

SURFACE TENSION AS EVIDENCE FOR COMPLEX FORMATION IN STRONGLY CONCENTRATED ELECTROLYTE SOLUTIONS

J. ČELEDA and J. ŽILKOVÁ

*Department of Nuclear Fuel Technology and Radiochemistry,
Prague Institute of Chemical Technology, 166 28 Prague 6*

Dedicated to Professor S. Škramovský on the occasion of his 75th birthday.

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Based on the Hildebrand–Guggenheim's "coverage" model, applied to the "step-function" model of highly concentrated electrolyte solutions worked out earlier, a mixing function was derived for the surface tension of aqueous mixtures of strong electrolytes of a concentration (normality) higher than 1 val/dm³. The conclusion derived from the model, that the complex formation in solution in this concentration range should lower its surface tension approximately in the extent corresponding to the drop in free charge concentration, was verified experimentally on the chloro complexes of Zn²⁺, Cd²⁺, and UO₂²⁺.

The surface tension has been used in the studies of chemical constitution almost exclusively as an auxiliary experimental parameter to determine the quantity "parachor", introduced by Sugden. In this way it was applied by Lakhani and Daroga¹ also to the investigation of aqueous electrolytes, and in this country by Škramovský² who was concerned mainly with parachors of hydrated ions, especially polyatomic anions.

The parachor of a solute, P_1 , calculated on the basis of the Hammick–Andrew's³ assumption of additivity of the parachors of the solution components from the equation

$$P_1 = (\sigma^{1/4} - c_0 P_0) c_1^{-1} \quad (1)$$

(c_0 and c_1 are molarities, subscript 0 refers to the solvent, σ is the measured surface tension of the solution), can be calculated from the approximate equation

$$P_1 = \Phi_1 [\sigma_0 + (\sigma_{01} - \sigma_0) V_1 / \Phi_1]^{1/4} \quad (2)$$

This equation was derived from the model described in the theoretical part by extrapolation to zero solute concentration (use was made of an expansion in series in powers of $\sigma_{01} - \sigma_0$, where σ_{01} is the effective surface tension assigned to the dissolved substance in a hypothetical liquid state where the same forces would act among its particles per unit area of the dissection plane as in its solution between solvated ions and solvent molecules). The expression in brackets represents the effective surface tension of the solute corrected for the difference between its apparent molar volume Φ_1 in the solution and its actual molar volume (including the solvation sphere) V_1 . The values of σ_{01} obtained from experimental data for aqueous electrolytes are at most by 20% higher than the surface tension of water, and since the approximation (2) holds

only for Φ_1 different from zero, the ratio of V_1/Φ_1 not exceeding several units, the whole bracket does not differ from $\sigma_0^{1/4}$ by more than $\pm 10\%$. Thus, the theoretical consideration leads to the conclusion that the measured values of P_1 are in substance proportional to the apparent molar volume of the solute Φ_1 and they yield about the same information about complex formation in solution as the apparent molar volumes themselves^{4,5}. The measured surface tension of the solution, σ , plays practically no role in the thus obtained "effective" parachors of electrolytes in view of the investigation of their chemical structure in solution. (For Φ_1 close to zero it is necessary to use another approximation for the calculation of P_1 , however the calculated values of P_1 are also very small not exceeding several cm^3/mol and the influence of σ again vanishes.)

For these reasons we were concerned with the question whether it would be possible to use to the mentioned purpose the surface tension itself, not combined with the molar volume. Our aim was to derive theoretical equations enabling to recognize the complex formation and estimate its extent from the measured surface tension of electrolyte mixtures, and to verify the theory on selected systems of electrolytes.

Our considerations were based on the Hildebrand-Guggenheim's "coverage" model, in which the surface tension of binary liquid mixtures is calculated from the reversible work of dilution of the components on the surface. The validity of mixing functions derived on this basis for ideal⁶ and regular⁷ binary mixtures was verified on a large assembly of organic binary mixtures (both nonpolar and strongly polar) by Škramovská⁸, who substantiated that the deciding role in the contributions of the components to the resulting surface tension is played by the individual sizes of "contacting surfaces" of their molecules, S_i , in accord with the more exact Hildebrand's variant of the model. The latter was therefore preferred to the first variant (with a single common mean value, S).

