

# Surface Behavior of Aqueous Solutions of Pyrrolidine and Piperidine

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The surface tension of aqueous solutions of pyrrolidine and piperidine at temperatures of 20, 25, 30, 40 and 50 °C have been measured over the mole fraction range. The surface tension value decreases significantly for the mixture rich in amine. Thermodynamic properties such as surface enthalpy and surface entropy for the systems studied were calculated from the experimental data.

## Introduction

Amines and their mixtures with water have been used in processes related to natural gas, ammonia synthesis, and so forth in the past decades to remove acidic gases as carbon dioxide and sulfur hydride through the reaction between these gases and the amines.<sup>1,2</sup> Certain alkanolamines could selectively remove one gas present in a mixtures of them (i.e., monoethanolamine (MEA), *N*-methyldiethanolamine (MDEA), or triethanolamine (TEA)<sup>3</sup>). Also, these reactions have been used to determine hydrodynamic parameters corresponding to aerated gas/liquid systems.

For these reasons, we are interested in the physical properties of these systems and their behavior in relation to the operation variables that are in many cases the mixture composition and the temperature.

In previous papers, other authors, in the last few years, have analyzed different amine–water systems in relation to important physical properties with influences in several industrial operations.<sup>4–6</sup> Densities, viscosities, and thermal conductivities have been measured for aqueous solutions of different amines and alkanolamines.

The aim of this work has been to measure and analyze the surface tension of binary aqueous solutions of pyrrolidine and piperidine over the entire concentration range at different temperatures.

## Experimental Section

Pyrrolidine (CAS number 123-75-1) and piperidine (CAS number 110-89-4) were supplied by Fluka and Riedel-de Haën, respectively, with a purity of >99% and >99.5%. Bi-distilled water was used to prepare the mixtures of water and amine. All of the mixtures were prepared by mass using an analytical balance (Kern 770) with a precision of 10<sup>-4</sup> g. The uncertainty of the samples' preparation in mole fraction was ±0.0002.

The surface tension was determined by 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 and flame dried before each measurement. The surface tension of pure water was determined and compared with the literature to confirm that this method contributes suitable results.<sup>7,8</sup> The uncertainty of the measurement was ±0.03

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**Table 1. Surface Tension,  $\sigma$ , for Water (1) + Pyrrolidine (2) from 20 °C to 50 °C**

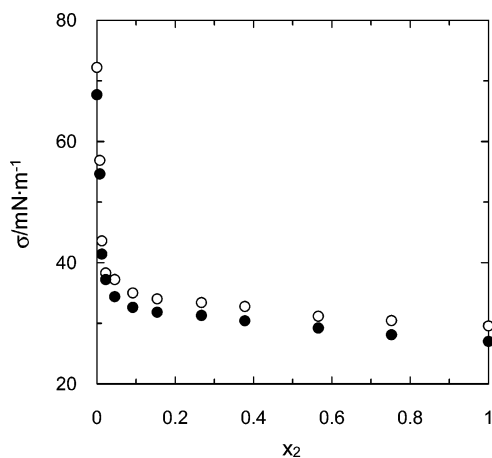
$x_2$	$t/^\circ\text{C}$				
	20	25	30	40	50
	$\sigma/\text{mN}\cdot\text{m}^{-1}$				
1.0000	30.27	29.75	29.02	27.87	26.75
0.9161	31.07	30.42	30.13	29.02	27.83
0.7844	32.10	31.45	31.30	30.40	29.20
0.6858	32.99	32.59	32.39	31.11	30.25
0.6093	33.89	33.54	33.07	31.95	31.05
0.5219	34.87	34.40	33.99	32.97	32.07
0.4212	35.97	35.45	35.11	34.44	33.15
0.3039	37.53	37.09	36.69	35.68	34.74
0.1792	39.70	39.74	39.00	38.01	37.30
0.1082	41.70	41.19	40.92	40.19	39.17
0.0564	46.07	45.61	45.21	44.76	43.89
0.0156	55.61	55.32	54.98	54.10	53.26
0.0000	72.70	72.05	71.28	69.32	67.88

mN·m<sup>-1</sup> The detailed experimental procedure has been described elsewhere.<sup>9</sup> In general, each surface tension value reported was an average of 10 measurements. The samples were thermostated in a closed vessel with stirring before surface tension measurements to prevent evaporation. Surface tension measurements were carried out at 20, 25, 30, 40, and 50 °C.

