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Surface Tension of Aqueous Solutions of Short *N*-Alkyl-2-pyrrolidinones

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The surface tension of aqueous solutions of 2-pyrrolidinone, 1-methyl-2-pyrrolidinone, and 1-ethyl-2-pyrrolidinone has been measured at temperatures from (20 to 50) °C over the whole range of concentrations. The surface tensions of these aqueous binary mixtures show more concentration dependence on the water-rich side. The addition of a small amount of *N*-alkyl-2-pyrrolidinone drastically reduces the surface tension of water. This effect is related to not only the presence of hydrophobic groups that tend to remain at the air−water interface but also the influence of the complex interactions between *N*-alkyl-2-pyrrolidinones molecules on the surface tension.

Introduction

Short-chain *N*-alkyl-2-pyrrolidinones are completely miscible over the entire composition range with water. They have been used as cosolvents in the petroleum industry to increase the selectivity and solvent power for extracting aromatic hydrocarbons. These pyrrolidinones are also used in pharmaceutical formulations and in the painless administration of therapeutic agents to the bloodstream in a controlled manner because they enhance the transdermal transport of drugs.

These cyclic amides have excellent thermal and chemical stability and are used as absorbents of sour gases from crude natural gas.[1] The mixed use of amides with certain amounts of water is preferred so that the mixture functions effectively. The knowledge of the physical properties of systems water + cyclic amides over the entire composition range and at different temperatures is very useful for different processes such as mass transfer operations. Surface tension has great importance[2] regarding the behavior and hydrodynamics in mass transfer operations, and the value of this property could play an important role in this kind of operations.

Previous studies have analyzed other cyclic amides with regards to surface tension, such as *N*-cyclohexyl-2-pyrrolidinone,[3] *N*-butyl-2-pyrrolidinone,[4] or *N*-hexyl-2-pyrrolidinone,[5] and certain kind of preaggregation was found before the presence of micelles in aqueous solution.

The present work has obtained the surface tension of different *N*-alkyl-2-pyrrolidinones + water at different temperatures and over the entire composition range to discover the influence of composition, temperature, and the role of substituents on the surface tension and the interactions and aggregation in this kind of system.

Experimental Section

Materials. 2-Pyrrolidinone (CAS no. 616-45-5), 1-methyl-2-pyrrolidinone (CAS no. 872-50-4), and 1-ethyl-2-pyrrolidinone (CAS no. 2687-91-4) were supplied by Fluka with a purity of ≥ 99 % for 2-pyrrolidinone and ≥ 98 % for the other compounds. All liquid mixtures were prepared by mass using an analytical balance (Kern 770) with a precision of $\pm 10^{-4}$ g. The maximum uncertainty of the sample preparations in mole fraction was ± 0.0006.

Table 1. Surface Tension σ for Water (1) + 2-Pyrrolidinone (2) from (20 to 50) °C

	T/°C				
	20	25	30	40	50
x_2	σ/mN·m^{-1}				
0.0000	72.65	72.05	71.21	69.52	67.92
0.0002	60.40	58.90	57.30	55.40	53.20
0.0006	55.69	54.60	53.93	52.20	51.05
0.0100	52.90	51.68	50.80	49.80	49.10
0.0150	52.40	51.19	50.23	49.30	48.70
0.0500	50.72	49.58	48.68	47.77	46.34
0.0700	50.26	49.28	48.45	47.00	45.89
0.1000	49.96	48.91	48.00	46.49	45.58
0.2000	48.91	48.08	47.09	45.89	45.13
0.3000	47.93	47.17	46.42	45.43	44.60
0.4000	47.54	46.87	46.19	45.28	44.53
0.5000	47.17	46.72	46.02	45.21	44.45
0.6000	47.10	46.64	45.81	44.91	44.15
0.7000	47.10	46.42	45.66	45.00	44.23
0.8000	46.94	46.42	45.66	44.68	43.85
0.9000	46.64	46.11	45.51	44.53	43.77
1.0000	46.31	45.81	45.22	44.12	43.19

Methods. Surface tension was determined using a Krüss K-11 tensiometer and the Wilhelmy plate method. A commercial platinum plate supplied by Krüss was employed. The platinum plate was cleaned with water and acetone and was flame dried before each measurement. The uncertainty of the measurement was ± 0.07 mN·m^{-1}. In general, each surface tension value reported was an average of ten measurements. Before the surface tension was measure, the samples were stirred in a thermostatted vessel that was closed to prevent evaporation. Surface tension measurements were carried out in the range of (20 to 50) °C. The measurement vessel was connected to a thermostat−cryostat bath (Selecta Frigiterm) controlled to ± 0.1 °C.

