

294. *Adsorption at the Surface of Solutions. Part II.
The Effect of Lithium Chloride on the Surface of
Water-Alcohol Solutions.*

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IN a number of recent investigations on the effect of salts on the surface tension of solutions containing capillary-active substances (*e.g.*, Seith, *Z. physikal. Chem.*, 1925, **117**, 257; Freundlich and Schnell, *ibid.*, 1928, **133**, 151; Palitzsch, *ibid.*, 1930, **147**, 51) the adsorption of the active substance has been calculated by the use of Gibbs's equation $\Gamma_2 = -d\sigma/d\mu_2$ in the form in which it is applied to binary systems. It can easily be shown that even if $d\mu_2$ is given its correct value as modified by the presence of the salt, this equation is not in

general applicable. Suppose that, as in Part I (preceding paper), the non-homogeneous region in the vicinity of the interface is contained between two surfaces. If a dividing surface, sensibly parallel with the actual interface, is placed in an arbitrary position between the two surfaces and if $\Gamma_1, \Gamma_2, \Gamma_3$ are the surface excesses of the three components S_1, S_2, S_3 , for the given position, we have, according to Gibbs,

$$\Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 + \Gamma_3 d\mu_3 + d\sigma = 0 \quad . \quad . \quad (1)$$

Now the dividing surface may be placed so that one and, in general, only one of the quantities $\Gamma_1, \Gamma_2, \Gamma_3$ is zero. If it is placed so that Γ_3 is zero, we have

$$\Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 + d\sigma = 0 \quad . \quad . \quad . \quad (2)$$

but it is not possible from a single equation of this kind to evaluate Γ_1, Γ_2 . However, the composition of a given ternary solution can be varied in two distinct ways: (1) the quantity of S_3 is kept constant while the proportions of S_1 and S_2 are varied, (2) the quantities of S_1 and S_2 are kept constant and the amount of S_3 is varied. From two such variations of a given solution we may obtain the two equations

$$\left. \begin{aligned} \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 + d\sigma &= 0 \\ \Gamma_1 d\mu_1' + \Gamma_2 d\mu_2' + d\sigma' &= 0 \end{aligned} \right\} \quad . \quad . \quad . \quad (3)$$

where $d\sigma, d\sigma'$ are the changes of the surface tension for changes $d\mu_1, d\mu_2; d\mu_1', d\mu_2'$, of the chemical potentials in variations of the two types. We thus obtain the values

$$\Gamma_1 = (d\sigma/d\mu_2 - d\sigma'/d\mu_2') / (d\mu_1'/d\mu_2' - d\mu_1/d\mu_2) \quad . \quad (4)$$

$$\Gamma_2 = (d\sigma/d\mu_1 - d\sigma'/d\mu_1') / (d\mu_2'/d\mu_1' - d\mu_2/d\mu_1) \quad . \quad (5)$$

(5) reduces to the Gibbs equation for a binary solution when $d\mu_2'/d\mu_1' = 0$, and $d\sigma/d\mu_1' = 0$, *i.e.*, when the effect of a change in the amount of S_3 on μ_2 is negligible in comparison with its effect on μ_1 , and causes no change of the surface tension. The first condition is not usually satisfied in the case of solutions of organic substances containing salts and unless the second condition is also unsatisfied the investigation loses most of its interest.

In order to evaluate Γ_1 and Γ_2 according to these equations for a solution of a salt S_3 in a mixed solvent containing S_1 and S_2 , it is thus necessary to find the change of the surface tension for the two types of variation postulated above, and also the changes of the chemical potentials of S_1 and S_2 in the same variations. The values of the latter, per molecule, are given in terms of the changes of the partial vapour pressures for the corresponding variations by

$$d\mu_1 = kT \cdot d \log p_1, \quad d\mu_2 = kT \cdot d \log p_2, \text{ etc.}$$