## Results and Discussion

A comparison between bibliographic data and our experimental data for the surface tension of pure amines employed in the present paper has been carried out. Specifically, Jasper<sup>10</sup> contributed a value of 29.48 mN·m<sup>-1</sup> for piperidine and 29.65 mN·m<sup>-1</sup> for pyrrolidine at 25 °C. A discrepancy of <0.4% of the compared values has been found.

**Effect of Composition.** In the present paper, we determined and analyzed the surface tension of aqueous solutions of pyrrolidine and piperidine. The experimental values of this physical property for the mixtures used in this study are listed in Tables 1 and 2 for different values of temperature and composition. The trends observed for the experimental data obtained for these mixtures are



**Figure 1.** Effect of composition on the surface tension of water (1) + piperidine (2) binary mixtures. ○,  $t = 25\text{ }^{\circ}\text{C}$ ; ●,  $t = 40\text{ }^{\circ}\text{C}$ .

**Table 2. Surface Tension,  $\sigma$ , for Water (1) + Piperidine (2) from 20 °C to 50 °C**

$x_2$	$t/^{\circ}\text{C}$				
	20	25	30	40	50
1.0000	30.11	29.56	29.09	27.90	27.00
0.7524	31.02	30.42	29.82	29.01	28.10
0.5657	31.38	31.15	30.92	30.01	29.20
0.3780	33.27	32.75	32.23	31.42	30.40
0.2672	33.90	33.39	32.88	32.10	31.26
0.1542	34.34	34.02	33.70	32.67	31.80
0.0920	35.44	34.99	34.54	33.69	32.61
0.0458	37.78	37.20	36.62	35.76	34.37
0.0228	38.56	38.27	37.98	37.43	37.18
0.0130	43.84	43.58	43.32	41.58	41.41
0.0076	57.25	56.85	56.45	55.56	54.62
0.0000	72.70	72.05	71.28	69.32	67.88

shown in Figure 1 for the water/piperidine system at different temperatures.

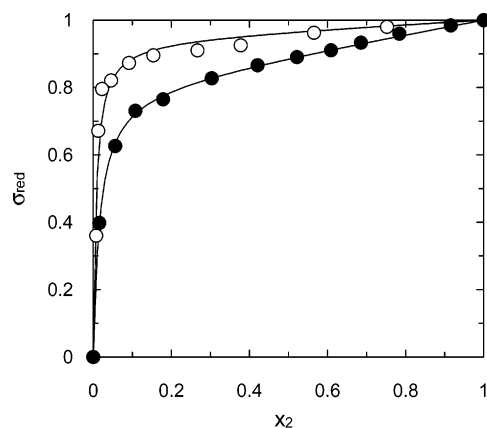
The behavior shown in this Figure proved that the addition of small quantities of amine to water provokes a drastic decrease in the surface tension value for all amine + water mixtures. The larger decreases in the surface tension was produced at a low concentration of amine because a decrease of 50% is produced with an amine concentration of  $\sim 0.015\text{ M}$ . The behavior shown for these two amine–water systems is similar that the observed by other authors for mixtures employing amines.<sup>11</sup>

For a given temperature, an equation developed by Connors and Wright<sup>12</sup> can fit the surface tension versus composition data and has been used by Navaza et al.<sup>11</sup> and Mahan et al.<sup>8</sup> with success on several occasions. This equation is expressed as a model with two adjustable parameters,  $a$  and  $b$  (eq 1).