In the application of Hildebrand's rigorous method of solution based on the calculation of the surface work of dilution, a difficulty in the derivation of theoretical mixing functions for solutions of two or more electrolytes is that the resulting functions contain parameters which cannot be determined by measuring the solutions of each electrolyte separately — it is necessary to evaluate them by an empirical adjustment directly from data on mixtures (assuming that no chemical reactions proceed between the components, which is not true in the formation of complexes). Therefore the theoretical equations derived from the mentioned method of solution cannot be used in the investigation of complexes in solutions and it was necessary to use a simplified model which, of course, is less exact. Hence, conclusions as to the complex formation arrived at in this way are rather only qualitative in nature.

THEORETICAL

The surface tension was again calculated as the work necessary to form a unit surface area in a reversible process, which however was not considered as a dilution process (where the work is done by osmotic forces) but was decomposed to two hypothetical reversible steps: a) dividing the solution by a dissecting plane and separating both

parts by counteracting the intermolecular attraction forces, *b*) rearrangement of particles in the newly formed surface.

The work attributed to the second step is in electrolyte solutions given by the osmotic work due to disintegration of the ionic atmosphere of each surface ion in that region of the solution which was separated from it, and further by the osmotic work due to changing surface concentration of the ions as a result of hydration interactions (attraction of small strongly hydrated ions into the bulk of the solution, repulsion of large ions with low hydration into the surface layer). A rough model consideration leads to the conclusion that both these quantities approach a constant value with increasing electrolyte concentration. With the ionic atmosphere, this limit corresponds to the quasi-lattice short-range order, where the whole charge of the atmosphere is practically concentrated in the distance of closest approach of the ions. It was shown in an earlier work^{9,10} that this limit is attained practically at concentrations about 1 val/dm³. The same can be roughly assumed also for the second effect, which also attains the saturation state at a quasi-lattice short-range ordering of the ions. At concentrations above this limit it is therefore possible to take both these effects into account at a given temperature for each electrolyte by a constant term D_i independent of the concentration; the whole concentration dependence of the surface tension can then be attributed to the separation work calculated under the assumption that the surface concentrations of the electrolytes are equal to their bulk concentrations.

In calculating the surface coverage corresponding to the components, the "step-function" model^{9,11} introduced earlier served as a base, making use of the fact that each type of influencing the water by the field of an ion attains saturation in its vicinity, and the intermediate region between this saturated zone and the uninfluenced solvent can be replaced by a sharp boundary. If we take into account the mutual penetration of the influenced zones with increasing solution concentration, then the volume fraction of the water which is not influenced by the ions is approximately given by^{11,12}

$$p_0 = \exp\left(-\sum_i c_i V_i\right), \quad (3)$$

where V_i are molar volumes of the influenced spheres of the individual ionic species of molarities c_i ; the same fraction is then assigned also to the uninfluenced water-water surface contacting in the dissecting plane. With the influenced surfaces, the influence of ions with centres located on one side of the dissecting plane overlaps with the influence of ions with centres on the other side.

With solutions of a single electrolyte, it is necessary to consider *a*) the water-water interaction corresponding to the surface tension of the pure water, σ_0 , *b*) the interaction between water and hydrated ions (mean-valued surface free energy σ_{01}), and finally *c*) electrolyte-electrolyte interaction (free energy σ_{11}). From the coverage

model modified in this way we obtain for the surface tension of highly concentrated aqueous electrolytes:

$$\sigma = \sigma_0 + D_1 + 2p_1(\sigma_{01} - \sigma_0) + p_1^2(\sigma_0 + \sigma_{11} - 2\sigma_{01}), \quad (4)$$

($p_1 = 1 - \sqrt{p_0}$ is the fraction of the water regions influenced in the dissecting plane by ions located on its one side). This is a quadratic function of p_1 , and when we express p_0 from Eq. (3) also by a power series approximated to the second degree we obtain for a solution of a single electrolyte:

$$\sigma = \sigma'_0 + A_1 c_1 + B_1 c_1^2 \quad (5)$$

with the following physical meaning of the constants:

$$A_1 = (\sigma_{01} - \sigma_0) V_1, \quad (6)$$

$$B_1 = \frac{1}{4}(\sigma_{11} + 2\sigma_0 - 3\sigma_{01}) V_1^2 \quad (7)$$

and σ'_0 is the surface tension of water including a constant correction D_1 (which can be even negative – if the influence of expelling the ions into the surface layer prevails).

