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Surface Properties of Aqueous Salt Systems

A.I.Rusanov and E.A.Faktor

Use of the Gibbs method and of a layer of finite thickness to calculate the thermodynamic characteristics of surface layers is examined. The chief properties of surface layers have been calculated for 35 aqueous salt systems from experimental data. The influence of the nature of the dissolved salt on the properties of solutions and surface layers is discussed on the basis of the calculated results. A list of 87 references is included.

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I. INTRODUCTION

Considerable experimental information has been accumulated on the surface tension of aqueous salt systems, but its processing is far from complete. Calculation is usually confined to finding the adsorption, although modern thermodynamics enables the composition and the entropy characteristics of the surface layer also to be calculated from sufficiently complete surface-tension data. These characteristics in turn make it possible to elucidate the effect of the nature of the ions on the structure and the properties of the surface layers.

The aim of the present paper is to generalise available published information from unified points of view by basing the thermodynamic calculations on a rigorous scheme and comparing characteristics of the same type for various aqueous salt systems. The most reliable published data on the surface tensions of solutions containing singly and multiply charged ions have been used for the calculations. A total of 35 aqueous salt systems have been considered.

II. SURFACE PHENOMENA IN AQUEOUS SALT SYSTEMS

1. Experimental Investigations of Surface Tension

Nearly linear increases in the surface tension of the solution with salt concentration were observed [1-6]. Quincke [2] formulated the empirical rule that solutions of different chlorides have roughly the same surface tension at the same volume concentration of the chloride ion. An attempt to extend this rule to other halides was less successful.

Whatmough [4] suggested that, when several salts were present together in solution, they made additive contributions to the surface tension.

More accurate results [7-9] revealed a fairly complicated relation between surface tension and solution composition. The earlier empirical relations were found to lack generality and be applicable only to dilute solutions. Nevertheless, the hypothetical linear composition dependence of the surface tension of a salt solution was used [10] to estimate by extrapolation the surface tension of a supercooled melt of the pure salt. This hypothesis, which is only an approximation, has been used also to solve several applied problems requiring no great accuracy in the calculation of surface tension [11,12].

An important contribution to developing ideas on the structure of the surface layer was made by Langmuir [13]. He assumed that the surface of a salt solution is covered by a film of water, below which the salt concentration is constant, and calculated the thickness of the film by means of the formula

$$\tau = -1000\,\Gamma_{1(2)}/c \qquad \text{(II, 1)}$$

where $\Gamma_{1(2)}$ is the adsorption of the salt and c the molar concentration of the solution. Extension of similar calculations to various aqueous salt systems showed [9,14,15] that the film thickness depends on the nature of the salt, but in all cases examined diminishes from 5–3 Å at low concentrations to 2 Å at high concentrations. Comparison with the size of a water molecule led to the important conclusion that the ions of a dissolved salt enter the surface monolayer when the solution is sufficiently concentrated.

Adsorption of a solute changes the potential difference between the solution and the surrounding medium. The dependence of this potential difference on solution composition was investigated by Frumkin [16,17], who discovered that most salt solutions give a small potential difference at their air interface, with the outer region of the double layer charged negatively. This indicates that anions are arranged on the average closer to the air than are cations. With solutions of the same concentration the negative charge increases in the sequence of anions

$$F^- < Cl^- < Br^- < I^- < CNS^-.$$

The reason is that less strongly hydrated ions pass more readily (and hence in greater quantity) into the surface layer, thus conferring a higher charge on the surface. According to Frumkin the nature of the cation has little effect on the surface charge.

Comparison of the adsorptions calculated by means of the relation

$$RT\Gamma_{1(2)} \approx 0.5\,(\sigma_0 - \sigma) \qquad \text{(II, 2)}$$

(in which R is the gas constant, T is the temperature, and σ and σ_0 are the surface tensions of the salt solution and pure water respectively) with the results of electrometric measurements indicated that the greater the adsorption of the salt the more strongly charged was the surface of the solution.

Pavlov [18] used empirical relations to calculate the surface tensions of salt solutions, and in many cases observed satisfactory agreement with experimental values obtained

by other workers. Having used incorrect premises in calculating the adsorption of the salt, he obtained positive values of $\Gamma_{1(2)}$.

In a study of the surface properties of aqueous salt systems Rebinder[19] directed attention to the behaviour of water as a surface-active compound. He obtained the complete surface-tension isotherm for the aqueous silver thallium(I) nitrate system at 90°C (the salt $AgTl(NO_3)_2$ melts at 82.5°C, above which temperature it is completely miscible with water). The surface-tension isotherm is well described by Shishkovskii's equation

$$\sigma - \sigma_0 = b \ln (ac + 1) \qquad \text{(II, 3)}$$

where a and b are constants, c is the concentration of water, and σ and σ_0 are the surface tensions of the molten salt and of the solution respectively.

Yashkichev[20] suggested a qualitative interpretation of results for the surface tension of salt solutions according to which the effect of the salt was governed by two factors acting in different directions. The first such factor was the effect of ions in disrupting the mutual order of the water molecules, which with negatively hydrated ions would tend to diminish surface tension. The other factor was the negative adsorption of ions, interaction of whose fields with water molecules of the surface layer should strengthen the tendency of the molecules to be drawn into the interior of the solution, which would correspond to an increase in surface tension. Such an explanation is, of course, greatly oversimplified and insufficiently informative, since negative adsorption of a salt is the starting point of the argument, but this does not provide sufficient grounds for such an assumption.

A series of studies[21-25] on foams, films, and drop entrainment from electrolyte solutions has shown that the stability of a foam depends on the nature of the dissolved salt and is increased by the presence of strongly hydrated ions. The critical rupture thickness on the spontaneous thinning of films of electrolyte solutions is inversely proportional to the concentration and energy of hydration of the ions. In several cases separation of electrolytes has been observed during drop entrainment[25].

2. The Jones–Ray Effect

A prolonged controversy ensued from the papers by Jones and Ray[26-28], who discovered by the capillary-rise method a minimum in the surface-tension isotherms for 13 aqueous salt systems. A depression of surface tension reaching 0.02 dyn cm^{-1} was observed in all cases in dilute solutions (below 0.002 N). The positive adsorption of the salt corresponding to this depression was explained by preferential attraction between salt ions and water molecules on the solution surface (at higher concentrations the forces retaining ions in solution increase more rapidly and the adsorption becomes negative).

According to Langmuir[29] the Jones–Ray effect is a consequence of the experimental technique: a film of water which may be several hundreds of ångströms thick would be present on the internal surface of the capillary, and would be thicker for salt solutions than for pure water. Such a film leads to a change in the effective radius of the capillary, which influences the measured results.

Langmuir's view was criticised[30], and the Jones–Ray effect was then confirmed[31] for aqueous potassium chloride by the ring-detachment method. Dole[32] also tried to obtain theoretically an equation for a surface-tension isotherm passing through a minimum. The deduction involved the postulated presence, on the surface of a dilute solution, of a monomolecular layer of water, whose interaction with the ions of the salt was far stronger than the interionic interaction in the solution. In order to bring into line with the experimental results, furthermore, it was postulated that only negative ions could be adsorbed and only on certain active centres (one per 10^5 water molecules). The calculated surface tensions were close to the experimental values, but Dole's postulates were too arbitrary to serve as evidence.

Bikerman[33] discussed the Jones–Ray effect in terms of the surface tension as the sum of three contributions. The work required for a water molecule to escape to the surface was assumed to be independent of concentration. The second term resulted from the lower salt concentration at the surface than in the bulk of the solution, so that formation of a surface layer entailed an increase in the bulk concentration of the solutions; this process was replaced in the calculations by compression of the ionic gas, and the corresponding work was computed solely on the basis of electrostatic interaction. The third term represented the work required to separate positive and negative ions. Calculations based on this scheme gave minimum surface tension for dilute potassium chloride solutions, but the third term was calculated from Jones and Ray's results. Moreover, the postulates involved (e.g. the assumed concentration independence of the first term) restrict considerably the concentration range in which the formulae might be applied.

The phenomena associated with the Jones–Ray effect was carefully examined by Passoth[34], who measured the surface tension by a modified maximum bubble pressure method enabling the time of formation of the bubble to be varied within wide limits. When the bubble formed slowly, the effect was observed with sodium and potassium chloride solutions, but no effect was observed when the rate was increased. Passoth concluded that the inner walls of the capillary were coated with a liquid film, whose thickness depended on solution concentration with slow formation of the bubble. Estimated thicknesses of this film were consistent with Langmuir's results.

A recent examination of the thermodynamic conditions of concentration buffering has shown that the Jones–Ray effect is impossible. It must thus be accepted that the effect is spurious, and is connected with the method adopted for measuring surface tension[34,36].

3. Use of Thermodynamics in the Analysis of Surface Phenomena in Aqueous Salt Systems

Two chief methods—the Gibbs method and the method of a layer of finite thickness—can be distinguished in the thermodynamics of surface phenomena. The former is based on the concept of a geometric surface, and utilises excess functions[37]. The excess entropy $\bar{S}$ and the excess mass of the ith component $\bar{m}_i$ are defined by the relations

$$\bar{S} \equiv S - s_v^{(\alpha)} V_\alpha - s_v^{(\beta)} V_\beta \qquad \text{(II, 4)}$$

$$\bar{m}_i \equiv m_i - \rho_i^{(\alpha)} V_\alpha - \rho_i^{(\beta)} V_\beta \qquad \text{(II, 5)}$$

where S is the entropy of the system, m_i is the mass (or the number of moles) of the ith component, $\rho_i^{(\alpha)}$ and $\rho_i^{(\beta)}$ are the densities of the ith component in the coexisting α and β phases, $s_V^{(\alpha)}$ and $s_V^{(\beta)}$ are the bulk entropy densities in these phases, and the sum of the volumes of regions of the system mutually separated by a dividing surface gives the total volume $V = V_\alpha + V_\beta$. The values of the excess

quantities depend on the position chosen for the dividing surface. The surface density of the excess of mass is termed the absolute adsorption

$$\Gamma_i \equiv \bar{m}_i/A \qquad \text{(II, 6)}$$

(in which A is the area of the dividing surface); while the combination

$$\Gamma_{i(j)} \equiv \Gamma_i - \Gamma_j \frac{\rho_i^{(\beta)} - \rho_i^{(\alpha)}}{\rho_j^{(\beta)} - \rho_j^{(\alpha)}} \qquad \text{(II, 7)}$$

is the Gibbs relative adsorption, which is invariant with respect to displacement of the dividing surface. The relative adsorption $\Gamma_{i(j)}$ is numerically equal to the absolute adsorption Γ_i for a dividing surface corresponding to the condition $\Gamma_j = 0$. Gibbs obtained the adsorption equation

$$d\sigma = -\bar{s}_{(j)}\,dT - \sum_{i \neq j} \Gamma_{i(j)}\,d\mu_i \qquad \text{(II, 8)}$$

where σ is the surface tension, μ_i is the chemical potential of the ith component, and $\bar{s}_{(j)}$ is defined by the relation

$$\bar{s}_{(j)} \equiv \frac{\bar{S}}{A} - \Gamma_j \frac{s_v^{(\beta)} - s_v^{(\alpha)}}{\rho_j^{(\beta)} - \rho_j^{(\alpha)}} \qquad \text{(II, 9)}$$

In the case of electrolyte solutions Eqn. (II, 8) contains electrode potentials instead of chemical potentials.

The chief merit of the Gibbs method is its mathematical simplicity. An important disadvantage, however, is that the use of geometric surfaces excludes consideration of the thickness of the surface layer, which is one of the principal problems of the theory of surface phenomena. An important role in the discussion of this problem was played by the method of a layer of finite thickness[38-40], an account of whose development and a modern presentation will be found in a monograph[41].