Results and Discussion

The present work analyzes the influence of mixture composition and temperature on the surface tension of systems formed by water and different short *N*-alkyl-2-pyrrolidinones. Tables 1, 2, and 3 show the value of surface tension determined for each system and for all of the compositions and temperatures

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Table 2. Surface Tension σ for Water (1) + 1-Methyl-2-pyrrolidinone (2) from (20 to 50) °C

	T/°C				
	20	25	30	40	50
x_2	σ/mN·m^{-1}				
0.0000	72.65	72.05	71.21	69.52	67.92
0.0002	63.96	61.50	59.25	57.00	55.00
0.0004	58.14	56.58	55.68	53.77	52.41
0.0006	55.21	54.22	53.41	52.05	50.87
0.0010	53.50	52.86	52.23	51.05	50.14
0.0050	52.40	51.68	50.87	49.69	48.78
0.0100	51.60	50.78	50.00	48.87	48.05
0.0300	50.20	49.41	48.53	47.17	45.56
0.1000	49.00	48.29	47.49	46.34	44.60
0.2000	48.05	47.49	46.61	45.50	43.70
0.4000	46.05	45.42	44.94	44.00	42.40
0.5000	45.26	44.62	44.00	43.12	41.81
0.6000	44.46	43.82	43.10	42.30	41.18
0.7000	43.66	43.00	42.38	41.50	40.46
0.8000	42.78	42.14	41.66	40.78	39.74
0.9000	41.98	41.34	40.94	40.14	39.27
1.0000	41.26	40.80	40.38	39.64	38.68

Table 3. Surface Tension σ for Water (1) + 1-Ethyl-2-pyrrolidinone (2) from (20 to 50) °C

	T/°C				
	20	25	30	40	50
x_2	σ/mN·m^{-1}				
0.0000	72.65	72.05	71.21	69.52	67.92
0.0002	65.16	62.84	60.76	58.13	53.44
0.0005	59.61	57.85	55.95	53.14	50.14
0.0010	56.30	54.77	53.23	51.00	49.00
0.0100	48.62	47.51	46.59	45.11	43.84
0.0200	44.12	43.28	42.53	41.40	40.20
0.0500	43.48	42.53	41.79	40.32	39.26
0.1000	42.11	41.22	40.42	39.30	38.32
0.2000	40.90	40.09	39.35	38.43	37.22
0.3000	40.28	39.44	38.52	37.59	36.48
0.4000	39.63	38.73	37.87	36.87	35.72
0.5000	39.25	38.23	37.31	36.20	35.26
0.6000	38.60	37.89	36.94	35.83	34.86
0.7000	38.04	37.01	36.39	35.35	34.72
0.8000	37.71	36.63	35.90	35.08	34.35
0.9000	37.09	36.17	35.63	34.72	34.00
1.0000	36.48	35.65	35.00	34.35	33.61

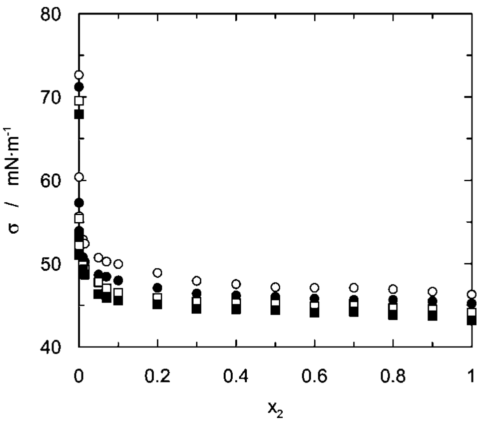

Figure 1. Influence of mixture composition and temperature on the water (1) + 2-pyrrolidinone (2) system. ○, T = 20 °C; ●, T = 30 °C; □, T = 40 °C; ■, T = 50 °C.

Table 4. Fit Parameters for Equation 1 for Water (1) + 2-Pyrrolidinone (2) Mixture

x_2	K_1 / mN·m^{-1}	K_2 / mN·K^{-1}·m^{-1}	δ / mN·m^{-1}
0.0000	75.97	0.16	0.07
0.0002	64.78	0.24	0.31
0.0006	58.58	0.15	0.22
0.0100	54.85	0.12	0.33
0.0150	54.26	0.12	0.37
0.0500	53.16	0.14	0.23
0.0700	52.95	0.15	0.16
0.1000	52.59	0.15	0.24
0.2000	51.19	0.13	0.24
0.3000	49.92	0.11	0.16
0.4000	49.36	0.10	0.14
0.5000	48.92	0.09	0.10
0.6000	49.02	0.10	0.14
0.7000	48.74	0.09	0.17
0.8000	48.94	0.10	0.11
0.9000	48.49	0.10	0.08
1.0000	48.41	0.11	0.05

employed in the present work. The value of the surface tension of pure water (72.05 mN·m^{-1} at 25 °C in the present work) has been used to confirm that the methodology used contributes suitable results (72.0 mN·m^{-1} at 25 °C,[6] 72.01 mN·m^{-1} at 25 °C[7]), and this comparison allows us to conclude that the deviations are very low.