In only one case, so far as we are aware, has the effect of a salt

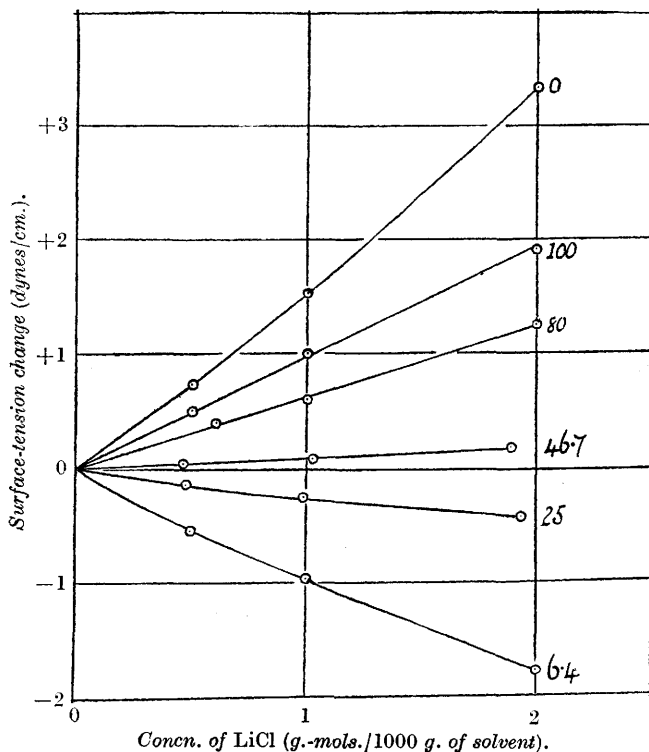
on the partial pressures of a mixed solvent been determined for a wide range of solutions, *viz.*, that of lithium chloride in water-alcohol mixtures (Shaw and Butler, *Proc. Roy. Soc.*, 1930, **129**, 519). It therefore seemed desirable to determine the surface tensions of these solutions and to evaluate Γ_1 and Γ_2 .

EXPERIMENTAL.

The surface tensions were determined by the capillary-rise method, using a U-tube having on the one side a fine capillary tube and on the other a wide

FIG. 1.

Surface-tension changes produced by lithium chloride in water-alcohol solutions.



(Numbers attached to curves represent the molar percentage of alcohol.)

tube of about 1 cm. radius. Two tubes were employed, one suitable for solutions with surface tensions between 20 and 40 dynes/cm., giving differences of level between 7.5 and 12 cm. over this range, and the other, used for aq. solutions only, giving a difference of level of 13.5 cm. for H_2O . Before the difference of level in the two limbs was read, the meniscus in the fine capillary was always brought to the same mark by varying the amount of liquid in the tube. The diameters of the capillaries at this point were not directly deter-

mined, but the tubes were calibrated, the first with EtOH and the second with H₂O ($\sigma = 21.93$ and 71.97 dynes/cm. respectively at 25°). The surface tensions were calculated by the equation $\sigma = h d g / 2(1/b_1 - 1/b_2)$, where h is the difference of level, d the density of the solution, g the force of gravity, and b_1, b_2 the radii of curvature of the liquid in the wide and the narrow tube. Knowing the approx. values of the surface tensions, as obtained by simple proportion, the relations between b_1, b_2 and the corresponding radii of the tubes r_1, r_2 were obtained from the table given by Sugden (J., 1921, **119**, 1483). The radii of the wide tubes as measured, and of the narrow tubes as determined in this way by the use of the calibration liquid, were: Tube I, $r_1 = 9.7$ mm., $r_2 = 0.07444$ mm.; tube II, $r_1 = 11.0$ mm., $r_2 = 0.1112$ mm. The differences of level were read by an accurate cathetometer reading to 0.05 mm., and the densities of the solutions were determined at 25° in a silica pycnometer.

The data and the calc. surface tensions are given in Table I.* Fig. 1 shows the change of surface tension caused by adding LiCl to the various H₂O-EtOH solutions. The effect is nearly linear with the concn. in all the solutions. It will be observed that, while the greatest increase of the surface tension is produced by the salt in pure H₂O, the greatest decrease is obtained in the solution containing the least proportion of EtOH, *viz.*, 6.4 mols. %. The effect of LiCl on less conc. solutions of EtOH would probably show features of interest, but since the v.p.'s of these solutions were not available, they were not included in the present investigation.

TABLE I.
Surface tensions of H₂O-EtOH-LiCl solutions.

Mol. fraction of EtOH.	Tube.	Concn. of LiCl (m).	$D_4^{25^\circ}$.	h (cm.).	σ , dynes/cm.	$\Delta\rho$.
1.00	I	0.000	0.7849	7.62	21.93	—
		0.500	0.8013	7.64	22.44	+0.51
		1.000	0.8164	7.66	22.93	+1.00
		1.995	0.8425	7.71	23.84	+1.91
0.80	I	0.000	0.8109	7.83	23.28	—
		0.608	0.8273	7.81	23.68	+0.40
		1.000	0.8373	7.78	23.88	+0.60
0.467	I	0.000	0.8652	8.12	25.78	—
		0.465	0.8761	8.03	25.82	+0.04
		1.025	0.8887	7.80	25.86	+0.08
0.25	I	0.000	0.9185	8.47	28.55	—
		0.474	0.9294	8.33	28.41	-0.14
		0.985	0.9405	8.20	28.30	-0.25
0.064	I	0.000	0.9600	7.98	28.12	-0.43
		0.000	0.9735	11.81	42.19	—
		0.500	0.9852	11.52	41.65	-0.54
0.00	II	1.000	0.9960	11.28	41.23	-0.96
		2.000	1.0180	10.82	40.41	-1.78
		0.000	0.9970	13.48	71.97	—
0.00	II	0.500	1.0082	13.47	72.71	+0.74
		1.000	1.0191	13.47	73.50	+1.53
		2.000	1.0411	13.51	75.31	+3.34

* The salt concns. are molalities—*i.e.*, the number of g.-mols. of the salt in 1000 g. of the solvent.

