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**PHYSICO-CHEMICAL PROPERTIES  
OF THE TERNARY SYSTEM UREA-AMMONIUM NITRATE-WATER.  
SURFACE TENSION**

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Received September 20th, 1983

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Surface tension of two binary systems ammonium nitrate-water and urea-water and of the ternary system ammonium nitrate-urea-water was measured as a function of concentration at 20 and 40°C. The experimental values were compared with those calculated from the relations which were proposed for calculating surface tensions of ternary systems from measured surface tensions of both binary systems.

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The system whose surface tension was measured is of interest both from the practical and theoretical point of view. It consists of a polar solvent-water, a uni-univalent fully dissociated electrolyte-ammonium nitrate whose ammonium ion is partly hydrolysed, and an organic substance-urea which, according to some authors<sup>1,2</sup>, behaves in water as a very weak base with dissociation constant  $1.5 \cdot 10^{-15}$  (25°C). Urea forms hydrogen bonds in aqueous solutions, and is able to replace water molecules from octahedral structure of liquid water. This also explains its high solubility in water. The existence of adducts of the type  $\text{NH}_4\text{NO}_3 \cdot \text{CO}(\text{NH}_2)_2$  and  $\text{NH}_4\text{NO}_3 \cdot 2 \text{CO}(\text{NH}_2)_2$  (ref.<sup>3</sup>) is assumed in the ternary system.

It was found out by a literature search that only the values of surface tension of binary solutions had been measured, moreover, in a rather limited extent<sup>4-12</sup>. The data by single authors differ rather considerably, not only as to their absolute values but also the course of the dependence on concentration, especially for the urea solutions. No data at all were found on the values of surface tension for the ternary system.

### **THEORETICAL**

For calculating surface tensions of multicomponent solutions  $\sigma_{\text{mix}}$ , the relation was proposed in our previous paper<sup>13</sup>

$$\sigma_{\text{mix}} = \sum_i y_i \sigma_i, \quad (1)$$

where  $y_i$  are the mole fractions of the  $i$ -th component in the surface layer and  $\sigma_i$  are the surface tensions of pure components. If a three-component system is concerned when solids 1 and 2 are dissolved in solvent 3 whose surface tensions  $\sigma_1$  and  $\sigma_2$  are not to be found out, this equation is rearranged in the following way:

$$\sigma^T = y_1^T \sigma_1 + y_2^T \sigma_2 + y_3^T \sigma_3 = y_1^T (\sigma_1 - \sigma_3) + y_2^T (\sigma_2 - \sigma_3) + \sigma_3. \quad (2)$$

For the binary solutions of both solid substances in solvent 3, it is possible to write the analogous relations

$$\sigma_{13}^B = y_1^B (\sigma_1 - \sigma_3) + \sigma_3 \quad (3)$$

and

$$\sigma_{23}^B = y_2^B (\sigma_2 - \sigma_3) + \sigma_3, \quad (4)$$

where  $\sigma^T$  is the surface tension of the ternary system and  $\sigma_{13}^B$  and  $\sigma_{23}^B$  are those of the respective binary solutions, and  $y_1^T, y_2^T, y_3^T$  are the mole fractions of the components in the surface layer of the ternary system and  $y_1^B, y_2^B$  are those of components 1 and 2 in the surface layer of the binary solutions 1,3 and 2,3.

From Eqs (3) and (4), it is possible to calculate  $(\sigma_1 - \sigma_3)$  and  $(\sigma_2 - \sigma_3)$  and insert into Eq. (2). For the surface tension of the ternary system we then get

$$\sigma^T = \left( \frac{y_1^T}{y_1^B} \right) (\sigma_{13}^B - \sigma_3) + \left( \frac{y_2^T}{y_2^B} \right) (\sigma_{23}^B - \sigma_3) + \sigma_3. \quad (5)$$

However, at the same solute mole fraction in a ternary and a binary solution, the mole fractions in surface phases of these two systems are not generally equal. As it has been derived in one of our previous works<sup>13</sup>, between the mole fractions in the surface and bulk phases holds the relation

$$y_1 = \frac{x_1}{x_1 + x_2 K_{12} + x_3 K_{13} + \dots}, \quad (6)$$

where  $K_{13} = \exp [(\Phi_1 - \Phi_3)/RT]$  and  $K_{23} = \exp [(\Phi_2 - \Phi_3)/RT]$  and  $\Phi_1, \Phi_2$  and  $\Phi_3$  are the adsorption potentials of components 1, 2 and 3, defined as the work needed to transfer one mole of molecules from the bulk into the surface phase.