Displacement of the equilibrium in a two-phase n-component system with a planar surface is described by the set of equations[41]

$$\begin{cases} a\,d\sigma = s_{\alpha\sigma}\,dT + v_{\alpha\sigma}\,dP - \sum_{i=1}^{n-1}\sum_{k=1}^{n-1} (x_i^{(\sigma)} - x_i^{(\alpha)})\, g_{ik}^{(\alpha)} dx_k^{(\alpha)} \\ a\,d\sigma = (s_{\alpha\beta} - s_{\alpha\sigma})\,dT - (v_{\alpha\beta} - v_{\alpha\sigma})\,dP - \sum_{i=1}^{n-1}\sum_{k=1}^{n-1} (x_i^{(\alpha)} - x_i^{(\beta)})\, g_{ik}^{(\alpha)} dx_k^{(\alpha)}, \end{cases} \qquad \text{(II, 10)}$$

where

$$\bar{s}_{\alpha\sigma} \equiv s^{(\sigma)} - s^{(\alpha)} - \sum_{i=1}^{n-1} (x_i^{(\sigma)} - x_i^{(\alpha)}) \left(\frac{\partial s}{\partial x_i}\right)^{(\alpha)} \qquad \text{(II, 11)}$$

$$v_{\alpha\sigma} \equiv v^{(\sigma)} - v^{(\alpha)} - \sum_{i=1}^{n-1} (x_i^{(\sigma)} - x_i^{(\alpha)}) \left(\frac{\partial v}{\partial x_i}\right)^{(\alpha)} \qquad \text{(II, 12)}$$

$$s_{\alpha\beta} \equiv s^{(\beta)} - s^{(\alpha)} = \sum_{i=1}^{n-1} (x_i^{(\beta)} - x_i^{(\alpha)}) \left(\frac{\partial s}{\partial x_i}\right)^{(\alpha)} \qquad \text{(II, 13)}$$

$$v_{\alpha\beta} \equiv v^{(\beta)} - v^{(\alpha)} - \sum_{i=1}^{n-1} (x_i^{\beta} - x_i^{(\alpha)}) \left(\frac{\partial v}{\partial x_i}\right)^{(\alpha)} \qquad \text{(II, 14)}$$

$$g_{ik} \equiv \left(\frac{\partial^2 g}{\partial x_i\,\partial x_k}\right)_{P,T}^{(\alpha)} \qquad \text{(II, 15)}$$

a is the molar surface, x_i is the mole fraction of the ith component, g is the molar Gibbs thermodynamic potential, and the s and v are molar entropies and volumes. The superscripts α and β denote the coexisting bulk phases, and σ indicates the surface layer. Physically the quantities $s_{\alpha\sigma}$ and $s_{\alpha\beta}$ represent entropy effects, and $v_{\alpha\sigma}$ and $v_{\alpha\beta}$ volume effects of transitions from the α phase to the surface layer and to the β phase respectively, i.e. effects accompanying formation of 1 mole of surface layer and of phase β from an infinite quantity of phase α. The quantities $s_{\alpha\sigma}$ and $v_{\alpha\sigma}$ are differential molar effects of adsorption. In the case of a liquid–vapour (α–β) equilibrium the quantities $s_{\alpha\beta}$ and $v_{\alpha\beta}$ are differential molar effects of vaporisation.

III. CALCULATION OF THERMODYNAMIC PROPERTIES OF SURFACE LAYERS

1. Calculation of Relative Adsorptions

For a strong uni-univalent electrolyte dissolved in water (the KA–H_2O system) the equation to the Gibbs adsorption isotherm is

$$-d\sigma = \Gamma_K + d\bar{\mu}_{K^+} + \Gamma_{A^-} d\bar{\mu}_{A^-} + \Gamma_{H^+} d\bar{\mu}_{H^+} + \Gamma_{OH^-} d\bar{\mu}_{OH^-} + \Gamma_{H_2O} d\mu_{H_2O} \qquad \text{(III, 1)}$$

where σ is the surface tension, Γ and $\bar{\mu}$ are the absolute adsorption and the electrochemical potential of the corresponding ion, and Γ_{H_2O} and μ_{H_2O} are the absolute adsorption and the chemical potential of undissociated water. Besides taking into account the phase equilibrium conditions, we should consider Eqn. (III, 1) in combination with the condition of equilibrium in the dissociation of water

$$\mu_{H_2O} = \bar{\mu}_{H^+} + \bar{\mu}_{OH^-} \qquad \text{(III, 2)}$$

and the condition of electrical neutrality

$$\Gamma_{H^+} + \Gamma_{K^+} = \Gamma_{OH^-} + \Gamma_{A^-} \qquad \text{(III, 3)}$$

According to thermodynamics the number of components in a given mixture is strictly defined, but their choice is arbitrary. For convenience we shall henceforward select as components the neutral substances HA and KA (almost completely absent from the bulk of the solution), and introduce for them, by analogy with (III, 2), the conditions

$$\mu_{KA} = \bar{\mu}_{K^+} + \bar{\mu}_{A^-};\ \mu_{HA} = \bar{\mu}_{H^+} + \bar{\mu}_{A^-} \qquad \text{(III, 4)}$$

From Eqns. (III, 1–4) we then obtain

$$-d\sigma = (\Gamma_{A^-} - \Gamma_{K^+})\,d\mu_{HA} + \Gamma_{K^+} d\mu_{KA} + (\Gamma_{OH^-} + \Gamma_{H_2O})\,d\mu_{H_2O} \qquad \text{(III, 5)}$$

and after allowing for the phase equilibrium conditions and eliminating $d\mu_{KA}$ we find that

$$-d\sigma = \Gamma_{A^-(K^+)} d\mu_{HA} + (\Gamma_{OH^-(K^+)} + \Gamma_{H_2O(K^+)})\,d\mu_{H_2O} \qquad \text{(III, 6)}$$

where the additional subscript (K^+) indicates conversion to relative adsorptions (with respect to the cation K^+).

The coefficient of $d\mu_{HA}$ in Eqns. (III, 5 and 6) represents the non-equivalence of adsorption of cation and anion of the dissolved electrolyte. If the compound HA is volatile, this coefficient can in principle be evaluated from the dependence of the surface tension on the vapour pressure of HA. When the non-equivalence of adsorption of the ions can be neglected, the first term on the right-hand side of (III, 5 and 6) vanishes, and the coefficient of $d\mu_{H_2O}$ becomes equal to the total adsorption of water in molecular and dissociated forms. These two adsorption equations then become formally identical with those for systems of non-electrolytes:

$$-d\sigma = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 \qquad \text{(III, 7)}$$

$$-d\sigma = \Gamma_{2(1)} d\mu_{(2)} \qquad \text{(III, 8)}$$

where $\Gamma_1 \equiv \Gamma_{KA} = \Gamma_{K^+}$ and $\Gamma_2 \equiv \Gamma_{H_2O} + \Gamma_{OH^-}$. Analogous formulae are obtained also for a solution of a weak electrolyte (when Γ_1 becomes the total adsorption of the electrolyte in molecular and dissociated forms). Formulae (III, 7 and 8) are obviously valid not only for an aqueous uni-univalent electrolyte but also for electrolytes of any type.

From (III, 8) the relative adsorption of water $\Gamma_{2(1)}$ can be calculated by means of the formula

$$\Gamma_{2(1)} = -\frac{1}{RT}\left(\frac{d\sigma}{d\ln a_2}\right)_T \qquad \text{(III, 9)}$$

where a_2 is the activity of water. If the salt is non-volatile and the vapour approximates to an ideal gas, we can use isothermal data on the vapour pressure P over the solution to calculate

$$\Gamma_{2(1)} = -\frac{P}{RT}\left(\frac{d\sigma}{dP}\right)_T \qquad \text{(III, 10)}$$

The relative adsorption of the salt $\Gamma_{1(2)}$ is easily found from formula (II, 8):

$$\Gamma_{1(2)} = -x_1^{(\alpha)}\Gamma_{2(1)}/(1-x_1^{(\alpha)}) \qquad \text{(III, 11)}$$

where $x_1^{(\alpha)}$ is the mole fraction of the salt in the solution. In Eqn. (III, 10) the vapour is regarded as ideal, but in (III, 11) the vapour density is neglected, so that both relations are valid only far from the critical point.

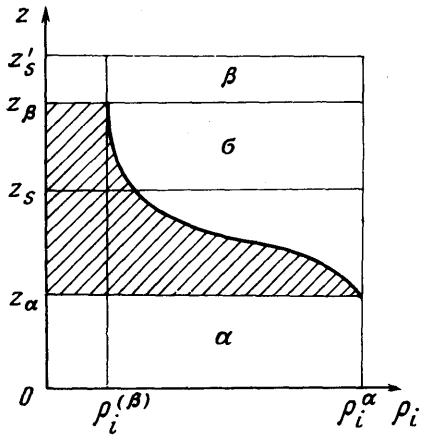


Figure 1. Density profile of ith component in surface layer.

2. Calculation of Composition of Surface Layer

Relation between adsorption and composition of surface layer

If the z-axis is directed perpendicularly to the surface from phase α towards phase β, the quantity $m_1^{(\sigma)}/A$ (the shaded area in Fig. 1) in a surface layer of thickness $\tau \equiv z_\beta - z_\alpha$ will be given by

$$m_1^{(\sigma)}/A = {}^{(\sigma)}_{m}x_1^{(\alpha)}/A = \Gamma_1 + \rho_1^{(\alpha)}\tau - (\rho_1^{(\alpha)} - \rho_1^{(\beta)})(z_\beta - z_s) \qquad \text{(III, 12)}$$

and similarly

$$m_2^{(\sigma)}/A = m^{(\sigma)}(1-x_1^{(\alpha)})/A = \Gamma_2 + \rho_2^{(\alpha)}\tau - (\rho_2^{(\alpha)} - \rho_2^{(\beta)})(z_\beta - z_s) \qquad \text{(III, 13)}$$

where

$$m^{(\sigma)} = m_1{}^{(\sigma)} + m_2{}^{(\sigma)},\quad x_1{}^{(\sigma)} = m_1{}^{(\sigma)}/m^{(\sigma)};$$

$m_i^{(\sigma)}$ is the number of moles of the ith component in the surface layer, and z_s is the coordinate of the dividing surface. These relations hold for any position of the dividing surface, not necessarily within the surface layer.

Passing to the relative adsorption

$$\Gamma_{2(1)} \equiv \Gamma_2 - \Gamma_1(\rho_2^{(\alpha)} - \rho_2^{(\beta)})/(\rho_1^{(\alpha)} - \rho_1^{(\beta)}) \qquad \text{(III, 14)}$$

and remembering that $A/m^{(\sigma)} = v^{(\sigma)}/\tau$, we obtain from (III, 12 and 13) the required relation

$$x_1^{(\sigma)} = \frac{x_1^{(\alpha)} - x_1^{(\beta)}\varkappa}{1-\varkappa}(1 - v^{(\sigma)}\Gamma_{2(1)}/\tau) - \frac{v^{(\sigma)}(x_1^{(\alpha)} - x_1^{(\beta)})}{v^{(\beta)}(1-\varkappa)} \qquad \text{(III, 15)}$$

where

$$\varkappa \equiv \rho^{(\beta)}/\rho^{(\alpha)} = v^{(\alpha)}/v^{(\beta)},\ \rho = \rho_1 + \rho_2;$$

and v is the molar volume. Equation (III, 15) shows that conversion from relative adsorptions to mole fractions in the surface layer necessitates specification of the thickness and the molar volume of the latter—two parameters which characterise unambiguously the situation of the surface layer in the system.