The above theory is an approximation to the second degree. Its significance is that it gives a physical meaning to the coefficients A_1 and B_1 in the linear and quadratic term, which enables us to deduce conclusions as to their role in mixed solutions containing two or more electrolytes which do not interact chemically. In such mixtures, we must consider besides the interaction constants $\sigma_{01}, \sigma_{02}, \sigma_{03} \dots$ and $\sigma_{11}, \sigma_{22}, \sigma_{33} \dots$ also the cross interactions between ions characterized by the constants $\sigma_{12}, \sigma_{13}, \sigma_{23}$ and so on, for which it can be assumed with respect to the short-distance character of the interactions (prevailing according to the model at higher concentrations) that approximately

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}). \quad (8)$$

It was found experimentally in earlier work^{10,11} that the molar influenced volumes of ions in aqueous solutions are with each kind of the influence approximately proportional to their charge, hence also in this case it can be assumed that the volumes V_i referred to 1 val will for various electrolytes only little differ from each other. The areas in which the influenced spheres of two or more different ions with centers on the same side of the section overlap can then be divided between them in the ratio of their normalities C . Hence, with regard to Eqs (6)–(8) we obtain the following expression for the surface tension of the mixed solution:

$$\sigma = \bar{\sigma}'_0 + \sum_i A_i C_i + \frac{1}{2} \sum_i \sum_j (B_i + B_j) C_i C_j, \quad (9)$$

where $\bar{\sigma}'_0$ is the corrected surface tension of water averaged over all electrolytes present (*i.e.*, over all D_i values) proportionally to their normalities C_i , A_i and B_i are constants determined empirically on solutions of each electrolyte separately on the basis of Eq. (5), referred to 1 val. The linear term in this equation is identical with the linear term in the more accurate equation derived by Hildebrand for binary mixtures with the consideration of different contacting areas S_i , if we replace the ratio of areas occupied by the components in the cross section, $S_i x_i / S_j x_j$ (x_i 's are molar fractions of the components), by the ratio of influenced volumes, $C_i V_i / C_j V_j$. In contrast to this equation, we can the parameters of the quadratic terms calculate from the parameters B_i found by measurement on single-electrolyte solutions. Hence follows the possibility to detect complex formation in mixed solutions of electrolytes from the comparison of the measured surface tension with values calculated from Eq. (9) for fully dissociated systems.

EXPERIMENTAL

The surface tension of electrolytes was measured by the bubble method¹³ modified according to Škramovský². The inner diameter of the capillary was 0.58 mm, the 11th bubble was measured. The temperature of measurement was 25°C. Solutions were prepared from redistilled water and reagent grade chemicals without further purification. The influence of surface active impurities was eliminated by their adsorption on preceding bubbles; experiments showed that ten bubbles set free before measuring ensured the attainment of constant results.

RESULTS AND DISCUSSION

Solutions of a Single Electrolyte

The parameters in Eq. (5) for solutions of a single fully dissociated electrolyte were calculated from the data of Škramovský and coworkers¹⁶. The approximation to the terms of the second order with respect to c_1 was quite sufficient in the measured range (0.5–5 val/dm³). The deviations are of the order of 0.1 mN/m (below 0.5%), *i.e.* in the limits of experimental errors, and they do not show a systematic dependence on c_1 . Adjusted parameters are summarized in Table I.

The difference of $\sigma'_0 - \sigma_0$ is in all cases smaller than 1 mN/m, hence the correction D_i is here of little significance and the approximation $D_i = \text{const.}$ used here is justified. (Large negative D_i values can be expected only in the case of surface active salts with very large ions.) With sodium salts (containing a small, strongly hydrated cation) the D_i value is larger, the same in the case of ammonium salts, whose cation forms a hydrogen bond with water, whereas potassium salts containing a larger, weakly hydrated cation have the σ'_0 value very close to σ_0 (= 72.58 mN/m) or even lower (as with KI, where also the anion is weakly hydrated). This is in accord with the physical meaning of D_i resulting from the model used.

The constant A is mostly in the range $0.7-1.0$ (mN/m) (dm^3/val). If we set V_i in Eq. (6) on the average equal to 0.15 dm^3/val , a value found from apparent molar volumes¹⁴ and conductivities⁹, we then obtain $\sigma_{0.1} = 78-80$ mN/m, which is only by 8–10% higher than σ_0 ; this corresponds to separation of water from the hydration sheaths of ions and not to separation of the hydration sheath from the ion. Hence, the ions in the surface layer preserve their firmly bound hydration sheath. For $\sigma_{1.1}$ we then obtain from the constant B according to Eq. (7) a value on the average about three times larger than σ_0 , which gives, assuming a distance of closest approach of the hydrated ions on the surface $a = 0.5$ nm, a value of the separation energy of about 50 kJ/mol. This is comparable with electrostatic interaction energies of hydrated cations with hydrated anions. The interpretation of the virial coefficients A and B on the basis of the proposed model leads hence to physically plausible results.

