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Surface Tension of Binary Mixtures of *N*-Methyldiethanolamine and Triethanolamine with Ethanol

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Surface tensions of binary mixtures of *N*-methyldiethanolamine and triethanolamine with ethanol were determined at (15 to 40) °C over the entire range of concentrations to analyze the influence of both variables. The Redlich–Kister equation was employed to fit surface tension deviation obtained from experimental values.

Introduction

Nowadays, research studies about physical properties of aqueous solutions of amines or their mixtures have been developed to contribute valuable data to use in unit design or control of chemical processes.[1,2] One of the most important uses of this kind of compound is for removal of sour gases from natural gas and petroleum streams.[3,4] The main objective of these processes is to minimize the environmental pollution and, specifically, the greenhouse effect. Also, other uses of this kind of substance are as surfactants, additives in detergents, and agriculture products.

Amines employed in this work are used in different industrial processes to capture carbon dioxide, and for this reason it is very important to characterize the behavior of these compounds with regard to the kinetics between acid gases and these amines in the capture process.[5,6] The use of ethanol as solvent in these kinds of chemical absorption processes could be interesting because certain studies have shown that it could improve the experimental results obtained in aqueous solution.[7,8]

The present work includes the measurement of surface tension of MDEA (and TEA) + ethanol mixtures to obtain experimental data of these physical properties that could be useful in absorption/desorption studies to find an explanation for the mass transfer process and gas–liquid kinetics.

Experiments

Materials. *N*-Methyldiethanolamine, MDEA (CAS Registry No. 105-59-9) and triethanolamine, TEA (CAS No. 102-71-6), were supplied by Fluka and Sigma-Aldrich, respectively, with a purity of > 98 %. Ethanol has been supplied by Panreac Química (CAS No. 64-17-5) with a purity of > 99 %. All liquid mixtures were prepared by mass using an analytical balance (Kern 770) with a precision of ± 10^{-4} g. The maximum uncertainty of the sample preparation in mole fraction was ± 0.002.

Methods. Surface tension was determined employing a Krüss K-11 tensiometer using the Wilhelmy plate method. The plate employed was a commercial platinum plate supplied by Krüss. The platinum plate was cleaned with water and acetone and flame-dried before each measurement. The uncertainty of the measurement was ± 0.04 $\mathrm{mN \cdot m^{-1}}$. In general, each surface tension value reported was an average of ten measurements. Before surface tension measurements were made, the samples were stirred in a thermostatted vessel that was closed to prevent evaporation. Surface tension measurements were carried out in the range of (15 to 40) °C with 5 °C steps. The measurement vessel was connected to a thermostat-cryostat bath (Selecta Frigiterm) controlled to ± 0.1 °C.

Results and Discussion

Punctual measurements have been carried out with the aim to check the experimental surface tension determination method for pure components. The experimental results have been compared with previously published data of our research team and other authors.[9–12] and low deviations have been observed (< 0.8 %).

Tables 1 and 2 show the experimental results of surface tension corresponding to ethanol binary solutions of MDEA and TEA determined at (15 to 40) °C over the entire concentration range.

As an example, Figure 1 offers a representation of the surface tension values determined over the entire range of concentration at different temperatures for both system studied in this work to analyze these variables upon this physicochemical property. Experimental trends shown in Figure 1 indicate that an increase in amine concentration in the mixture produces an increase of the value of surface tension. Pure ethanol has a low value of surface tension in relation with the corresponding value for pure water (72.01 $\mathrm{mN \cdot m^{-1}}$),[13] and then, the experimental behavior observed in the present work is so different than the trend observed in previous studies[9,10] for aqueous solutions of these amines (see Figure 1). For example, in aqueous solutions, a small quantity of amines produces an important decrease in the value of surface tension[9,10] with a very characteristic behavior on this kind of mixture. The behavior observed when these amines are employed in aqueous solution is related to different

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Table 1. Surface Tension, σ, for MDEA (1) + Ethanol (2) from t = (15 to 40) °C