In the case of equilibrium between solution and vapour with neglect of the density of the latter $\varkappa \to 0$ formula (III, 15) simplifies to[42,43]

$$x_1^{(\sigma)} = x_1^{(\alpha)}(1 - v^{(\sigma)}\Gamma_{2(1)}/\tau), \qquad \text{(III, 16)}$$

which coincides also with the expression for adsorption from a binary liquid solution at its interface with a solid[44].

Use of thermodynamic equations to calculate composition of surface layer

In order to calculate $x_1^{(\sigma)}$ by means of Eqn. (III, 16) it is first necessary to find the Gibbs relative adsorption. However, it can be calculated also by use of the thermodynamics of surface layers, e.g. from the constant-pressure temperature dependence of surface tension, an equation for which is obtained by fixing the pressure in Eqns. (II, 10) and eliminating one of the derivatives, e.g. $(dx_{n-1}/dT)_P^{(\alpha)}$. For a binary system we then have

$$a\left(\frac{d\sigma}{dT}\right)_P = -s_{\alpha\sigma} + \frac{x_1^{(\sigma)} - x_1^{(\alpha)}}{x_1^{(\beta)} - x_1^{(\alpha)}}s_{\alpha\beta} \qquad \text{(III, 17)}$$

which holds in practice even in the presence of a foreign gas (e.g. air[45]) in the system. In the case of a non-volatile salt ($x_{X_1}^{(\beta)} = 0$) we find from (III, 17) that

$$x_1^{(\sigma)} = x_1^{(\alpha)} - \frac{(d\sigma/dT)_P \cdot v^{(\sigma)}/\tau + s_{\alpha\sigma}}{s_{\alpha\beta}}x_1^{(\alpha)} \qquad \text{(III, 18)}$$

where $v^{(\sigma)} = a\tau$, which enables the composition of the surface layer of a binary solution to be calculated from the constant-pressure temperature dependence of surface tension. The differential molar entropy effects in (III, 18) are defined[41]

$$s_{\alpha\sigma} = -(d\sigma/dT)_{x_1}^{(\alpha)}\, v^{(\sigma)}/\tau;\quad s_{\alpha\beta} = RB/T$$

the constant B being evaluated from the temperature dependence of the vapour pressure $\ln P = A - B/T$. Surface-tension isobars are found from the composition dependence of σ and P, and are then differentiated to determine $(d\sigma/dT)_P$.

The composition of a surface layer of given thickness can be calculated also from isothermal data on the dependence of surface tension on solution composition. For a binary system the surface-tension isotherm

$$a\,d\sigma = \left[(x_1^{(\beta)} - x_1^{(\alpha)})\frac{v_{\alpha\sigma}}{v_{\alpha\beta}} - (x_1^{(\sigma)} - x_1^{(\alpha)})\right]g_{11}^{(\alpha)}dx_1^{(\alpha)} \qquad \text{(III, 19)}$$

follows from (II, 10).[46] When liquid–vapour (α–β) equilibrium is established far from the critical point, it can be assumed that

$$|v_{\alpha\beta}| \gg |v_{\alpha\sigma}| \qquad \text{(III, 20)}$$

and the first term in square brackets can be neglected. From (III, 19) we then obtain

$$x_1^{(\sigma)} = x_1^{(\alpha)} \frac{(d\sigma/dx_2^{(\alpha)})_T v^{(\sigma)}}{g_{11}^{(\alpha)} \cdot \tau} \qquad \text{(III, 21)}$$

The quantity $g_{11}^{(\alpha)}$ is calculated by means of the formula

$$g_{11}^{(\alpha)} = \frac{RT}{1 - x_1^{(\alpha)}} \frac{\partial \ln a_1}{\partial x_1^{(\alpha)}},$$

where a_1 is the activity of the first component. The molar volume is determined to a first approximation with no salt present in the surface layer. On the assumption of the same composition dependence of molar volume in the surface layer and in the solution, the calculated values of $x_1^{(\sigma)}$ are then used to make a second approximation refining the value of $v^{(\sigma)}$, and so on.

It follows from formulae (III–16, 18, and 21) that calculation of the composition of the surface layer requires that its thickness τ should be specified. Thermodynamics imposes certain restrictions on the choice of this quantity.

3. Estimation of Minimal Possible Thickness of Surface Layer

It has been shown[44,47] in the thermodynamics of surface phenomena that conditions of stability impose limitations on the thickness of the surface layer. These conditions can be used to find the minimum possible thickness for every mixture composition at every temperature. The requirement that the compositions of solution and surface layer should vary in parallel

$$(dx_1^{(\sigma)}/dx_1^{(\alpha)}) \geqslant 0$$

can be used as such a condition for binary systems. Application of this inequality to Eqn. (III, 15) and the assumption that molar volumes are additive yield

$$\tau \geqslant \Gamma_{2(1)} [v^{(\alpha)} - x_1^{(\alpha)}(v_1 - v_2)] + x_1^{(\sigma)} d\Gamma_{2(1)}/dx_1^{(\alpha)} \qquad \text{(III, 22)}$$

On the other hand, it follows from the self-evident inequality $0 \leqslant x_1^{(\sigma)} \leqslant 1$ that

$$\tau \geqslant \Gamma_{2(1)} v_2 \qquad \text{(III, 23)}$$

where v_1 and v_2 are the molar volumes of the components, and

$$v^{(\alpha)} \equiv v_2 + (v_1 - v_2) x_1^{(\alpha)}$$

is the additive molar volume of phase α. Analogous relations (but written for an equimolecular surface) were obtained for films adsorbed on a solid[44].

Use of other stability conditions for surface layers of finite thickness also leads to inequalities of the type (III, 22 and 23). The minimum possible thickness is then found directly from data on the composition of the surface layer[41,46].

4. Calculation of Excess Entropy

Considerable interest attaches not only to relative adsorption and the composition of the surface layer but also to the entropy characteristics of the latter, especially in connection with its structure. Calculations of these characteristics for binary liquid solutions were first published by the Reviewers[43,45]. The excess entropy depends by definition (II, 4) on the position of the dividing surface. However, the quantity $\bar{s}(j)$, introduced by analogy with the relative adsorption, is invariant with respect to displacement of the dividing surface and according to (II, 9) is equal to the excess entropy for a surface corresponding to the condition $\Gamma_j = 0$.

To obtain a relation for calculating the excess entropy we make use of an equation linking the molar entropies of solution and surface layer of finite thickness $s^{(\alpha)}$ and $s^{(\sigma)}$ with the temperature derivative of the surface tension. For a liquid–vapour equilibrium in a binary system, with the density of the vapour phase neglected, this equation becomes[41]

$$s^{(\sigma)} = s^{(\alpha)} - \frac{A}{m^{(\sigma)}} \left(\frac{d\sigma}{dT}\right)_{x_1^{(\alpha)}} + \left(\frac{\partial s}{\partial x_1}\right)^{(\alpha)} (x_1^{(\sigma)} - x_1^{(\alpha)}) \qquad \text{(III, 24)}$$

According to a general rule[41] a similar relation should apply to the excess functions. On passing to the latter $m^{(\sigma)}/A$ is replaced by the sum of the absolute adsorptions $\Gamma_1 + \Gamma_2$, and $x_1^{(\sigma)}$ by $\Gamma_1/(\Gamma_1 + \Gamma_2)$. Hence the entropy of the surface layer $s^{(\sigma)} \equiv S^{(\sigma)}/m^{(\sigma)}$ is replaced by $\bar{s}/(\Gamma_1 + \Gamma_2)$, where $\bar{s}$ is the excess entropy per unit surface. From this we obtain

$$\bar{s} = s^{(\alpha)}(\Gamma_1 + \Gamma_2) - (d\sigma/dT)_{x_1^{(\alpha)}} + (\partial s/\partial x_1^{(\alpha)})[\Gamma_1 - x_1^{(\alpha)}(\Gamma_1 + \Gamma_2)] \qquad \text{(III, 25)}$$

Passing to relative adsorptions, we find from (III, 25) that

$$\bar{s}_{(1)} = -(d\sigma/dt)_{x_1^{(\alpha)}} + [s^{(\alpha)} - (\partial s/\partial x_1)^{(\alpha)} x_1^{(\alpha)}]\,\Gamma_{2(1)} \qquad \text{(III, 26)}$$

$$\bar{s}_{(2)} = -(d\sigma/dT)_{x_1^{(\alpha)}} + [s^{(\alpha)} + (\partial s/\partial x_1)^{(\alpha)}(1 - x_1^{(\alpha)})]\,\Gamma_{1(2)} \qquad \text{(III, 27)}$$

whence

$$\bar{s}_{(2)} = \bar{s}_1 + \bar{s}^{(\alpha)}(\Gamma_{1(2)} - \Gamma_{2(1)}) \qquad \text{(III, 28)}$$

In the practical application of formulae (III, 26 and 27) to the calculation of excess entropies from experimental values of $(d\sigma/dT)_{x_1(\alpha)}$ the molar entropy of the solution is first calculated by means of the formula

$$s^{(\alpha)} = s_1 x_1^{(\alpha)} + s_2(1 - x_1^{(\alpha)}) + (\Delta h - \Delta g)/T \qquad \text{(III, 29)}$$

where Δh is the molar heat of mixing, which can be determined from calorimetric data, and Δg is the molar Gibbs free energy of mixing.

5. Calculation of Molar Entropy of Surface Layer

Calculation of molar entropy of surface layer from data on excess entropy

As in the calculation of composition, the entropy of the surface layer can be calculated either from excess Gibbs functions or directly by means of formulae relating to the surface layer. To obtain relations between the excess entropy and the molar entropy of the surface layer we return to Fig. 1, replace the density profile by the entropy profile, and write down the consequent self-evident relation

$$\bar{s} = S^{(\sigma)}/A - s_v^{(\alpha)}\tau + (s_v^{(\alpha)} - s_v^{(\beta)})(z_\beta - z_s) \qquad \text{(III, 30)}$$

Considering (III, 30) together with (III, 12) and passing to molar quantities

$$S^{(\sigma)} = s^{(\sigma)} m^{(\sigma)},\ s_v^{(\alpha)} = \frac{s^{(\alpha)}}{v^{(\alpha)}},\ s_v^{(\beta)} = \frac{s^{(\beta)}}{v^{(\beta)}},\ \rho_1^{(\alpha)} = \frac{x_1^{(\alpha)}}{v^{(\alpha)}},\ \rho_1^{(\alpha)} = \frac{x_1^{(\beta)}}{v^{(\beta)}}$$

we find from (II, 9) that

$$s^{(\sigma)} = \frac{v^{(\sigma)}}{\tau}\bar{s}_{(1)} + \frac{\varkappa\,(x_1^{(\alpha)}s^{(\beta)} - x_1^{(\beta)}s^{(\alpha)})\,v^{(\sigma)}/v^{(\alpha)} + (s^{(\alpha)} - s^{(\beta)}\varkappa)\,x_1^{(\sigma)}}{x_1^{(\alpha)} - x_1^{(\beta)}\varkappa} \quad \text{(III, 31)}$$

where $x_1^{(\sigma)}$ is defined by (III, 15) with the same meaning of κ. Thus formula (III, 31), when considered in combination with (III, 15), enables the molar entropy of the surface layer to be calculated from its excess entropy. We again stress that the thickness and the molar volume of the surface layer must be specified: these two parameters define unambiguously the position of the surface layer in the heterogeneous system.

On passing to a solution–vapour ($\alpha-\beta$) system and neglecting the vapour density, we find from (III, 15 and 31) that

$$s^{(\sigma)} = s^{(\alpha)} + (\bar{s}_{(1)} - \Gamma_{2(1)}s^{(\alpha)})\,v^{(\sigma)}/\tau \quad \text{(III, 32)}$$

which can be used to calculate the molar entropy of the surface layer from the excess functions.