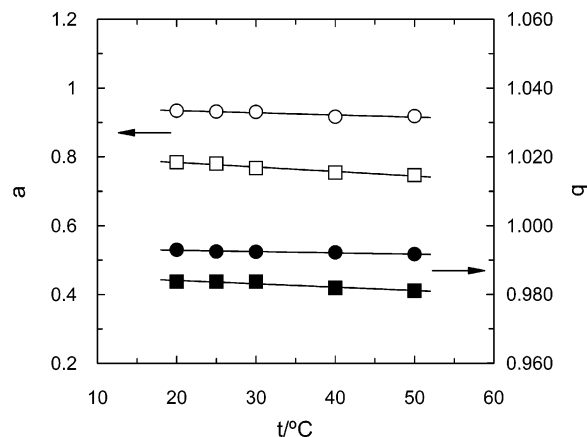
$$\sigma_{\text{red}} = \frac{\sigma - \sigma_w}{\sigma_w - \sigma_a} = \left(1 + \frac{a \cdot x_w}{1 - b \cdot x_w}\right) \cdot x_a \quad (1)$$

where  $\sigma$ ,  $\sigma_w$ , and  $\sigma_a$  are the surface tension of the mixture, water, and amine, respectively, and  $x_w$  and  $x_a$  are the mole fractions of water and amine.

Figure 2 shows the good fit found with eq 2 in relation to the surface/composition data for both systems studied at 25 °C. In this Figure, we have plotted the reduced surface tension (left side of eq 2) versus mixture composition.



**Figure 2.** Experimental and calculated (eq 1) data of reduced surface tension versus composition of the mixture. ○, Water (1) + piperidine (2); ●, water (1) + pyrrolidine (2).  $t = 25\text{ }^{\circ}\text{C}$ .



**Figure 3.** Fitting parameters corresponding to eq 1. Water (1) + piperidine (2) system: ○,  $a$ ; ●,  $b$ . Water (1) + pyrrolidine (2) system: □,  $a$ ; ■,  $b$ .

Also, in Figure 3 the  $a$  and  $b$  data have been plotted in relation to temperature. A small effect of the temperature on these parameter is observed. Using  $a$  and  $b$  parameters from eq 1, we can calculate the binding constant,  $K$ , using eq 2.

$$K = \frac{a}{1 - a} \quad (2)$$

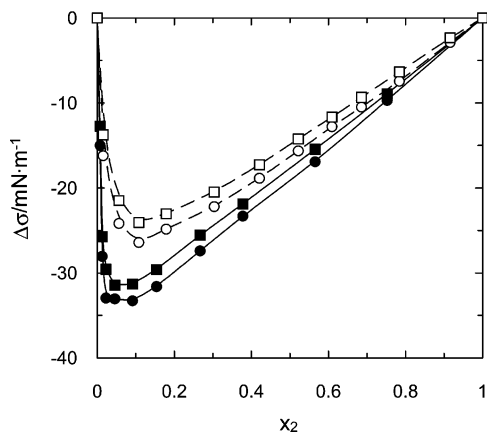
For the systems analyzed, in all cases a decrease in the  $K$  value is produced when temperature increases and indicates that when the temperature increases the water surface is a less favorable site for the amines.

The surface tension deviation from linearity has been defined as the difference between the surface tension of the mixture and that expected on the basis of a mole fraction average as expressed in eq 3.

$$\Delta\sigma = \sigma_m - \sum_i (x_i \cdot \sigma_i) \quad (3)$$

In Figure 4, we plotted this deviation against the mole fraction of amines, and a clear deviation is observed for the two amine mixtures.

**Effect of Temperature.** The effect of the temperature on the value of the surface tension has been analyzed, and the behavior observed is shown in Figures 1 and 4. A decrease in this property is produced when the operation temperature increases. Also, a linear trend was observed when the plot of surface tension versus temperature was



**Figure 4.** Surface tension deviations as a function of the mole fraction of amines ( $x_2$ ). Water (1) + piperidine (2): ●,  $t = 25$  °C; ■,  $t = 50$  °C. Water (1) + pyrrolidine (2): ○,  $t = 25$  °C; □,  $t = 50$  °C.

**Table 3.** Fit Parameters Corresponding to Equations 1 and 2

$t/^\circ\text{C}$	$a$	$b$	$K$
Water (1) + Pyrrolidine (2)			
20	0.784	0.984	3.6
25	0.780	0.984	3.5
30	0.767	0.984	3.3
40	0.754	0.982	3.1
50	0.747	0.981	3.0
Water (1) + Piperidine (2)			
20	0.934	0.993	14.2
25	0.931	0.993	13.5
30	0.930	0.992	13.3
40	0.916	0.992	10.9
50	0.918	0.992	11.2