For the same mole fraction in the bulk phase  $x_1^T = x_1^B = x_1$ , the ratio of mole fractions in the surface phase of a ternary and binary systems is then given by the relation

$$\frac{y_1^T}{y_1^B} = \frac{x_1 + x_2^B K_{13}}{x_1 + x_2^T (K_{13} + K_{23}) + x_3^T K_{13}} = \frac{x_1 + x_2^T K_{13} + x_3^T K_{13}}{x_1 + x_2^T (K_{13} + K_{23}) + x_3^T K_{13}} \quad (7)$$

and analogously for the ratio of mole fractions of the second solute. These ratios approach unity in case that  $K_{13}$  and  $K_{23}$  approach unity, that means in the systems where mole fraction in the surface and bulk phases is approximately the same. In this case it is possible to calculate surface tension of the ternary system from measured surface tensions of binary systems by the simplified form of Eq. (5):

$$\sigma^T = \sigma_{13}^B + \sigma_{23}^B - \sigma_3, \quad (8)$$

where  $\sigma_{13}^B$  and  $\sigma_{23}^B$  are the surface tensions of component 1 and 2, respectively, in solvent 3 at the same concentration of solute as in three-component system.

If the dependence of surface tensions in both binary solutions is rather nonlinear, it is necessary to calculate the ratio  $y_1^T/y_1^B$  according to Eq. (7) in which the constants  $K_{12}$  and  $K_{23}$  are evaluated from the measurements of surface tensions in binary solutions, e.g. by plotting  $1/(\sigma^B - \sigma_3)$  versus  $1/x$ . This dependence will be linear if the dependence of surface tension of solution on concentration is described by Eq. (1). From the slope of this line  $A$  and intercept on the  $y$ -axis  $B$ , it is possible to calculate  $K_{13}$  and  $K_{23}$  by the relation

$$K = \frac{A}{A + B}. \quad (9)$$

## EXPERIMENTAL

*Substances used:* Urea, A.R. (Lachema), was purified by recrystallization from methanol, A.R. (Lachema). The solution saturated at 40°C was filtered through a sintered glass and cooled to 0°C. The solid phase was separated and dried under reduced pressure over magnesium perchlorate, A.R., at room temperature for the period of at least 14 days. Ammonium nitrate, A.R. (Lachema) was recrystallized from redistilled water and as well dried over magnesium perchlorate under reduced pressure at room temperature.

Redistilled water was used for preparation of solutions. The binary and ternary solutions were prepared by weighing all the components. The stock solutions were stored at 0–3°C, protected from light.

*To measure surface tensions,* the drop weight method was used as comparative method. Redistilled water was used as a standard. The apparatus and the method of measurement were described in previous work<sup>14</sup>. Here it is necessary only to say that with concentrated solutions, drying-up the capillary edges takes place very easily, which makes the next forming drop wet only part of the ground surface, and so the drop formed has then lower mass. Therefore, it is necessary to pay extreme attention for the entire ground surface of capillary to be wetted by the solution all the time.

## RESULTS AND DISCUSSION

The dependence of surface tensions of the binary solutions urea–water and ammonium nitrate–water on mass concentration was measured at 20 and 40°C. The experimental

values are given in Table I and Figs 1 and 2. Further, the surface tension of the ternary system ammonium nitrate–urea–water at 20 and 40°C for mass ratios of ammonium nitrate and urea equal approximately to 5 : 1, 2 : 1, 1 : 1, 1 : 2 and 1 : 5 was measured, the overall mass concentration of salts being approximately 33, 50 and 66%. The measured values are in Table II and Figs 3–5.

TABLE I  
Surface tensions ( $10^{-3} \text{ Jm}^{-2}$ ) of binary solutions at 20 and 40°C

Urea–water			Ammonium nitrate–water		
$w_U$	$\sigma_{20^\circ}$	$\sigma_{40^\circ}$	$w_A$	$\sigma_{20^\circ}$	$\sigma_{40^\circ}$
0.0000	72.91	70.10	0.0000	72.91	70.10
0.0196	73.27	70.39	0.0464	74.16	70.97
0.0451	73.32	70.30	0.1045	74.65	72.00
0.1002	73.58	70.75	0.2021	76.67	73.40
0.1954	74.10	71.30	0.2992	78.76	75.19
0.2947	74.96	72.32	0.3558	79.24	76.58
0.3935	75.54	72.85	0.4505	82.32	78.08
0.4932	76.39	73.86	0.5002	82.91	79.74
0.5947	77.46	75.15	0.6078	86.10	82.90

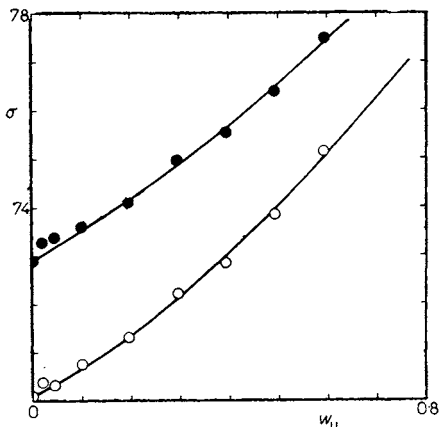


FIG. 1  
Surface tensions  $\sigma$  ( $10^{-3} \text{ Jm}^{-2}$ ) of the urea solutions, ● 20°C, ○ 40°C