Calculation of molar entropy of surface layer from entropies of coexisting phases

The molar entropy of the surface layer $s^{(\sigma)}$ can be calculated directly from the thermodynamic equations for a layer of finite thickness. A suitable formula can be obtained from the definition (II, 11) of the differential molar entropy effect of adsorption. For a binary system we have

$$s_{\alpha\sigma} = s^{(\sigma)} - s^{(\alpha)} - (\partial s/\partial x_1)^{(\alpha)}\,(x_1^{(\sigma)} - x_1^{(\alpha)}) \quad \text{(III, 33)}$$

Taking into account the above expression for $s\alpha\sigma$, we hence obtain Eqn. (III, 24), which is quite convenient for calculating $s^{(\sigma)}$ from the entropy of the solution $s^{(\alpha)}$ and the temperature variation of surface tension.

The entropy of the surface layer can be calculated also by means of the formula

$$s^{(\sigma)} = s^{(\beta)} - s_{\alpha\beta} + s_{\alpha\sigma} - (\partial s/\partial x_1)^{(\alpha)}\,(x_1^{(\beta)} - x_1^{(\sigma)}) \quad \text{(III, 34)}$$

obtained by subtracting (II, 11) from (II, 13). Since the salt is non-volatile, $x_1^{(\beta)} = 0$, and we finally obtain [45]

$$s^{(\sigma)} = s^{(\beta)} - RB/T - (d\sigma/dT)_{x_1^{(\alpha)}}v^{(\sigma)}/\tau + (\partial s/\partial x_1)^{(\alpha)}x_1^{(\sigma)} \quad \text{(III, 35)}$$

The molar entropy of the vapour $s^{(\beta)}$ is evaluated from the formula

$$s^{(\beta)} = s_0^{\beta} - R\ln P \quad \text{(III, 36)}$$

where $s_0^{(\beta)}$ is the entropy of 1 mole of water vapour at 1 atm, and P (in atm) is the aqueous vapour pressure over the solution.

Among Eqns. (III–24, 32, and 35) the most convenient for practical application is (III, 24), which gives the smallest calculated error [43,48]. However, the use both of this equation and of (III, 32) requires the availability of calorimetric data, from which $s^{(\alpha)}$ can be calculated, and then the entropy of the surface layer. Adsorption data are also required when Eqn. (III, 34) is applied. However, formula (III, 36), which involves calculating the entropy of phase β and the entropy effect $s\alpha\beta$, can be used in approximate form (neglecting the last term) even in the absence of calorimetric data.

IV. EFFECT OF NATURE OF DISSOLVED IONS ON PROPERTIES OF SURFACE LAYER

In this Section we shall discuss results calculated by means of the above formulae for binary aqueous salt systems studied hitherto. Calculations have been made at one or more temperatures depending on the completeness and quality of the experimental data. The calculated thermodynamic characteristics of surface layers of various aqueous salt systems at the same temperature permit the systems to be compared and the effects of cations and anions on the structure and properties of the surface layer to be elucidated. The temperature 25 °C was chosen for this purpose. Most published surface-tension data relate to the range 10–30 °C, which permits interpolation for 25 °C. Furthermore, heats of mixing [49–51] as well as activity coefficients [52] are most often given for this temperature. Calculations at other temperatures are also important for revealing the temperature dependence of these properties of surface layers.

[References containing data on surface tension and activity coefficients for aqueous salt solutions.]

Salt	Surface tension	Activity coeff.	Salt	Surface tension	Activity coeff.
LiCl	9, 10, 55–57	58, 59	$NaNO_3$	3, 7, 60, 70, 75	52
NaCl	7, 14, 28, 60, 61	58, 59	KNO_3	3, 62, 70, 72, 75	52
KCl	9, 61, 62	52, 58, 59	$CsNO_3$	26	52
RbCl	48, 63, 86	52, 64	NH_4NO_3	3, 7, 19, 65, 75	52, 76
CsCl	48, 86	52	$AgNO_3$	9, 19, 77	52
NH_4Cl	55, 58	58, 59	$Ba(NO_3)_2$	7, 65	52
$MgCl_2$	68, 75	52	$Zn(NO_3)_2$	66, 68	52
$CaCl_2$	15, 56, 65–67	52	Na_2SO_4	7, 65 70, 75, 78	52
$SrCl_2$	59, 68, 69	52	K_2SO_4	7, 27, 62, 70	52
$BaCl_2$	27, 59	52	$(NH_4)_2SO_4$	3, 65, 75	52
$MnCl_2$	65, 68	52	$CuSO_4$	69, 70, 75	52
LiBr	3, 10, 56	52	$MgSO_4$	68, 72, 75, 79	52
NaBr	45, 65	58	$ZnSO_4$	59, 72, 75	52
KBr	3, 7, 10, 71, 72	52	$Al_2(SO_4)_3$	65, 80	52
LiI	3, 10	52	$K_3[Fe(CN)_6]$	58, 65	52
NaI	10, 36, 61	58, 59	Na_2CO_3	3, 8, 75, 81	52
KI	61, 62	58, 59	K_2CO_3	19, 70, 75	52
$LiNO_3$	3, 73, 74	52			

The Table summarises the published sources used. The second column gives references to determinations of surface tension, and the third column the sources of data on activity coefficients or vapour pressures. The molar entropies of the pure components have been taken from Refs. 53 and 54.

1. Dependence of Relative Adsorption on Energy of Hydration of Ions of Dissolved Salt

When calculating relative adsorptions in aqueous salt systems, we must bear in mind that the concentrations of hydroxide and hydrogen ions are far smaller than those of the ions of the dissolved salt. From the electrical neutrality of the surface layer (III, 3) we may then suppose that the condition of equivalent adsorption of cation and anion of the salt is a quite good approximation. Formulae (III, 9–11) have therefore been used to compute relative adsorptions.

The calculated adsorptions show (Figs. 2–15) that the relative adsorption of water $\Gamma_{2(1)}$ is positive in all the systems examined. The adsorption isotherms pass through an extremum in aqueous potassium, rubidium, and caesium chlorides, aqueous lithium and zinc nitrates, and aqueous ammonium sulphate (in potassium chloride solution it is perceptible only at 40 °C [61]). The relative adsorption of the salt $\Gamma_{1(2)}$ is negative, and in most cases increases numerically with concentration.

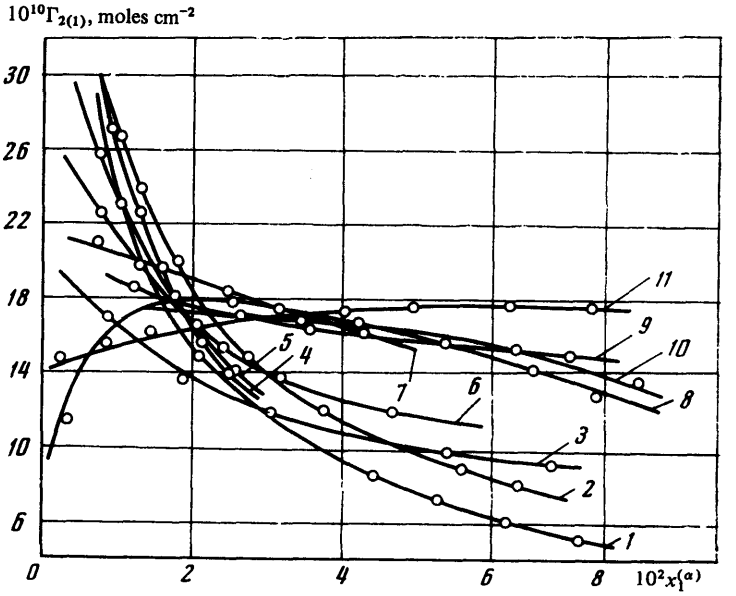


Figure 2. Relative adsorption of water at 25°C in aqueous solutions of: 1) $MgCl_2$; 2) $CaCl_2$; 3) LiCl; 4) $BaCl_2$; 5) $SrCl_2$; 6) $MnCl_2$; 7) CsCl; 8) RbCl; 9) KCl; 10) NaCl; 11) NH_4Cl.

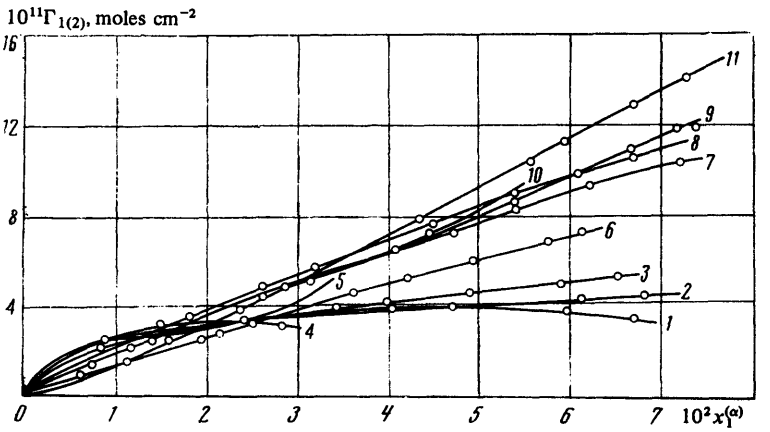


Figure 3. Relative adsorption of salt at 25°C in aqueous solutions of: 1) $MgCl_2$; 2) LiCl; 3) $CaCl_2$; 4) $BaCl_2$; 5) $SrCl_2$; 6) $MnCl_2$; 7) RbCl; 8) NaCl; 9) KCl; 10) CsCl; 11) NH_4Cl.

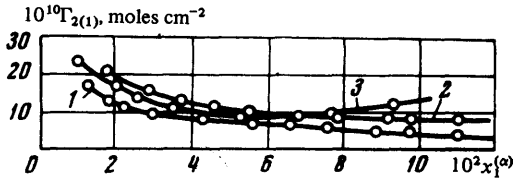


Figure 4. Relative adsorption of water at 25°C in aqueous solutions of: 1) LiBr; 2) NaBr; 3) KBr.

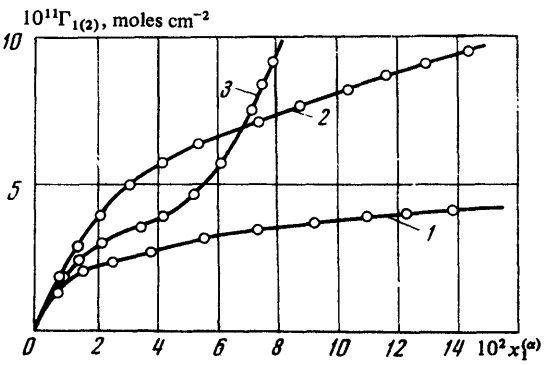


Figure 5. Relative adsorption of salt at 25°C in aqueous solutions of: 1) LiBr; 2) NaBr; 3) KBr.

In order to interpret the adsorption data we must consider the relation between the relative adsorption and the nature of the ions adsorbed. Consideration is usually given to published ionic hydration energies when adsorption isotherms for different salts are compared[82,83]. Indeed, the ability of an ion to pass from the bulk of the solution to the surface layer is largely determined by the strength of bonding of the ion with solvent molecules, i.e. by its hydration. However, data on the energy of hydration of individual ions generally relate to infinite dilution[49,84], so that the concentration dependence of this energy must be taken into account when discussing adsorption over a wide concentration range. Use for this purpose of Mishchenko's qualitative theory[49], which classifies solutions of electrolytes according to the form of isotherm for their integral heats of distribution, shows that substances whose dissolution becomes continuously less exothermic exhibit the most substantial change (weakening) of hydration with increase in solution concentration. Among the systems examined, aqueous solutions of lithium chloride, bromide, iodide, and nitrate, magnesium chloride and sulphate, calcium and barium chlorides, and zinc nitrate and sulphate belong to this group.