**Table 4.** Fit Parameters Corresponding to Equation 4

water (1) + piperidine (2)			water (1) + pyrrolidine (2)		
$x_2$	$K_1$	$K_2$	$x_2$	$K_1$	$K_2$
	$\text{mN}\cdot\text{m}^{-1}$	$\text{mN}\cdot\text{K}\cdot\text{m}^{-1}$		$\text{mN}\cdot\text{m}^{-1}$	$\text{mN}\cdot\text{K}\cdot\text{m}^{-1}$
1.0000	32.20	0.11	1.0000	32.64	0.12
0.7524	32.82	0.10	0.9161	33.19	0.11
0.5657	33.00	0.07	0.7844	33.94	0.09
0.3780	35.11	0.09	0.6858	34.98	0.09
0.2672	35.57	0.09	0.6093	35.92	0.10
0.1542	36.17	0.09	0.5219	36.76	0.09
0.0920	37.33	0.09	0.4212	37.78	0.09
0.0458	39.99	0.11	0.3039	39.47	0.09
0.0228	39.44	0.05	0.1792	41.64	0.09
0.0130	45.79	0.09	0.1082	43.32	0.08
0.0076	59.04	0.09	0.0564	47.38	0.07
0.0000	76.37	0.17	0.0156	57.29	0.08
			0.0000	76.37	0.17

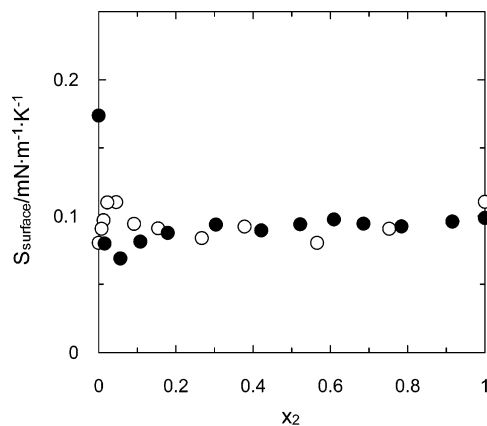
carried out. Our research group has observed this behavior for other binary systems.<sup>7,11</sup>

In previous papers by our group and other authors,<sup>8,13</sup> the surface tension versus temperature data have been fit with a linear regression employing eq 4.

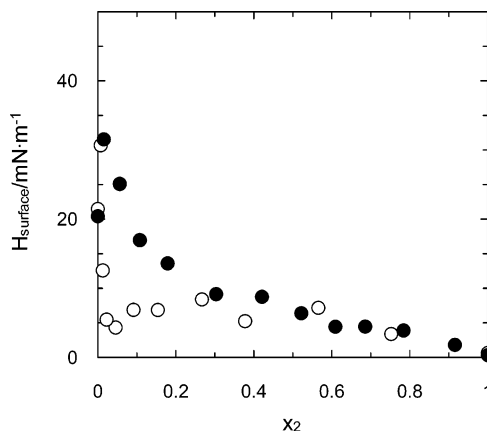
$$\sigma = K_1 - K_2 \cdot t \quad (4)$$

where  $\sigma$  is the surface tension,  $t$  is the temperature, and  $K_1$  and  $K_2$  are fitting coefficients corresponding to eq 4. The values for the fit parameters of eq 4 are listed in Table 4.

**Surface Thermodynamics.** The last point has been related to the thermodynamic properties of the surface for this kind of mixture. The surface enthalpy and entropy



**Figure 5.** Surface entropy for water (1) + piperidine (2) (○) and water (1) + pyrrolidine (2) (●) systems.



**Figure 6.** Surface enthalpy for water (1) + piperidine (2) (○) and water (1) + pyrrolidine (2) (●) systems.  $t = 25$  °C.

have been calculated using equations employed by Glinski et al.<sup>14</sup> (eqs 5 and 6).

$$S = -\left(\frac{\partial\sigma}{\partial T}\right)_{C,P} \quad (5)$$

$$H = \sigma - T\left(\frac{\partial\sigma}{\partial T}\right)_{C,P} \quad (6)$$

In relation to the trend observed for the entropy and observed in Figure 6, this entropy has a constant value along the entire composition range, and near pure water, a notable increase in its value is produced. Other authors have found maxima for other systems<sup>8</sup> related to the molecular organization of amines in the water surface.

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