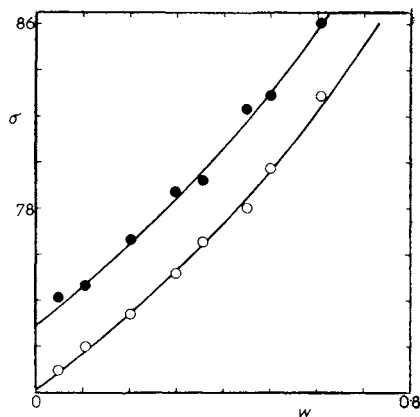


FIG. 2  
Surface tensions  $\sigma$  ( $10^{-3} \text{ Jm}^{-2}$ ) of the ammonium nitrate solutions, ● 20°C, ○ 40°C

The experimental values of surface tensions of both binary systems were substituted into Eq. (1). The values of  $1/(\sigma_{13}^B - \sigma_3)$  versus  $1/x_1$  and  $1/(\sigma_{23}^B - \sigma_3)$  versus  $1/x_2$  were plotted;  $1/x_1$  and  $1/x_2$  were calculated from the relations

$$1/x_1 = (M_3 - M_1)/M_3 + (M_1/M_3)(1/w_1)$$

and

$$1/x_2 = (M_3 - M_2)/M_3 + (M_2/M_3)(1/w_2), \quad (10)$$

TABLE II

Surface tensions ( $10^{-3} \text{ Jm}^{-2}$ ) in the ternary system urea–ammonium nitrate–water

$w_U$	$w_A$	$w_{H_2O}$	20°C			40°C		
			$\sigma_{exp}$	$\sigma_I$	$\sigma_{II}$	$\sigma_{exp}$	$\sigma_I$	$\sigma_{II}$
Overall concentration of salts approximately 0.6667 mass %								
0.0000	0.6667	0.3333	87.82	—	—	84.17	—	—
0.1126	0.5562	0.3312	85.48	85.04	84.34	82.11	81.31	81.24
0.2160	0.4394	0.3446	83.01	82.90	81.87	79.69	79.58	78.75
0.3298	0.3378	0.3324	81.23	81.04	79.93	78.20	78.06	77.08
0.4359	0.2239	0.3402	79.90	79.80	78.80	77.01	77.16	76.26
0.5548	0.1100	0.3352	78.66	78.84	78.22	76.11	76.34	75.76
0.6667	0.0000	0.3333	78.06	—	—	75.80	—	—
Overall concentration of salts approximately 0.5000 mass %								
0.0000	0.5000	0.5000	83.00	—	—	79.65	—	—
0.0831	0.4153	0.5016	81.55	81.42	81.09	78.43	78.22	77.97
0.1668	0.3335	0.4997	80.15	80.13	79.60	76.82	76.95	76.53
0.2523	0.2501	0.4976	79.06	79.02	78.39	76.01	76.02	75.53
0.3328	0.1663	0.5009	78.13	78.02	77.51	74.74	75.20	74.75
0.4153	0.0830	0.5017	77.48	77.13	76.82	74.35	74.56	74.27
0.5000	0.0000	0.5000	76.52	—	—	74.03	—	—
Overall concentration of salts approximately 0.3333 mass %								
0.0000	0.3333	0.6667	79.12	—	—	75.96	—	—
0.0563	0.2814	0.6683	78.65	78.32	78.19	75.43	75.21	75.11
0.1106	0.2211	0.6683	77.87	77.50	77.30	74.47	74.44	74.28
0.1669	0.1669	0.6632	77.24	76.78	76.55	73.94	73.85	73.66
0.2221	0.1110	0.6669	76.66	76.16	75.96	73.40	73.41	73.15
0.2778	0.0556	0.6666	75.85	75.62	75.50	73.06	72.90	72.79
0.3333	0.0000	0.6667	75.13	—	—	72.40	—	—

where  $w_1$  and  $w_2$  are mass fractions. Both systems give at both temperatures linear dependences, from the slopes and intercepts on  $y$ -axis of which the values  $K_{13}$  (the urea–water system): 0.50902 (at 20°C), 0.59154 (at 40°C), and  $K_{23}$  (the ammonium nitrate–water system): 0.39401 (at 20°C), 0.36039 (at 40°C) were calculated.