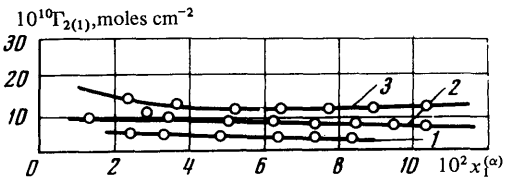


Figure 6. Relative adsorption of water at 25°C in aqueous solutions of: 1) LiI; 2) NaI; 3) KI.

A similar conclusion concerning the variation of hydration with concentration can be reached by comparing values of df/dc (where f is the mean activity coefficient and c the concentration). Positive values of df/dc indicate partial dehydration of the ions. Comparison of these derivatives for solutions of alkali-metal chlorides shows that, with increase in concentration, ionic dehydration is most significant with lithium chloride solution[20].

As example we shall examine in detail the series of solutions of alkali-metal chlorides. In infinitely dilute solutions the hydration energies $-\Delta H_0$ of the lithium, sodium, potassium, rubidium, caesium, and ammonium cations are respectively 127, 101, 81, 75, 67, and 78 kcal g-ion^{-1}.[49] However, the above discussion shows that bonding with water molecules becomes weaker with increase in concentration (energetic and coordinative dehydration) more noticeably with the lithium ion, which is most strongly hydrated at infinite dilution, than with the other cations, which facilitates transfer of these ions from the bulk of the solution to the surface layer. In sufficiently concentrated solutions the adsorption may thus become greater (numerically less) than that from solutions of the other chlorides.

The above considerations apply also to solutions of lithium bromide, iodide, and nitrate, magnesium chloride and sulphate, calcium and barium chlorides, and zinc nitrate and sulphate, and correspond to results obtained over a considerable concentration range. Fig. 3 shows that at concentrations $x_1^{(\alpha)} = 0.03$ and above the numerical value of the adsorption is significantly smaller from solutions of lithium, magnesium, and calcium chlorides than from solutions of other chlorides. Similarly, with the alkali-metal bromides (Fig. 5) adsorption from lithium bromide solution is greater (numerical value smaller) than from sodium and potassium bromide solutions beginning from $x_1^{(\alpha)} = 0.01$. The conclusions reached are supported also by the adsorption isotherms for solutions of iodides (Fig. 7), nitrates (Fig. 9), and sulphates (Fig. 11).

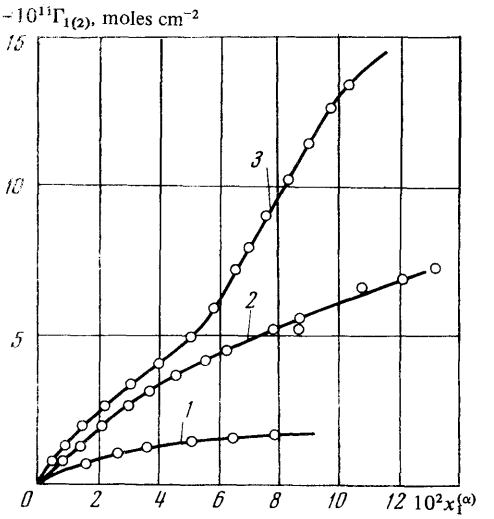


Figure 7. Relative adsorption of salt at 25°C in aqueous solutions of: 1) LiI; 2) NaI; 3) KI.

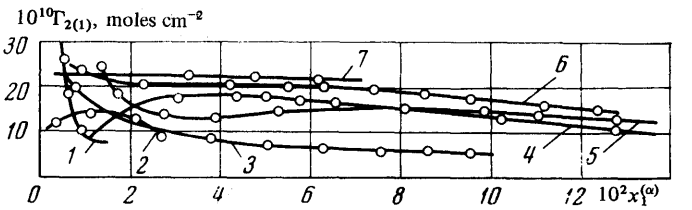


Figure 8. Relative adsorption of water at 25°C in aqueous solutions of: 1) $Ba(NO_3)_2$; 2) $LiNO_3$; 3) $Zn(NO_3)_2$; 4) $NaNO_3$; 5) NH_4NO_3; 6) $AgNO_3$; 7) KNO_3.

In very dilute solutions, however, it must be expected that the relative positions of the isotherms will correspond to the hydration energies for infinite dilution. The diagrams show, nevertheless, that the adsorption isotherms almost coalesce at low salt concentrations. Additional calculations were therefore made for the chlorides of various metals. With $x_1^{(\alpha)} = 0.004$ adsorption of the salt at 25°C (expressed as -10^{-11} mole cm^{-2}) is respectively 0.4, 0.6, 0.8, and 0.9 in aqueous rubidium, ammonium, lithium, and barium chlorides. Thus at such concentrations adsorption decreases with increase in the energy of hydration of the cation. In the above series it is

least with the barium ion, which is the most vigorously hydrated in infinitely dilute solution[49] ($-\Delta H_0$ = 320 kcal g-ion^{-1}).

For nitrate solutions calculations were made of the adsorption with $x_1^{(\alpha)}$ = 0.002 at 25°C. The values obtained for aqueous caesium, lithium, and zinc nitrates (respectively 0.3, 0.6, and 0.9 measured in -10^{-11} mole cm^{-2}) are also consistent with the energies of hydration of the cations at infinite dilution[49] ($-\Delta H_0$ = 67, 127, and 496 kcal g-ion^{-1}).

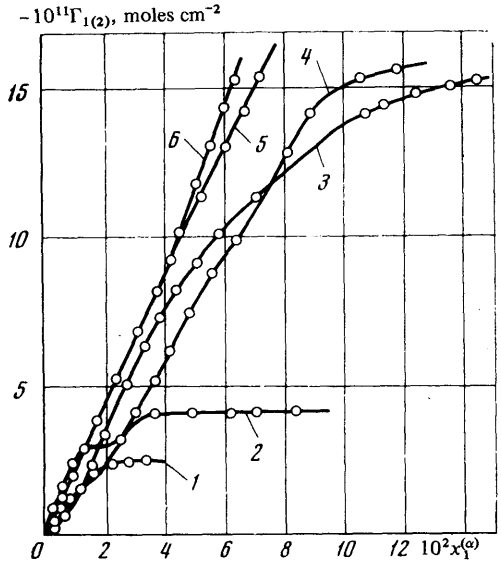


Figure 9. Relative adsorption of salt at 25°C in aqueous solutions of: 1) $LiNO_3$; 2) $Zn(NO_3)_2$; 3) $NaNO_3$; 4) NH_4NO_3; 5) $AgNO_3$; 6) KNO_3.

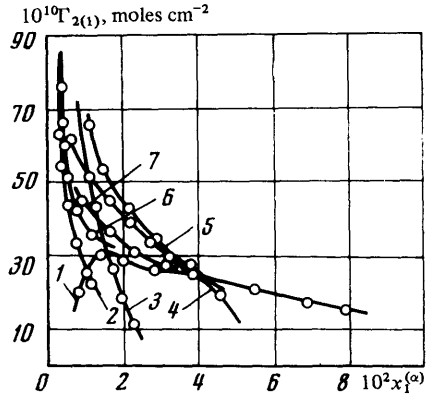


Figure 10. Relative adsorption of water at 25°C in aqueous solutions of: 1) $(NH_4)_2SO_4$; 2) $Al_2(SO_4)_3$; 3) $CuSO_4$; 4) $MgSO_4$; 5) $ZnSO_4$; 6) K_2SO_4; 7) Na_2SO_4.

In other cases (when the salts exhibit no marked difference in the concentration dependence of the hydration energy) the relative positions of the salt-adsorption isotherms correspond throughout the concentration range to the hydration energies at infinite dilution, e.g. for lithium, sodium, and potassium halides (Figs. 13–15). In conformity with Mishchenko's classification, solutions of lithium chloride, bromide, and iodide are of the same type according to the form of the isotherms for the integral heats of dissolution, while solutions of the sodium halides belong to another type, and those of the potassium halides to a third type. This means that the variation (increase or decrease) in the energy of hydration of the anions is roughly the same in each of the three cases. The relative positions of the adsorption isotherms should then correspond to these hydration energies at infinite dilution. For the chloride, bromide, and iodide ions we have[49] $-\Delta H_0$ = 84, 76, and 67 kcal g-ion^{-1}. The diagrams show that the numerical value of the adsorption diminishes in this sequence in all three cases.

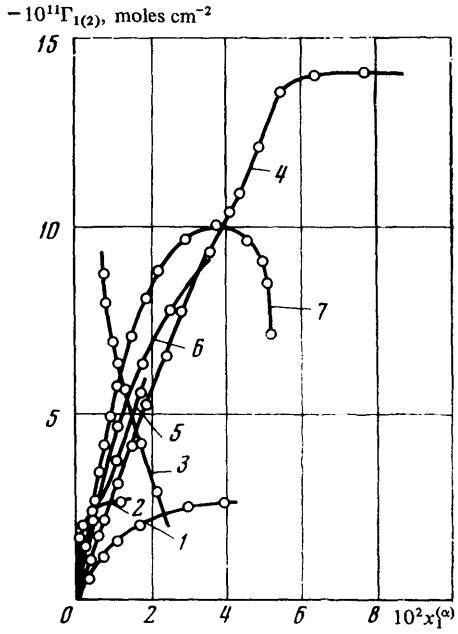


Figure 11. Relative adsorption of salt at 25°C in aqueous solutions of: 1) $ZnSO_4$; 2) K_2SO_4; 3) $CuSO_4$; 4) $(NH_4)_2SO_4$; 5) $Al_2(SO_4)_3$; 6) Na_2SO_4; 7) $MgSO_4$.

As already mentioned, calculations of adsorption have been made for several temperatures where suitable data on surface tension and activity coefficients were available. Comparison of results for 25° and 40°C indicates only a slight change (in most cases within the limits of error of the calculation) in the relative adsorption with temperature[43,61]. Only in aqueous ammonium chloride is a significant increase in $\Gamma_{1(2)}$ produced by raising the temperature from 25° to 40°C.[55] The evident reason is that the energy of hydration of the ammonium ion diminishes more rapidly with rise in temperature than do those of metal ions.

Increase in the numerical adsorption of surface-inactive non-volatile substances is accompanied by an increase in the surface tension of the solution (a direct consequence of the Gibbs adsorption equation). However, the surface

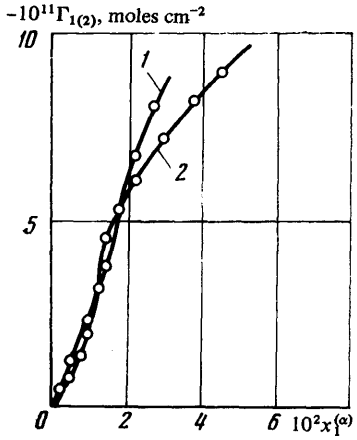


Figure 12. Relative adsorption of carbonates at 25°C from aqueous solutions of: 1) Na_2CO_3; 2) K_2CO_3.