	$\sigma/(\mathrm{mN \cdot m^{-1}})$					
	t/°C					
x_1	15	20	25	30	35	40
0.0000	22.72[a]	22.31[a]	21.85	21.41[a]	21.04[a]	20.62[a]
0.0253	23.45	23.11	22.79	22.49	22.16	21.92
0.0321	23.58	23.24	22.92	22.63	22.27	22.04
0.1033	24.92	24.59	24.32	24.06	23.77	23.58
0.1629	26.03	25.70	25.45	25.26	24.94	24.81
0.1705	26.18	25.83	25.59	25.38	25.08	24.98
0.2474	27.58	27.24	27.02	26.79	26.53	26.44
0.3713	29.85	29.47	29.28	28.95	28.75	28.63
0.4806	31.80	31.40	31.18	30.84	30.62	30.49
0.5506	33.02	32.60	32.39	32.01	31.78	31.66
0.7035	35.58	35.06	34.92	34.48	34.24	34.07
0.7452	36.25	35.71	35.58	35.08	34.84	34.66
0.8227	37.51	36.91	36.71	36.09	35.80	35.57
0.9368	39.11	38.42	38.10	37.39	37.00	36.73
1.0000	39.99	39.26	38.92	38.08	37.63	37.25

[a] Vázquez et al.[12]

Table 2. Surface Tension, σ, for TEA (1) + Ethanol (2) from t = (15 to 40) °C

	$\sigma/(\mathrm{mN \cdot m^{-1}})$					
	t/°C					
x_1	15	20	25	30	35	40
0.0000	22.72[a]	22.31[a]	21.85	21.41[a]	21.04[a]	20.62[a]
0.0795	24.10	23.69	23.32	23.02	22.71	22.35
0.1461	25.40	25.02	24.70	24.41	24.12	23.81
0.2209	27.12	26.77	26.42	26.11	25.78	25.46
0.3266	29.68	29.34	28.97	28.61	28.21	27.79
0.4581	33.17	32.72	32.29	31.87	31.42	30.89
0.6263	37.65	37.11	36.57	36.02	35.48	34.82
0.7725	41.56	40.89	40.24	39.61	39.00	38.21
0.8489	43.57	42.86	42.16	41.47	40.83	39.97
0.9304	45.78	44.96	44.22	43.47	42.77	41.84
1.0000	47.64	46.77	45.88	45.16	44.42	43.40

[a] Vázquez et al.[12]

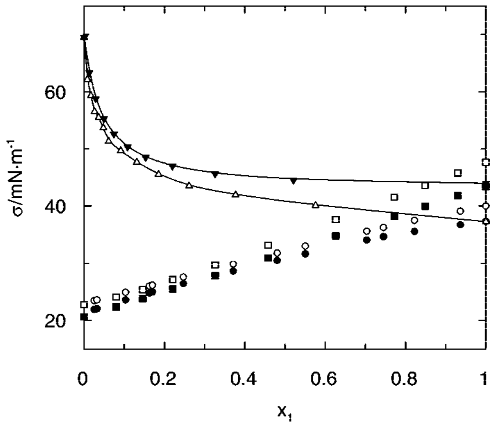

Figure 1. Surface tension, σ, for MDEA (1) + ethanol (2) systems: ○, 15 °C; ●, 40 °C. For the TEA (1) + ethanol (2) system: □, 15 °C; ■, 40 °C; △, MDEA (1) + water (2) at 40 °C;[10] ▼, TEA (1) + water (2) at 40 °C.[11]

processes: (i) the tendency of certain solutes to locate at the air–water interface that produces a fast decrease in surface tension when solute concentration increases and (ii) aggregation processes between solute molecules in aqueous solution that produce a slight modification in surface tension when solute concentration is varied. In binary mixtures of these amines (MDEA and TEA) with ethanol, these characteristic behaviors are not observed, and then, these processes do not take place.