The values of surface tension of the ternary system were calculated from surface tensions of both the binaries on the one hand by Eq. (8) ( $\sigma_I$ ), on the other hand

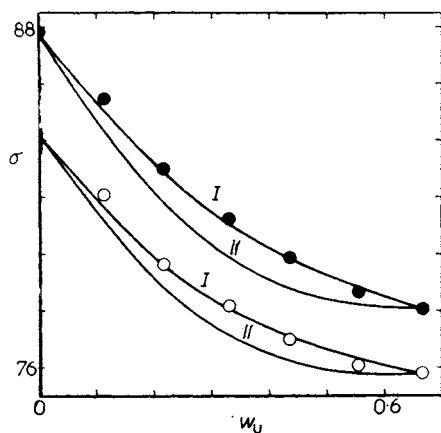


FIG. 3

Surface tensions  $\sigma$  ( $10^{-3} \text{ Jm}^{-2}$ ) in the system urea–ammonium nitrate–water. Overall concentration of salts 0.6667 mass %. Comparison of calculated curves *I* and *II* with experimental values, ● 20°C, ○ 40°C

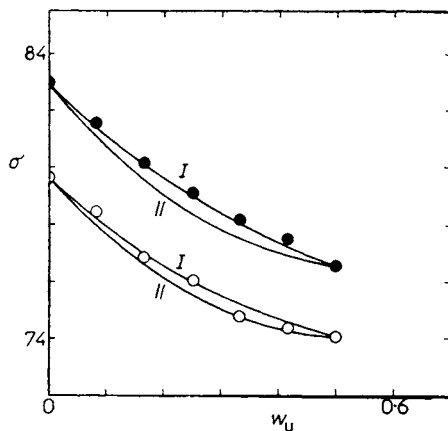


FIG. 4

Surface tensions  $\sigma$  ( $10^{-3} \text{ Jm}^{-2}$ ) in the system urea–ammonium nitrate–water. Overall concentration of salts 0.5000 mass %. Comparison of calculated curves *I* and *II* with experimental values, ● 20°C, ○ 40°C

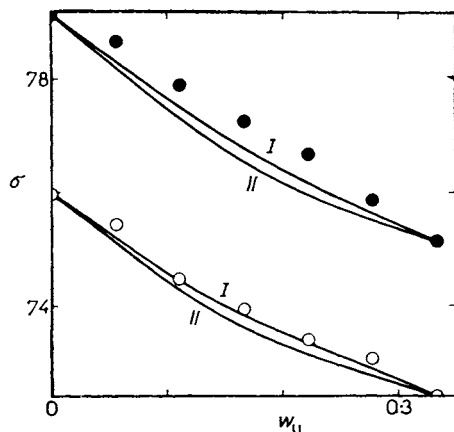


FIG. 5

Surface tensions  $\sigma$  ( $10^{-3} \text{ Jm}^{-2}$ ) in the system urea–ammonium nitrate–water. Overall concentration of salts 0.3333 mass %. Comparison of calculated curves *I* and *II* with experimental values, ● 20°C, ○ 40°C

by Eq. (5) ( $\sigma_{II}$ ) in which modified Eq. (7) was used for calculating  $y^T/y^B$ :

$$y_1^T/y_1^B = \frac{w_1 M_2 M_3 + w_2 M_1 M_3 K_{13} + w_3 M_1 M_2 K_{13}}{w_1 M_2 M_3 + w_2 M_1 M_3 K_{13}/K_{23} + w_3 M_1 M_2 K_{13}}, \quad (11)$$

$$y_2^T/y_2^B = \frac{w_2 M_1 M_3 + w_1 M_2 M_3 K_{23} + w_3 M_1 M_2 K_{23}}{w_2 M_1 M_3 + w_1 M_2 M_3 K_{23}/K_{13} + w_3 M_1 M_2 K_{23}}. \quad (12)$$

The given values were substituted for  $K_{13}$  and  $K_{23}$ . The values of surface tensions of the ternary system ammonium nitrate-urea-water calculated by both ways mentioned are compared with the experimental values in Table II and in Figs 3–5. As it is evident from the table and figures, the simple Eq. (8) complies better than the theoretically more justifiable Eq. (5) for the system measured though the dependences of surface tensions of both binaries on concentration are not linear. The averages of absolute values of deviations of the surface tensions calculated according to Eq. (8) from experimental values are at 20°C  $\Delta_I$  (20°C) = -0.310%, at 40°C  $\Delta_I$  (40°C) = -0.219%, and of surface tensions calculated according to Eq. (5)  $\Delta_{II}$  (20°C) = -0.881% and  $\Delta_{II}$  (40°C) = -0.576%, therefore at both temperatures more than twofold.

The surface tensions calculated according to Eq. (5) are always lower than the values measured. This might be caused by the fact that the dissolution of electrolyte – ammonium nitrate – displaces urea from the bulk phase into the surface phase.

*The authors wish to express their thanks to Mr J. Špür and Mr L. Jettmar for their technical cooperation.*

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Translated by J. Linek.