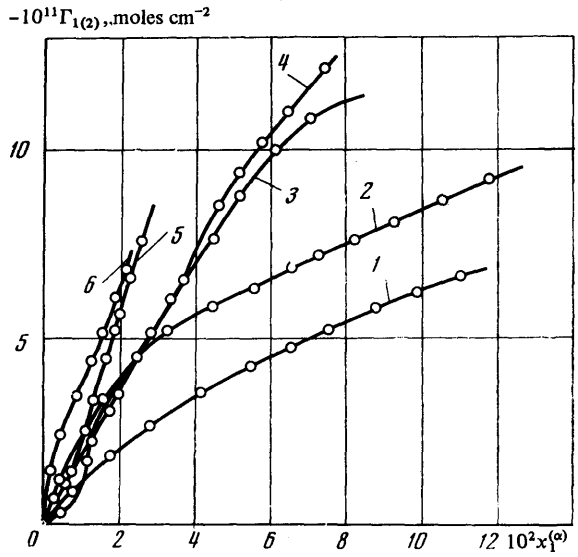


Figure 13. Relative adsorption of sodium salts at 25°C from aqueous solutions of: 1) NaI; 2) NaBr; 3) NaCl; 4) $NaNO_3$; 5) Na_2CO_3; 6) Na_2SO_4.

tension depends also on structural changes occurring in the solution under the influence of ions of the dissolved salt (this fact is reflected in the Gibbs equation by the activity coefficients). On the one hand, disruption of the structure of water by ions facilitates the transfer of water molecules to the surface layer and thus tends to diminish surface tension. On the other hand, the fields due to the ions, whose concentration in the solution may exceed considerably their concentration in the surface layer, promote the transfer of molecules into the interior of the solution and increase surface tension[20]. The presence of opposing tendencies provides an explanation for the fairly closely similar surface tensions exhibited by solutions of salts containing markedly different ions. For example, the presence of lithium ions structures a solution[85] and hinders the transfer of water molecules to the surface layer, which corresponds to an increase in surface tension relative both to pure water and to potassium chloride solution (potassium ions are known to loosen the structure of water[85]). But Fig. 3 shows that the adsorption of potassium chloride is numerically greater than that of lithium chloride. Hence on this basis the presence of potassium chloride in solution should produce a greater increase in surface tension. As a result, the surface-tension isotherms of these two solutions are quite close (Fig. 16).

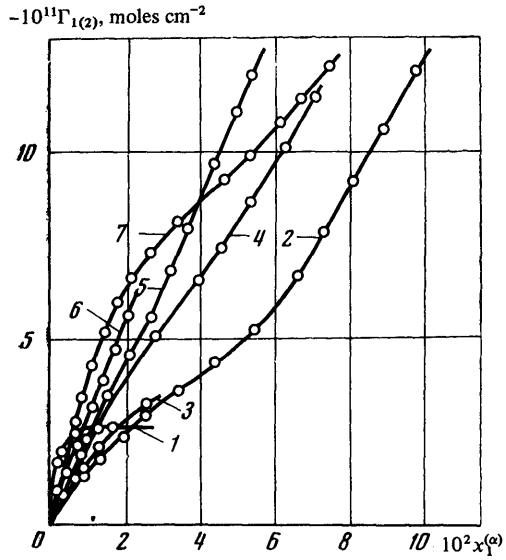


Figure 14. Relative adsorption of potassium salts at 25°C from aqueous solutions of: 1) K_2SO_4; 2) KI; 3) KBr; 4) KCl; 5) KNO_3; 6) $K_3[Fe(CN)_6]$; 7) K_2CO_3.

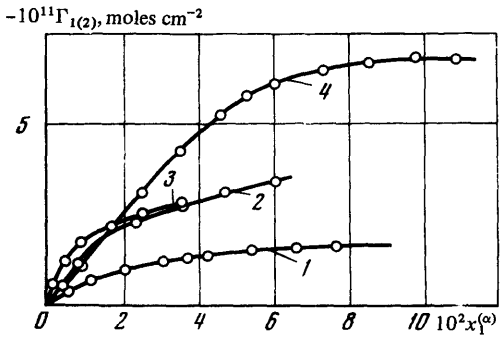


Figure 15. Relative adsorption of lithium salts at 25°C from aqueous solutions of: 1) LiI; 2) LiBr; 3) $LiNO_3$; 4) LiCl.

2. Composition and Minimum Possible Thickness of Surface Layer in Aqueous Salt Systems

A value of τ exceeding the minimum possible thickness must be specified in order to calculate the composition of the surface layer by means of formulae (III—16, 18, and 21), as in the calculation of its molar entropy. Thus the choice of thickness for the calculation entails estimation of its minimum possible value.

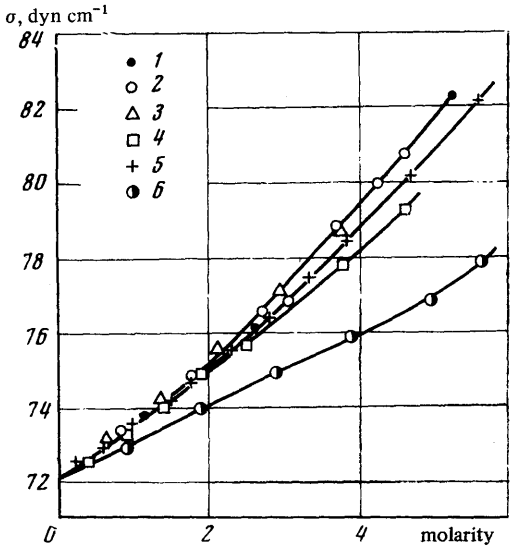


Figure 16. Surface tension at 25°C of solutions of ammonium and alkali-metal chlorides[48,55,61]: 1) LiCl; 2) NaCl; 3) KCl; 4) RbCl; 5) CsCl; 6) NH_4Cl.

The estimation has been based on the inequalities (III, 22 and 23). The larger of the two values of τ_{min} obtained from these inequalities are plotted against composition in Figs. 17–20. In most cases the minimum possible thickness decreases with increase in solution concentration. The diagrams show also that, with the exception of solutions of sulphates and carbonates, τ_{min} does not exceed 5 Å even at low salt concentrations. It is noticeable also that the minimum possible thickness falls more rapidly with concentration in solutions of sulphates.

The inequality (III, 23) can be used also to make the interesting estimation of the maximum possible thickness of a layer of pure water on the surface of the solution if such a layer can exist (an analogous method has already been applied to aqueous sodium chloride[14]). Another possibility for estimating the thickness of a film of water on the surface of a salt solution is to solve Eqns. (III, 18 and 21 [sic]) for τ with $x_1^{(\sigma)} = 0$. The hypothetical absence of salt in the surface layer implies a transition from a real surface layer to a model in which vapour and salt solution are separated by a film of water of thickness τ.

Calculations by different methods for solutions of lithium and sodium chlorides show (Fig. 21) that the film of water becomes thinner with increase in solution concentration, and that the water present on the surface of concentrated solutions is insufficient to form a monolayer. This implies that in these systems the ions of the salt enter a monolayer at the solution—vapour interface—a conclusion which is consistent with earlier results[8,9,15,16,45].

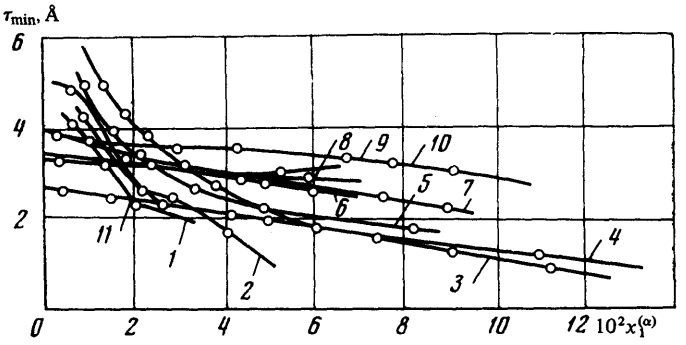


Figure 17. Concentration dependence of minimum possible thickness of surface layer at 25°C in aqueous solutions of chlorides: 1) $SrCl_2$; 2) $MgCl_2$; 3) $CaCl_2$; 4) LiCl; 5) $MnCl_2$; 6) RbCl; 7) NaCl; 8) KCl; 9) CsCl; 10) NH_4Cl; 11) $BaCl_2$.

Estimation of the minimum possible thickness was followed by calculation of the composition of the surface layer. In the case of carbonate and sulphate solutions the calculations were based on a layer 10 Å thick, and in the remaining cases 5 Å was chosen. These values are acceptable on purely thermodynamic grounds, since they deliberately exceed the minimum possible thickness.

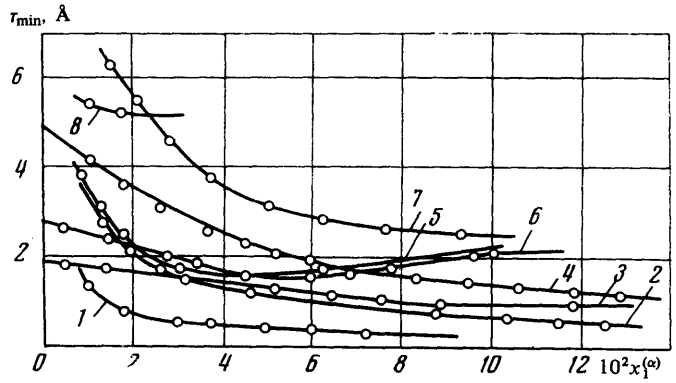


Figure 18. Concentration dependence of minimum possible thickness of surface layer at 25°C in aqueous solutions of alkali-metal halides and carbonates: 1) LiI; 2) LiBr; 3) NaI; 4) NaBr; 5) KBr; 6) KI; 7) Na_2CO_3; 8) K_2CO_3.

Choice of the same thickness (e.g. 5 or 10 Å) for the surface layers of several salt solutions helps to reveal several regularities indicating a relation between the nature of the ions and the properties of the surface layer.

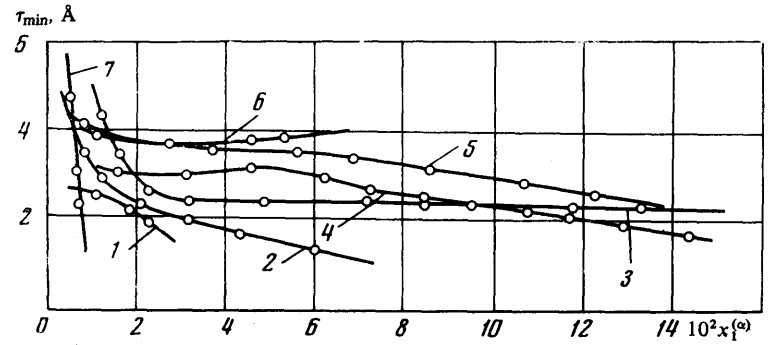


Figure 19. Concentration dependence of minimum possible thickness of surface layer at 25°C in aqueous solutions of nitrates: 1) $LiNO_3$; 2) $Zn(NO_3)_2$; 3) NH_4NO_3; 4) $NaNO_3$; 5) $AgNO_3$; 6) KNO_3; 7) $Ba(NO_3)_2$.

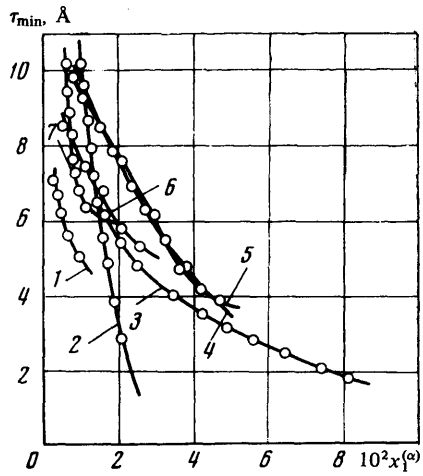


Figure 20. Concentration dependence of minimum possible thickness of surface layer at 25°C in aqueous solutions of sulphates: 1) K_2SO_4; 2) $CuSO_4$; 3) $(NH_4)_2SO_4$; 4) $MgSO_4$; 5) $ZnSO_4$; 6) Na_2SO_4; 7) $Al_2(SO_4)_3$.