An example of the experimental data obtained in the present work for the surface tension is shown in Figure 1, which includes the data for the system formed by water + 2-pyrrolidinone over the entire range of composition and for different temperatures.

The behavior shown in this Figure proves that the addition of small quantities of 2-pyrrolidinone to water produces a drastic decrease in the surface tension value. The larger decrease in the surface tension was produced at a low concentration of 2-pyrrolidinone. The behavior shown for this system is similar to that observed for the other mixtures studied in the present work and is in agreement with previous studies in systems with this kind of compound.[4,5]

In relation to the influence of temperature on the value of surface tension, the experimental results show that when temperature increases, a continuous decrease in the value of surface tension is observed. (See Figure 1 and Tables 1, 2, and 3.) The observed behavior in relation to the influence of temperature on the surface tension value is common, and it has been detected for different systems.[8,9]

In a previous work,[10] the surface tension versus temperature data were fit using a linear model (eq 1) that used the equation developed by Jasper[11]

$$\sigma = K_1 - K_2 \cdot T \qquad (1)$$

where σ is the surface tension, T is the temperature, and K_1 and K_2 are fitting coefficients corresponding to eq 1. The values for the fit parameters of eq 1 and the root-mean-square deviation, δ, are listed in Tables 4, 5, and 6.

The experimental data shown in Figure 2 for all systems analyzed in the present work at 25 °C indicate that when the mixtures are enriched in *N*-alkyl-2-pyrrolidinone, the surface tension tends to be at a constant value close to the corresponding value for each pure *N*-alkyl-2-pyrrolidinone after the initial decrease in the surface tension with low additions of organic compound. This kind of behavior indicates that the systems employed in the present study produce aggregation processes[12] that influence the surface tension. Figure 2 shows the behavior observed for these experimental systems using *N*-alkyl-2-pyrrolidinone with different hydrophobic chain lengths. The experimental results shown in Figure 2 indicate that when the chain length increases, the decrease in the value of the surface tension from the pure water data is larger. Also, Figure 2 includes the bibliographic data corresponding to the system formed by water and *N*-butyl-2-pyrrolidinone[4] that confirm the

Table 5. Fit Parameters for Equation 1 for Water (1) + 1-Methyl-2-pyrrolidinone (2) Mixture

x_2	K_1 / $mN\cdot m^{-1}$	K_2 / $mN\cdot K^{-1}\cdot m^{-1}$	δ / $mN\cdot m^{-1}$
0.0000	75.97	0.16	0.07
0.0002	68.86	0.29	0.65
0.0004	61.47	0.19	0.30
0.0006	57.85	0.14	0.17
0.0010	55.67	0.11	0.12
0.0050	54.68	0.12	0.14
0.0100	53.74	0.12	0.19
0.0300	53.22	0.15	0.12
0.1000	51.88	0.14	0.16
0.2000	50.99	0.14	0.17
0.4000	48.43	0.12	0.17
0.5000	47.45	0.11	0.10
0.6000	46.48	0.11	0.16
0.7000	45.64	0.10	0.17
0.8000	44.67	0.10	0.08
0.9000	43.62	0.09	0.11
1.0000	42.93	0.08	0.15

Table 6. Fit Parameters for Equation 1 for Water (1) + 1-Ethyl-2-pyrrolidinone (2) Mixture

x_2	K_1 / $mN\cdot m^{-1}$	K_2 / $mN\cdot K^{-1}\cdot m^{-1}$	δ / $mN\cdot m^{-1}$
0.0000	75.97	0.16	0.07
0.0002	72.40	0.37	0.43
0.0005	65.65	0.31	0.20
0.0010	60.81	0.24	0.25
0.0100	51.50	0.16	0.21
0.0200	46.53	0.13	0.13
0.0500	46.10	0.14	0.15
0.1000	44.37	0.12	0.22
0.2000	43.11	0.12	0.13
0.3000	42.53	0.12	0.21
0.4000	41.94	0.13	0.20
0.5000	41.53	0.13	0.24
0.6000	40.94	0.13	0.25
0.7000	39.83	0.11	0.26
0.8000	39.43	0.11	0.30
0.9000	38.79	0.10	0.19
1.0000	38.01	0.09	0.20

behavior and the trends observed in the analysis of the experimental data of the present work. This behavior is due to the hydrophobic nature of the alkyl group that increases with increasing chain length, and the trend for the organic molecules to accumulate at the air−liquid interface increases, too, producing a decrease in the value of the surface tension.

