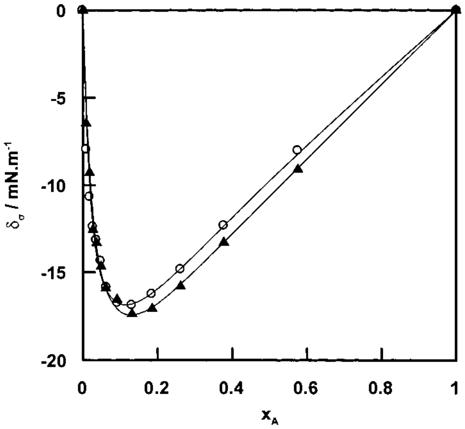

Figure 3. Surface tension deviation, δ_σ, as a function of mole fraction of *N*-methyldiethanolamine, x_A: (▲) 25 °C; (○) 50 °C; (—) calculated from eqs 2 and 3.

Table 4. Surface Tension (σ/mN m^{-1}) of *N*-Methyldiethanolamine + 2-Amino-2-methyl-1-propanol + Water

	% mass MDEA/% mass AMP					
t/°C	0/50	10/40	20/30	30/20	40/10	50/0
25	39.58	41.58	42.76	45.10	47.30	49.80
30	38.98	41.12	42.40	44.52	46.40	49.00
35	38.37	40.82	41.84	43.88	45.80	48.00
40	37.76	40.12	41.12	43.40	45.07	47.40
45	37.14	39.58	40.80	42.68	44.65	46.50
50	36.50	39.00	40.15	42.40	44.10	45.80

Table 5. Surface Tension Parameters K_1 and K_2 (Eq 1) for *N*-Methyldiethanolamine (A) + Water (B)

x_A	K_1	K_2	x_A	K_1	K_2
0.000	76.0852	−0.1626	0.091	55.9114	−0.1531
0.008	68.3981	−0.1610	0.131	53.7714	−0.1525
0.017	64.5190	−0.1602	0.185	51.6676	−0.1512
0.026	62.7209	−0.1597	0.261	49.7323	−0.1509
0.036	61.3304	−0.1577	0.377	47.9167	−0.1495
0.048	59.3626	−0.1562	0.576	45.2952	−0.1474
0.061	57.3257	−0.1543	1.000	41.4900	−0.1022

to the data for each solute (where σ_W and σ_A are the surface tensions of pure water and pure alkanolamine, respectively, and x_W and x_A are the mole fractions of water and alkanolamine). The values of the fitted parameters *a* and *b* in eq 2 are listed in Table 6. The experimental and estimated surface tensions for *N*-methyldiethanolamine +

Table 6. Surface Tension Parameters *a* and *b* (Eq 2) for *N*-Methyldiethanolamine + Water

	t/°C					
parameters	25	30	35	40	45	50
a	0.731	0.735	0.745	0.767	0.804	0.821
b	0.9772	0.9767	0.9750	0.9733	0.9716	0.9711

water are compared in Figure 2. The deviations are less than 0.2% in all such plots.

The surface tension deviation is defined as the difference between the surface tension of the mixture and that expected on the basis of a mole fraction average

$$\delta_\sigma = \sigma - (\sigma_W x_W + \sigma_A x_A) \tag{3}$$

Plotting δ_σ against the mole fraction of *N*-methyldiethanolamine (Figure 3) shows that the deviation from a mole fraction average is larger for a temperature of 25 °C than for a temperature of 50 °C.

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