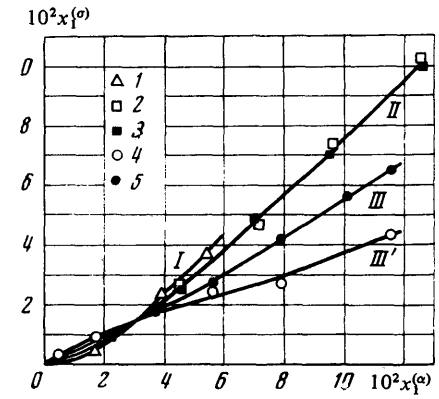


Figure 22. Composition of surface layer 5 Å thick in aqueous solutions of chlorides of: I) calcium; II) lithium; III, III′) ammonium at: 1,2,4) 25°C; 3,5) 40°C.

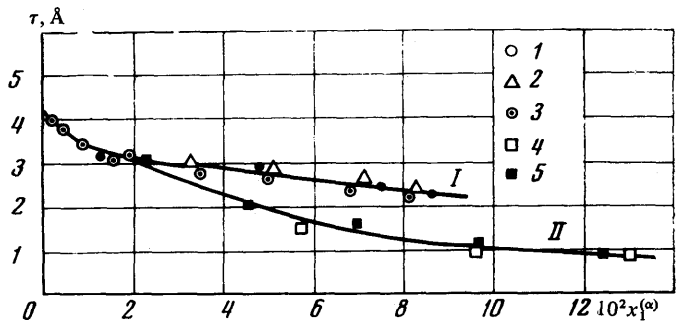


Figure 21. Thickness at 25°C of layer of water on surface of solutions of: I) sodium chloride; II) lithium chloride from: 1) formula (III, 17); 2) inequality (III, 22); 3) Ref. 14; 4) formula (III, 17); 5) inequality (III, 22).

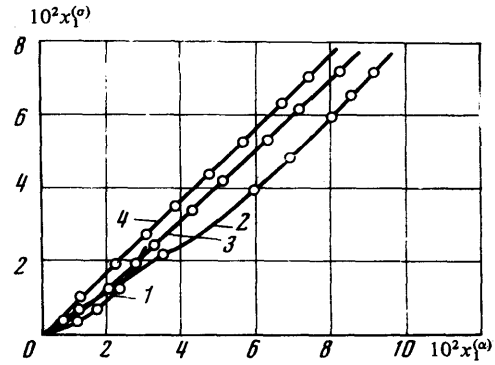


Figure 23. Composition of surface layer 5 Å thick in aqueous solutions at 25°C of lithium salts: 1) nitrate; 2) chloride; 3) bromide; 4) iodide.

Parallel calculations of composition by means of Eqns. (III–16, 18, and 21) for solutions of alkali-metal and ammonium chlorides showed good agreement [43, 55, 61], so that composition in the remaining systems was calculated only by means of (III, 16). Plots of the results show (Figs. 22–27) that the surface layer is in all cases depleted in salt relative to the solution, which corresponds to negative relative adsorption of the salt. This is a natural and necessary feature, since the parameters are directly related by formula (III, 16).

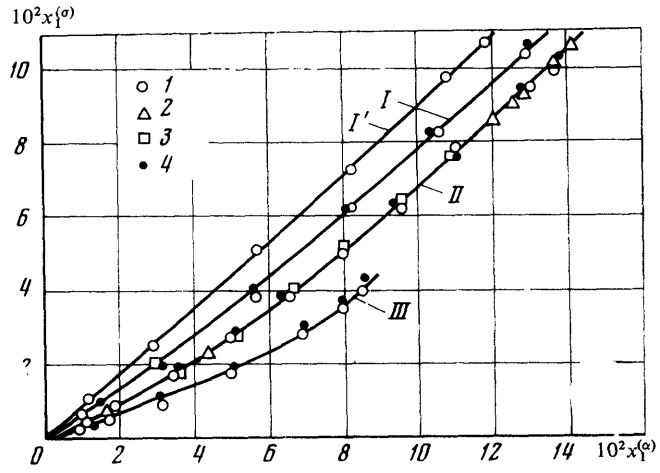


Figure 24. Composition of surface layer 5 Å thick in aqueous solutions of sodium halides: I) iodide; I') iodide (10 Å); II) bromide; III) chloride at: 1–3) 25°C:, 4) 40°C.

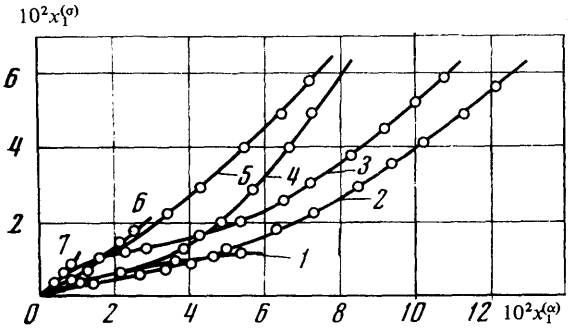


Figure 25. Composition of surface layer 5 Å thick at 25°C in aqueous solutions of nitrates: 1) KNO_3; 2) $AgNO_3$; 3) $NaNO_3$; 4) NH_4NO_3; 5) $Zn(NO_3)_2$; 6) $LiNO_3$; 7) $Ba(NO_3)_2$.

Comparison of the isotherms for the lithium halides shows (Fig. 23) that, for solutions of the same composition, the salt content of the surface layer diminishes in the sequence LiI > LiBr > LiCl throughout the concentration range. A similar pattern is exhibited by the halides of sodium (Fig. 24) and of potassium [55]. Thus the results obtained for adsorption and composition indicate that iodides penetrate into the surface layer more readily than do bromides and chlorides (and bromides in turn more readily than chlorides). As already mentioned, the increase in salt contents of lithium, sodium, and potassium halides in the sequence—chloride < bromide < < iodide—corresponds to the hydration energies of these ions.

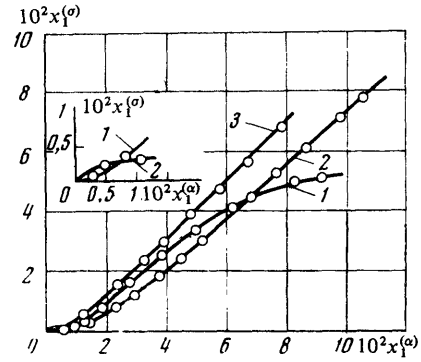


Figure 26. Composition of surface layer 5 Å thick at 25°C in aqueous solutions of alkali-metal bromides: 1) KBr; 2) NaBr; 3) LiBr.

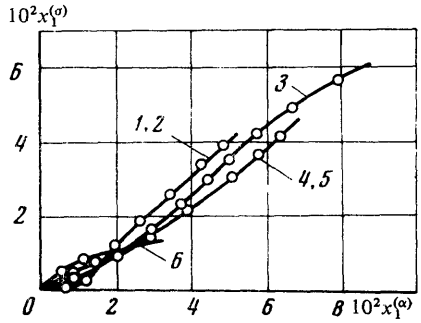


Figure 27. Composition of surface layer 10 Å thick at 25°C in aqueous solutions of sulphates and carbonates: 1) $CuSO_4$; 2) $ZnSO_4$; 3) K_2CO_3; 4) $(NH_4)_2SO_4$; 5) Na_2SO_4; 6) Na_2CO_3.

The isotherms for the composition of the surface layer in solutions of lithium, calcium, and ammonium chlorides show (Fig. 22) that at low concentrations ($x_1^{(\alpha)} < 0.03$) the quantity of salt in the surface layer diminishes in the sequence $NH_4Cl > LiCl > CaCl_2$, i.e. with increase in the energy of hydration of the cation at infinite dilution ($-\Delta H_0 = 78$, 127, and 386 kcal g-ion^{-1}). [49] The relative positions of the isotherms change in more concentrated solutions, which is explained by differences in the concentration dependence of the hydration energy for these ions [49].

A similar situation is observed with the surface layers of solutions of alkali-metal bromides and of sulphates (Figs. 26 and 27). The concentration of salts containing

the most strongly hydrated cations (lithium bromide and copper and zinc sulphates respectively) is lower in the surface layers of dilute solutions than are those of the other bromides and sulphates. For the above reasons the relative positions of the composition isotherms change with increase in concentration of the solution.

In conclusion we note that rise in temperature from 25° to 40°C has little effect on the composition of the surface layer in solutions of salts having a metal cation (Figs. 22 and 24).

3. Entropy of Surface Layers

Excess entropy

After the molar entropy of the solution $s^{(\alpha)}$ and the relative adsorption have been calculated, formulae (III, 26–28) can be used to estimate the excess entropies $\bar{s}_{(1)}$ and $\bar{s}_{(2)}$. The first calculations of excess entropy in binary systems were published by the Reviewers[43] (with unary systems excess entropy can be determined by means of the Gibbs adsorption equation).

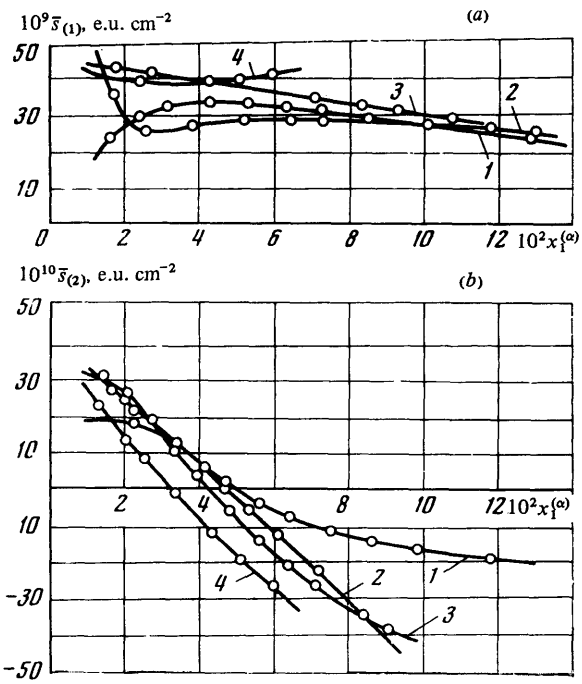


Figure 28. Excess entropies at 25°C in aqueous solutions of: 1) $NaNO_3$; 2) NH_4NO_3; 3) $AgNO_3$; 4) KNO_3.

The calculated results show that $\bar{s}_{(1)}$ is positive and in all cases exceeds $\bar{s}_{(2)}$ (e.g. Figs. 28 and 29 together with Refs. 43, 55, 61, and 68). Since $\bar{s}_{(1)}$ and $\bar{s}_{(2)}$ represent the excess entropies for the surfaces $\Gamma_1 = 0$ and $\Gamma_2 = 0$ respectively, the fact that $\bar{s}_{(1)} > \bar{s}_{(2)}$ implies that the dividing surface, for which $\Gamma_1 = 0$, is located below the surface corresponding to the condition $\Gamma_2 = 0$ (Fig. 1).

In all the systems examined the quantity $\bar{s}_{(2)}$ diminishes with increase in concentration, in some cases (e.g. nitrate solutions) becoming negative. Such a negative value (with $\bar{s}_{(1)} > 0$) does not necessarily mean that the molar entropy of the surface layer is smaller than the entropy of the solution. It may be due merely to variation in the position of the surface $\Gamma_2 = 0$ with concentration. Upward movement of this surface (increase in its coordinate z_S in Fig. 1) corresponds to a decrease in $\bar{s}_{(2)}$ down to negative values.