Calculation of Adsorptions.

The values of Γ_1 , Γ_2 were calculated by equations (4) and (5); for solutions containing 0.0, 0.5, and 1.0*m*-lithium chloride the partial pressures given by Shaw and Butler (*loc. cit.*) were used, and for solutions containing 2.0*m*-lithium chloride values obtained by graphical interpolation from those determined for 1.0*m* and 4.0*m* were used.

The following approximations have been made in the calculations. (1) The relative changes of the chemical potentials of water and alcohol in a binary solution for a variation of the composition at constant temperature and pressure are given by $N_1 \cdot d\mu_1 + N_2 \cdot d\mu_2 = 0$, or $d\mu_1/d\mu_2 = -N_2/N_1$ where N_2 and N_1 are the molar fractions of the two substances in the given solution. The effect of a small proportion of a third component on this ratio is comparatively small and it is assumed that $d\mu_1/d\mu_2$ has this value in all the solutions. (2) Since the slopes of the curves $\sigma - \log p_1$, $\sigma - \log p_2$, for constant salt concentration are only slightly affected by the presence of the salt, $d\sigma/d\mu_2$ has been given the value $-\Gamma_2^0$, and $d\sigma/d\mu_1$ the value $-\Gamma_1^0 = N_1/N_2 \cdot \Gamma_2^0$, where Γ_2^0 is the value of the adsorption of alcohol in the binary water-alcohol solution of the given composition, as determined in Part I (preceding paper). Under these conditions (4) and (5) become

$$\Gamma_1 = (-\Gamma_2^0 - d\sigma'/kT \cdot d \log p_2') / (N_2/N_1 + d \log p_1' / d \log p_2') \quad (6)$$

$$\Gamma_2 = (N_1 \Gamma_2^0 / N_2 - d\sigma'/kT \cdot d \log p_1') / (N_1/N_2 + d \log p_2' / d \log p_1') \quad (7)$$

where $d\rho'$ is the change of surface tension for a variation of the salt content which gives rise to changes $d \log p_1'$ and $d \log p_2'$ in the partial pressures of alcohol and water. Since sufficient points are not available to determine accurately the slopes of the curves near any given solution, these variations have been evaluated for the intervals 0—0.5*m*, 0.5—1.0*m*, 1.0—2.0*m* LiCl. The results of the calculations are given in Table II.

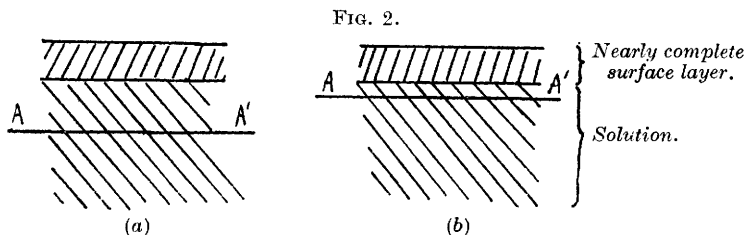
TABLE II.

Adsorption from solutions of lithium chloride in aqueous alcohol.

EtOH, mols. %.	Interval, 0.0—0.5 <i>m</i> -LiCl.		Interval, 0.5—1.0 <i>m</i> -LiCl.		Interval, 1.0—2.0 <i>m</i> -LiCl.	
	Γ_1 .	Γ_2 .	Γ_1 .	Γ_2 .	Γ_1 .	Γ_2 .
100	—	41	—	18	—	19
80	4.6	34	2.2	33	-0.6	18
50	15	40	5.0	40	-0.8	31
25	53	57	21	52	7	44
6.4	103	42	47	41	27	39
0.0	133	—	67	—	41	—

Discussion.

The accuracy of the values obtained by combining such a variety of data over somewhat wide intervals is necessarily rather low and errors of the order of 10—20% would not be surprising. Nevertheless, some definite conclusions as to the structure of the surface can be drawn. It will be seen that both in water and in alcohol the adsorption diminishes as the concentration of the salt is increased, in agreement with the calculations of Goard (J., 1925, 127, 2451) of the adsorption of water from aqueous salt solutions. The adsorption of alcohol over the lower range of salt concentrations is close to the maximum adsorption of binary water-alcohol solutions, and corresponds with an approximately unimolecular layer of alcohol molecules. The value in water for the same interval (133×10^{13} mols./cm.²) may also be reasonably attributed to a single layer of water molecules, for the volume occupied by a single molecule in