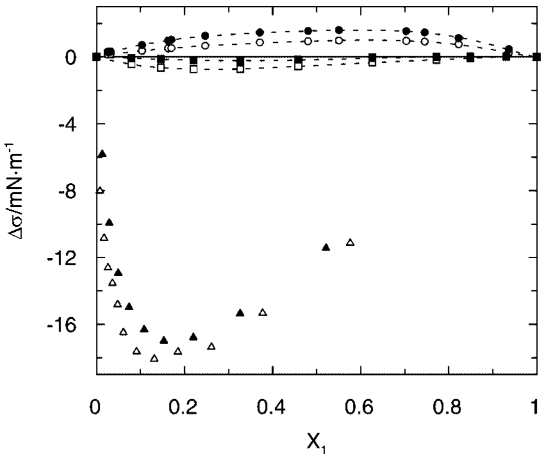

Figure 2. Surface tension deviations, $\Delta\sigma$, for MDEA (1) + ethanol (2) systems: ○, 25 °C; ●, 40 °C. For the TEA (1) + ethanol (2) system: □, 20 °C; ■, 40 °C; △, MDEA (1) + water (2) at 25 °C;[10] ▲, TEA (1) + water (2) at 25 °C.[11]

Table 3. Fit Parameters Corresponding to the Redlich−Kister Equation for MDEA (1) + Ethanol (2) from t = (15 to 40) °C

	$\Delta\sigma/\mathrm{mN \cdot m^{-1}}$					
	t/°C					
parameter	15	20	25	30	35	40
A_0	−2.89	−4.22	−10.14	−12.65	−11.97	−14.40
A_1	41.84	51.38	91.94	117.0	119.4	140.1
A_2	−81.05	−97.23	−170.8	−221.4	−226.4	−267.5
A_3	47.53	56.85	98.56	130.1	132.8	159.0
δ	0.06	0.08	0.1	0.13	0.13	0.14

Table 4. Fit Parameters Corresponding to the Redlich−Kister Equation for TEA (1) + Ethanol (2) from t = (15 to 40) °C

	$\Delta\sigma/\mathrm{mN \cdot m^{-1}}$					
	t/°C					
parameter	15	20	25	30	35	40
A_0	−2.16	−0.98	2.04	−0.97	−1.42	−0.68
A_1	−0.25	−2.83	−8.89	0.96	4.02	3.90
A_2	−12.9	−19.5	−23.3	−4.16	6.38	11.8
A_3	5.40	14.1	22.7	−0.71	−12.2	−16.1
δ	0.02	0.01	0.01	0.01	0.02	0.02

With regard to the influence of temperature upon surface tension values in binary mixtures studied, a common behavior was observed for both systems when temperature was increased producing a clear decrease in the value of surface tension with a linear trend. This trend is frequently observed in this kind of system[12] for all the compositions studied, and it allows use of a linear equation to fit experimental data.

The surface tension deviations corresponding to the mixtures employed in the present work were defined by eq 1

$$\Delta Y = Y_m - (x_1 \cdot Y_1 + x_2 \cdot Y_2) \qquad (1)$$

Deviations calculated employing eq 1 by means of experimental surface tension data of pure components and mixtures show that deviation character is different for each system. Positive deviations have been found for mixtures of ethanol + MDEA, while negative ones have been obtained for the other mixture (ethanol + TEA) (see Figure 2). The negative character of deviations for the mixture formed by ethanol + MDEA changes with regard to the aqueous mixture that shows negative deviations[9] such as numerous systems of amines with water.[14] The deviations obtained are very different in relation to those obtained for the system of these amines and water as Figure 2 shows. This behavior is due to the interactions formed by amines and the other mixture compound.

The deviation values were fitted using a Redlich–Kister type equation (eq 2), and the corresponding results obtained for fitting parameters are shown in Tables 3 and 4. Figure 2 shows the fit of the Redlich–Kister equation to the calculated values of surface tension deviations.

$$\Delta\kappa_s = x_1 \cdot x_2 \cdot \sum_{j=1}^{4} q_j \cdot x_2^{(j-1)/2} \qquad (2)$$

Also, the root-mean-square deviations (δ) were calculated by means of eq 3

$$\delta = \left(\frac{\sum_i (z_{\text{exptl}} - z_{\text{calcd}})^2}{n_{\text{data}}} \right)^{1/2} \qquad (3)$$

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