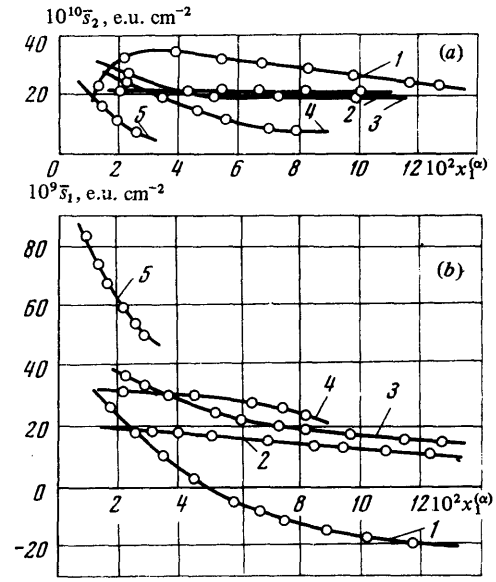


Figure 29. Excess entropies at 25°C in aqueous solutions of: 1) $NaNO_3$; 2) NaI; 3) NaBr; 4) NaCl; 5) Na_2SO_4.

Molar entropy of Surface layer

The molar entropy of a surface layer 5 Å thick was calculated by means of formulae (III—24, 32, and 35) for solutions of alkali-metal halides and ammonium chloride at 25° and 40°C (the calculation for aqueous sodium iodide was repeated with $\tau = 10$ Å); the results showed satisfactory agreement[43,45,55,61]. For the remaining systems Eqn. (III, 24) was used to calculate entropy at 25°C, since this method is the most accurate. Figs. 30–35 illustrate (*a*) the dependence of the entropy of the surface layer $s^{(\sigma)}$ on the composition of the layer and (*b*) the molar entropies of the solutions $s^{(\alpha)}$ as a function of solution composition.

The entropy of the solution is in all cases smaller than that of the coexisting surface layer: $s^{(\sigma)} > s^{(\alpha)}$. However, this difference is not entirely attributable to surface phenomena, since the solution shows a substantial difference in composition in bulk and at the surface. It is therefore of interest also to compare the entropy characteristics of solution and surface layer having the same salt concentration. Even in this case $s^{(\sigma)} > s^{(\alpha)}$. In aqueous lithium chloride with $x_1^{(\alpha)} = 0.045$, for example, $s^{(\alpha)} = 16.1$ e.u. mole^{-1}. With the same salt concentration in the surface layer, however, the entropy of the latter is $s^{(\sigma)} = 16.8$ e.u. mole^{-1}. In aqueous caesium chloride with $x_1^{(\alpha)} = 0.020$ we have similarly $s^{(\alpha)} = 17.5$ e.u. mole^{-1},

whereas with the same salt concentration in the surface layer $s^{(\sigma)} = 18.6$ e.u. mole^{-1}. Comparison of the entropies of surface layer and solution both containing 1 mole % of the salt gives for $s^{(\alpha)}$ and $s^{(\sigma)}$ the respective values 17.0 and 17.6 e.u. mole^{-1} (Figs. 30–34).

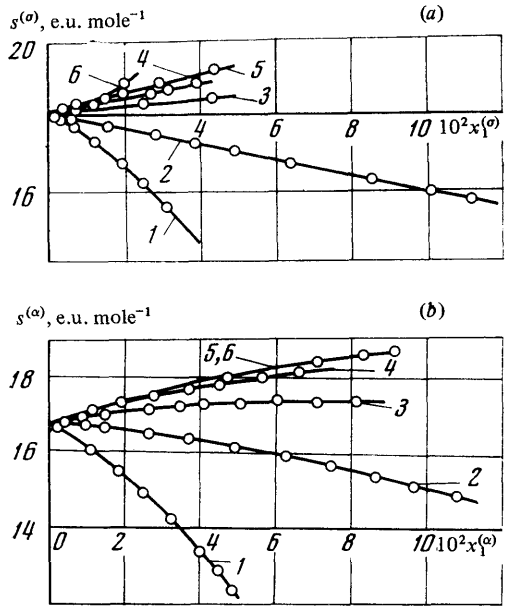


Figure 30. Composition dependence of molar entropy at 25°C in: *a*) surface layer 5 Å thick; *b*) solution for aqueous: 1) $MgCl_2$; 2) LiCl; 3) NaCl; 4) KCl; 5) RbCl; 6) CsCl.

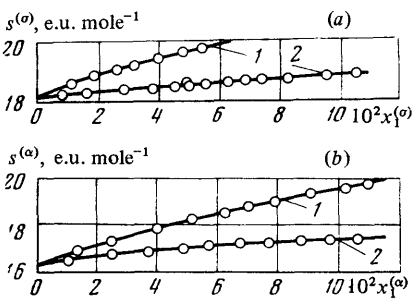


Figure 31. Composition dependence of molar entropy at 25°C in: *a*) surface layer 5 Å thick; *b*) solution for aqueous: 1) KI; 2) NaI.

The above examples show that the greater entropy of the surface layer is due not only to depletion with the salt but also to definite structural changes in the layer (with loosening of the surface structure on passing to the vapour). Nevertheless, a parallel variation in the entropies of solution and surface layer must be noted: increase in the salt concentration is accompanied by decreases in $s^{(\sigma)}$ and $s^{(\alpha)}$ in aqueous lithium chloride, magnesium chloride, and lithium nitrate, and by increases in the remaining cases. Such variation of entropy with concentration seems reasonable: increase in the content of the positively hydrated lithium and magnesium ions orders both the solution and the surface layer [85] with a consequent decrease in entropy; but accumulation of the large, weakly hydrated rubidium, caesium, and ammonium ions produces an increase in entropy.

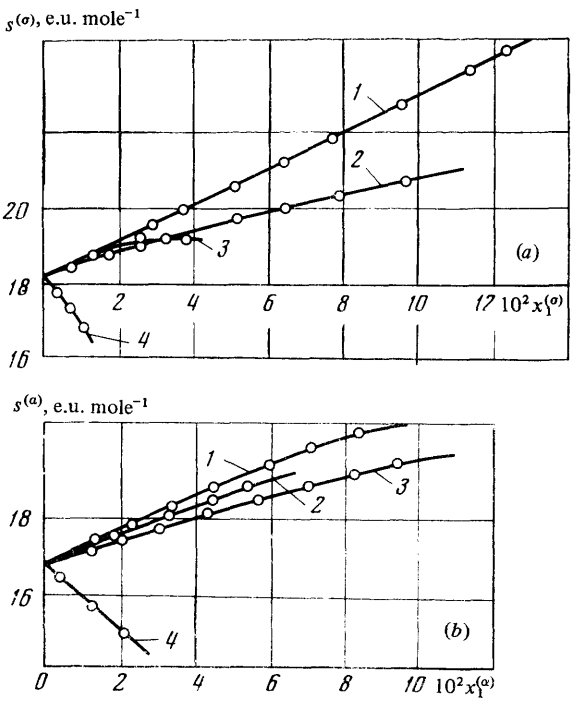


Figure 32. Composition dependence of molar entropy at 25°C in: *a*) surface layer 5 Å thick; *b*) solution for aqueous: 1) NH_4NO_3; 2) $NaNO_3$; 3) $AgNO_3$; 4) $LiNO_3$.

Comparison of the entropies of surface layers in different aqueous salt systems will reveal the effects of individual ions on the structure of the solution. Change in structure is due firstly to reorientation of water molecules by ion–dipole interaction. Among ions of the same valency the smallest will be the most effective. Secondly, the introduction of ions would tend to distort and disrupt the structure of water, and the more strongly the larger their size. Bonner [87] has concluded from ample experimental data that the combined effect of the above two factors would be minimal with sodium among singly charged ions. This conclusion is fully supported by the results obtained (Figs. 30 and 33). The entropy isotherm for the surface layer in aqueous sodium chloride is very nearly horizontal, which means little increase in entropy with the accumulation of salt in the surface layer: i.e. the introduction of sodium ions in fact causes minimal disruption of the structure on the surface layer.

Fig. 33(*a*) illustrates the molar entropies $s^{(\sigma)}$ as functions of composition of surface layer for aqueous solutions

of sodium chloride, bromide, iodide, and nitrate. At low salt concentrations the entropies are almost identical. But with increase in the salt content of the surface layer ($x_1^{(\sigma)} > 0.03$) the difference in behaviour among the halide ions affects the entropies of the surface layer (the chloride ion has less effect than have bromide and iodide ions on the structure of water [49]). Differences in the entropies of the solutions $s^{(\alpha)}$, however, are observed (Fig. 33*b*) at far higher concentrations ($x_1^{(\alpha)} > 0.08$). We reach the same conclusion from the molar entropies of solutions and surface layers in aqueous potassium chloride and iodide (Fig. 34).

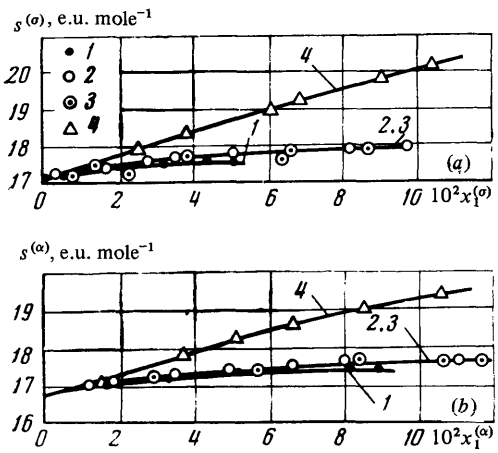


Figure 33. Composition dependence of molar entropy in: *a*) surface layer 5 Å thick; *b*) solution for aqueous: 1) NaCl; 2) NaBr; 3) NaI; 4) $NaNO_3$.

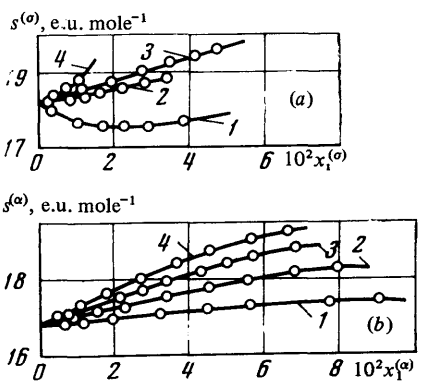


Figure 34. Composition dependence of molar entropy in: *a*) surface layer 5 Å thick; *b*) solution for aqueous: 1) KBr; 2) KCl; 3) KI; 4) KNO_3.

The entropy characteristics of solutions of rubidium and caesium chlorides (Fig. 35) are especially interesting. The isotherms of the molar entropies of the solutions coincide throughout the concentration range. Beyond the concentration $x_1^{(\sigma)} = 0.02$ the entropy of the surface layer increases more rapidly with the concentration of caesium chloride in the layer than with that of rubidium chloride.

The examples cited show that in several cases differences in behaviour among ions are more strongly developed in the surface layer than in the solution. The differences in the values of the corresponding thermodynamic functions of the systems therefore become appreciable sooner (at lower concentrations) in the surface layer than in the solution.

In conclusion we note that, among all the properties of surface layers, the entropy is most sensitive to variation in temperature, and increases appreciably on passing from 25° to 40°C. [43,45,55,61]

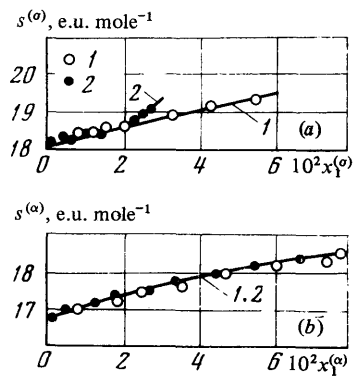


Figure 35. Composition dependence of molar entropy at 25°C in: *a*) surface layer 5 Å thick; *b*) solution for aqueous: 1) RbCl; 2) CsCl.

The Review has shown that thermodynamic calculations based on experimental data for surface tension and discussion of the thermodynamic characteristics obtained for surface layers are useful for studying the structure of aqueous salt systems and the effect of the nature of dissolved ions on the properties of solutions and surface layers.

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Laboratory of Surface Phenomena,
Faculty of Chemistry,
Leningrad State University