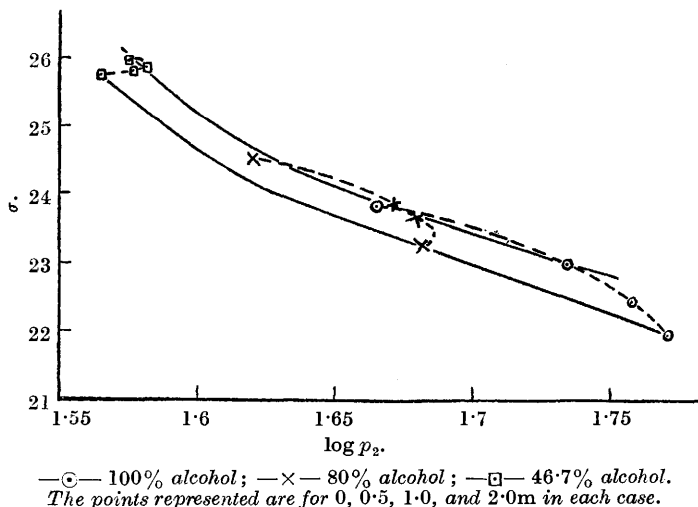
liquid water at 25° is $v = 29.8 \times 10^{-24}$ cm.³, and if we take $v^{\frac{2}{3}}$ as the area per molecule we find 102×10^{13} for the number of mols. per cm.². At the higher salt concentrations in both cases the average distance of the ions from the surface is less. In alcohol this might be accounted for by a change in the orientation of the surface molecules, but it is more difficult to account for the effect of water in this way.

In the mixed solutions at the smaller salt concentrations the adsorption of alcohol remains effectively constant for all solutions containing from 6 to 100 mols. % of alcohol. In the 6.4 % alcoholic solution there are adsorbed, not only an approximately unimolecular layer of alcohol, but also nearly as many water molecules as from water itself. We may suppose that at the surface of this solution, as in Fig. 2a, there is an approximately complete layer of alcohol molecules and that the average limit of approach of the ions to the surface is nearly as far below this layer as it is from the surface of solutions in water. This will be the case if the ions are hydrated by a single sheath of water molecules which prevent them from coming into closer contact with the surface layer. The total adsorption of alcohol measured is not only that in the surface layer but also that in the solution above the line AA'. The latter,

however, is only a small fraction of the whole for a dilute solution.

As the alcohol content of the solutions increases, the adsorption of water steadily diminishes. This cannot be entirely due, if the position of the line AA' remains unchanged, to the decreased water content of the solution, for in that case the decrease in Γ_1 would be accompanied by a large increase of Γ_2 . But since the water sheaths of the ions, which we have supposed to keep the ions below the adsorbed layer, are replaced to an increasing extent by alcohol molecules as the concentration of the latter grows, and since the composition of the bulk of the solution approximates more closely to that of the surface layer, it is natural that the line AA' should move

FIG. 3.



upwards (Fig. 2*b*) until in pure alcohol it coincides with the lower limit of a unimolecular layer.

Finally, the adsorptions diminish in the mixed solutions, as they do in the pure solvents, with increase of salt concentration, and it must be supposed that the ions penetrate the surface layer to an increasing extent in such cases.

There is one other point of interest. If the values of σ for solutions containing a large proportion of alcohol are plotted against $\log p_2$, the points for the higher salt concentrations tend to fall on the same curve (Fig. 3). The reason for this can be seen by considering equation (1). If we make $\Gamma_3 = 0$ as before, and choose variations such that $d\mu_2 = 0$, we have $\Gamma_1 = -(d\sigma/d\mu_1)_{\mu_2}$. The condition $d\mu_2 = 0$ is satisfied for points lying on any vertical line in Fig. 3. It is

evident that if we vary the salt concentration and the composition of the solvent simultaneously in such a way that μ_2 remains constant, at the higher salt concentrations the variation of σ is very small. Therefore for these solutions Γ_1 is also small. The behaviour shown in Fig. 3 is thus in accordance with the values of Γ_1 already obtained for solutions containing a large proportion of alcohol.

Summary.

1. A method is given of applying the equations of Gibbs to determine the adsorption at the surface of ternary solutions.

2. The surface tensions of water-alcohol-lithium chloride solutions have been determined at 25° by the capillary-rise method, and the adsorptions of water and alcohol with respect to lithium chloride have been evaluated.

3. It is shown that, at small concentrations of lithium chloride, there is present at the surface of solutions containing more than 6 mols. % of alcohol an approximately complete unimolecular layer of alcohol. The ions are separated from the under surface of this layer by a layer of solution, the thickness of which decreases as the alcoholic content increases and which disappears in pure alcoholic solutions. This behaviour is attributed to the hydration of the ions. At higher lithium chloride concentrations the ions penetrate the surface to an increasing extent.

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