For all 1 : 2 electrolytes, the increment of the σ value per 1 mol/dm³ is above $C = 0.5$ val/dm³ about twice as large as for 1 : 1 electrolytes at the same concentration, as exemplified by interpolated values of σ (mN/m) for carbonate and hydrocarbonate:

Interpolated values	KHCO ₃	K ₂ CO ₃
$\sigma(1.0\text{M}) - \sigma(0.5\text{M})$	0.62	1.28
$\sigma(1.5\text{M}) - \sigma(0.5\text{M})$	1.27	2.92
$\sigma(2.0\text{M}) - \sigma_0$	2.89	5.95

TABLE I

Constants in Eq. (5) for Surface Tension of Aqueous Electrolytes Determined from Experimental Data (25°C)

Electrolyte	Range of c_1 mol dm ⁻³	σ'_0 mN m ⁻¹	A_1 mN m ⁻¹ dm ³ mol ⁻¹	B_1 mN m ⁻¹ dm ⁶ mol ⁻²
NaCl	0.90–5.07	73.16	1.01	0.150
KCl	0.77–3.76	72.76	1.07	0.136
NaBr	1.07–5.54	73.23	1.00	0.099
NH ₄ Br	1.08–5.20	73.31	1.01	0.061
KJ	0.75–5.79	72.42	0.90	0.060
KNO ₃	0.58–2.78	72.60	0.90	0.060
NH ₄ NO ₃	1.33–7.58	73.22	0.90	0.032
KHCO ₃	0.49–2.27	73.00	1.15	0.060
K ₂ CO ₃	0.48–5.53	72.76	1.52	0.70
Na ₂ S ₂ O ₃	0.30–1.68	73.09	1.50	0.80
(NH ₄) ₂ SO ₄	0.80–3.73	73.55	1.30	0.45

This is in accord with the assumption that one charge unit corresponds in the case of strong, fully dissociated electrolytes of a different valence type approximately to the same hydration volume V_i , hence to the same occupied surface in the coverage model and thus to the same increment of the surface tension in the high concentration range. Accordingly it can be expected that a change of the $\text{Me}^{n+} + n \text{X}^-$ system to $\text{MeX}^{(n-1)+} + (n-1) \text{X}^-$ will be connected in strongly concentrated aqueous solutions with a drop in the surface tension exceeding substantially the experimental errors. This can be made use of in detecting such an association in cases where other methods lose their applicability at higher concentrations.

Mixed Solutions

The preceding conclusion was verified on isomolar chloride solutions in which the cation forming no complexes with Cl^- ions was at constant concentration of Cl^- replaced gradually by a complexing cation. In the case of an isomolar series of solutions of two strong electrolytes at constant normality $C = C_1 + C_2$ the variable quadratic term in Eq. (9) vanishes and the equation takes the form of a linear function:

$$\sigma = \bar{\sigma}'_0 + K_1 C_1 + K_2 C_2, \quad (10)$$

where $K_i = A_i + B_i C$ with constant C are constants; after substituting $C_1 = C - C_2$ we obtain

$$\sigma = k_1 + k_2 C_2, \quad (11)$$

where $k_2 = A_2 - A_1 + (B_2 - B_1) C$ is for the isomolar series a constant and $k_1 = \bar{\sigma}'_0 + A_1 C + B_1 C^2$ is approximately constant independent of C_2 , if $\bar{\sigma}'_0$ is only little variable. On replacing gradually the first electrolyte by the second one, the surface tension changes linearly from the value corresponding to the pure first electrolyte to that corresponding to the other one.

This conclusion was verified on nonassociated mixtures of electrolytes of the types 1 : 1 and 1 : 2 (Fig. 1). The linear form of the dependence holds within the range of experimental errors.