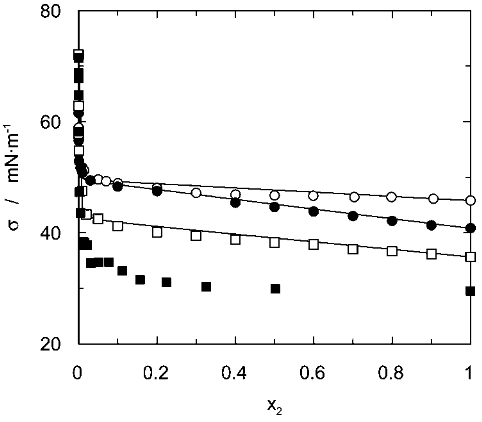

Figure 2. Influence of mixture composition and fit results of eq 2 for: ○, water (1) + 2-pyrrolidinone (2) system; ●, water (1) + 1-methyl-2-pyrrolidinone (2) system; and □, water (1) + 1-ethyl-2-pyrrolidinone (2) system at $T = 25$ °C; ■, water (1) + 1-butyl-2-pyrrolidinone (2) system at $T = 23.5$ °C.[4]

Table 7. Fit Parameters for Equation 2 for Water (1) + 2-Pyrrolidinone (2) Mixture

T/°C	a	b	K	δ
20	0.8385	0.99980	5.19	0.95
25	0.8573	0.99985	6.01	0.82
30	0.8670	0.99986	6.52	0.86
40	0.8620	0.99988	6.25	0.85
50	0.8534	0.99989	5.82	0.93

Table 8. Fit Parameters for Equation 2 for Water (1) + 1-Methyl-2-pyrrolidinone (2) Mixture

T/°C	a	b	K	δ
20	0.7177	0.99976	2.54	0.73
25	0.7219	0.99980	2.60	0.59
30	0.7278	0.99982	2.67	0.54
40	0.7314	0.99984	2.72	0.56
50	0.7392	0.99984	2.83	0.83

Table 9. Fit Parameters for Equation 2 for Water (1) + 1-Ethyl-2-pyrrolidinone (2) Mixture

T/°C	a	b	K	δ
20	0.8128	0.99928	4.34	1.07
25	0.8133	0.99941	4.36	1.16
30	0.8150	0.99950	4.40	1.26
40	0.8246	0.99960	4.70	1.29
50	0.8256	0.99971	4.73	1.54

For a given temperature, an equation developed by Connors and Wright[13] can fit the surface tension versus composition data and has been successfully used by different authors.[14] This equation is expressed as a model with two adjustable parameters, a and b (eq 2)

$$\frac{\sigma - \sigma_1}{\sigma_2 - \sigma_1} = \left(1 + \frac{a \cdot x_1}{1 - b \cdot x_1}\right) \cdot x_2 \tag{2}$$

where σ, σ_1, and σ_2 are the surface tensions of the mixture, water, and n-alkyl-pyrrolidinone, respectively, and x_1 and x_2 are the mole fractions of water and n-alkyl-pyrrolidinone, respectively.

Figure 2 shows the good fit found with eq 2 in relation to the surface/composition data for these systems studied at 25 °C. A low effect of the temperature on these parameter values has been observed. Using a and b parameters from eq 2, it is possible to calculate the binding constant, K, using eq 3

$$K = \frac{a}{1 - a} \tag{3}$$

For the systems analyzed, in all cases, a decrease in the K value (Tables 7, 8, and 9) is produced when the temperature increases. This indicates that when the temperature increases, the *N*-alkyl-pyrrolidinone concentration at the air−liquid surface decreases because of the interaction between water−amide or amide−amide. Also, in Tables 7, 8, and 9, it is possible to observe that the K value for water−pyrrolidinone is less than the corresponding value for water−*N*-methyl-2-pyrrolidinone. When the chain length increases (*N*-ethyl-2-pyrrolidinone), K increases in relation to the value obtained for *N*-methyl-2-pyrrolidinone. This behavior is due to the order of the interactions' magnitudes: *N*-methyl-2-pyrrolidinone > *N*-ethyl-2-pyrrolidinone > pyrrolidinone.[1]

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