For a mixed solution of two electrolytes A and B of which the first one associates with the ions of the second one present in a stoichiometric excess to a complex of normality C_a , we obtain from Eq. (9) a linear relation of the form

$$\sigma = \sigma(A + B) + [\sigma(a + B) - \sigma(A + B)] C_a / C_A, \quad (12)$$

where $\sigma(A + B)$ denotes surface tension of the solution corresponding according to Eq. (9) or (10) to full dissociation, and $\sigma(a + B)$ is the surface tension of a solu-

tion with the component A fully complexed, i.e. for $C_a = C_A$. The degree of conversion into a complex can accordingly be estimated from the surface tension of the mixed solution by linear interpolation between both extreme values.

The results measured during replacing the Na^+ ions by complex forming cations UO_2^{2+} , Zn^{2+} , and Cd^{2+} (Fig. 2) show that the surface tension of the solution is indeed significantly depressed, and this even below the value corresponding to a pure sodium chloride solution (dashed curve 2, Fig. 2). Curve 1 in Fig. 2 corresponds to theoretical values of the surface tension obtained from the described model for a full association of the complexing cation to the first degree to MeCl^+ , curve 2 for a full association to the second degree to MeCl_2 with an eventual bonding of the surplus free Cl^- ions with MeCl_2 to form MeCl_3^- or MeCl_4^{2-} anions (whereby the total number of charges does not change) and the line 3 corresponds to a state in which all Cl^- ions are bound in the MeCl_4^{2-} complex and only replacement of free Me^{2+} by Na^+ cations takes place.

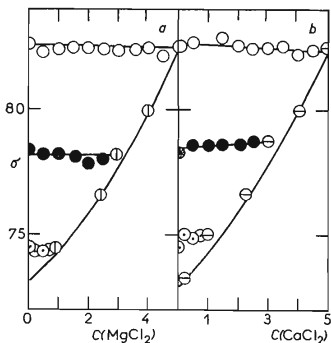


FIG. 1

Surface Tension of Aqueous Electrolytes σ (mN/m) in Isomolar Series of Normality C (val/dm³)

a LiCl + MgCl₂; *b* MgCl₂ + CaCl₂; ○ $C = 5$, ● $C = 3$, ⊙ $C = 1$, ⊕ $C(\text{LiCl}) = 0$, ⊖ $C(\text{MgCl}_2) = 0$.

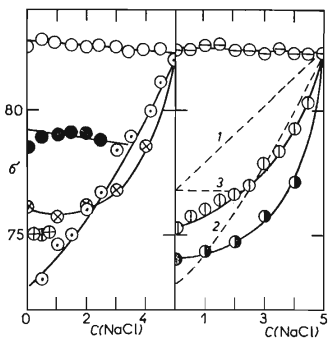


FIG. 2

Surface Tension of Aqueous Electrolytes σ (mN/m) in Isomolar Series of Normality $C = 5$ val/dm³

○ LiCl + NaCl, ⊗ $\frac{1}{2}$ UO₂Cl₂ + NaCl, ⊙ $\frac{1}{2}$ CaCl₂ + NaCl, ● $\frac{1}{2}$ ZnCl₂ + NaCl, ⊕ $\frac{1}{2}$ CdCl₂ + NaCl, ⊖ only NaCl, theoretical curves: 1 MeCl⁺ + Cl⁻; 2 MeCl₂; 3 $\frac{1}{2}[\text{MeCl}_4]^{2-} + \text{M}^+$; ● $C(\text{LiCl}) + C(\text{NaCl}) = 3$ val/dm³, ⊕ $C(\text{LiCl}) + C(\text{NaCl}) = 1$ val/dm³.

The drop of the experimental values below these curves observed at a large stoichiometrical excess of Cl^- against Me^{2+} (smallest with Cd^{2+} , largest with Zn^{2+} , whose complexes are most stable of all three ions under study) can be caused by the fact that the voluminous complex anions lower the term D_i expressing the influence of the surface reorganization to negative values, or simply by a partial association of these large anions with Na^+ . This effect makes the possibility of a quantitative evaluation of the ratio of the complex forms on the basis of Eq. (12) to appear difficult. In the range of lowest Cl^- : Me^{2+} ratios, the evaluated concentrations of the complexes (calculated as MeCl^+) lie within the range of the published stability constants found by other methods¹⁵.

The results obtained with systems for which the complex formation was proved by other methods substantiate that the association of ions in a complex connected with a drop in the concentration of free charges lowers significantly the surface tension of strongly concentrated electrolyte solutions; this can serve as a means for a rather sensitive detection of this association at high concentrations at which the potentiometric and conductivity methods cannot be used and where the spectral analyses fail because of the absence of a characteristic electron or vibration spectrum (*viz.*, complexes of a very low bonding order).

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