368. *The Effects of Sodium Chloride and Aniline Hydrochloride upon the Surface Tensions and Partial Vapour Pressures of Aqueous Aniline Solutions.*

By James C. Speakman.

Worley (J., 1914, **105**, 210) noted that addition of sodium chloride to an aqueous aniline solution caused a decrease of surface tension, although its addition to water was well known to cause an increase, and he explained this qualitatively by attributing the lowered surface tension to an increase in the adsorption of aniline in the surface as a result of its being salted out. It was decided to subject this interpretation to quantitative examination, and generally, to determine how far the surface behaviour of aqueous aniline solutions, as previously observed (J., 1935, 776), was affected by addition of salts. The surface tensions and the partial vapour pressures of aniline have therefore been measured for aqueous solutions containing (*a*) sodium chloride (which has a salting-out effect), (*b*) aniline hydrochloride (which has an opposite, " salting-in " effect), and (*c*) both these solutes together. The bearing of the data upon the salting-out effect and related phenomena has also been considered.

Experimental.

The methods used for determining surface tensions and partial vapour pressures were as already described (J., 1933, 1449; 1935, 777). All measurements were made at 20·0°.

Seith (*Z. physikal. Chem.*, 1925, **117**, 265) made some surface-tension measurements, by means of the vibrating-jet method, on solutions of aniline containing sodium chloride. His results do not cover a wide concentration range, but they are somewhat lower than those now found. The discrepancy increases with the surface adsorption, and it is conceivable that his method, which involves surfaces of rapidly fluctuating area, may give rise to some error when applied to solutions showing strong adsorption.

Materials and Solutions.—The aniline was purified as before (*loc. cit.*). The sodium chloride was of A.R. quality and was dried. Aniline hydrochloride was prepared immediately before use by dissolving the base in the acid (" Special for Analysis "). Boiled-out distilled water was always used. Solutions were prepared by weighing out the aniline, adding an appropriate volume of 4*M*-sodium chloride and/or 2*M*-hydrochloric acid, and diluting them to a definite volume. As they became somewhat discoloured during several days' standing, they were used while fresh. All concentrations are given as molarities; the densities of the solutions are, however, known with sufficient accuracy (see below) to enable these to be converted into other units. Observations have been made on solutions of aniline, covering the whole concentration range up to saturation, in the following six liquids : water (*loc. cit.* 1935), 1·00*M*- and 2·00*M*-sodium chloride, 0·50*M*- and 1·00*M*-aniline hydrochloride, 1·00*M*-sodium chloride + 1·00*M*-aniline hydrochloride.

A special procedure was adopted for preparing saturated solutions of aniline. The solubility being approximately known, a solution of 4—5% lower concentration was prepared in the usual way; a small excess of aniline was then added, and the liquid warmed, shaken, and cooled to 20·0° before use. Saturated solutions were used only for determinations of vapour pressure, and not for those of surface tension, the latter being deduced by a short extrapolation (cf. *loc. cit.*, 1935).

Densities.—The densities of some of the solutions at 20·0° were measured with a pyknometer.

and from the results those of others were inferred. Table I gives the densities of the salt solutions containing no aniline; as the aniline concentration is increased, the density also increases slightly and linearly according to the equation $\rho_c = \rho_0 + 0{\cdot}0045c$, where ρ_c is the density at aniline concentration c. (The accuracy is ± 0·05%.)

TABLE I.

Densities of salt solutions at 20·0°.

Salt	NaCl	NaCl	NH_2Ph,HCl	NH_2Ph,HCl	$NaCl+NH_2Ph,HCl$
Concn., *M*	1·00	2·00	0·50	1·00	each 1·00
ρ_0	1·0380	1·0757	1·0119	1·0251	1·0636

Solubilities.—The solubilities of aniline in the salt solutions were determined by keeping a saturated solution (prepared as described above) in a stoppered flask immersed in the thermostat for several days until clear. A portion of the aqueous phase was then drawn off in a warmed pipette and diluted, and aliquot portions were analysed by the bromate method (*loc. cit.*, 1935). The results, averages of two or three determinations, are in Table II.

FIG. 1.

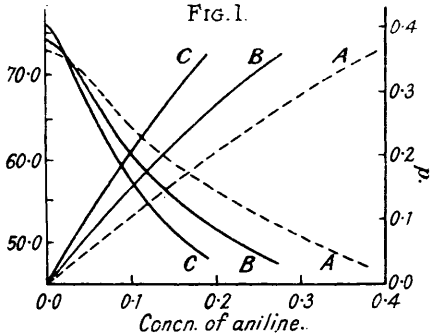


FIG. 2.

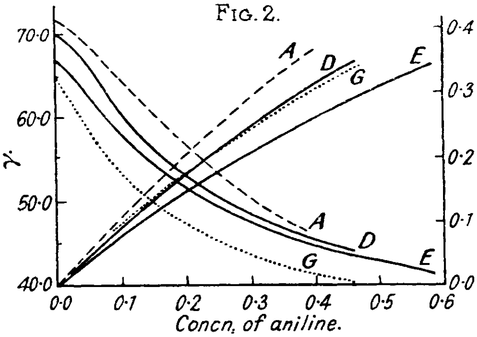


FIG. 3.

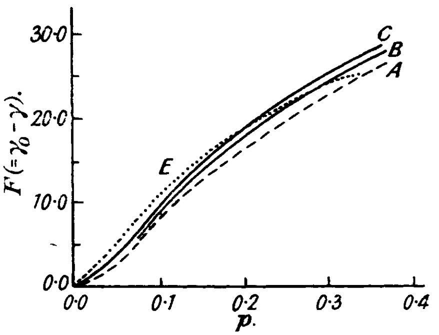
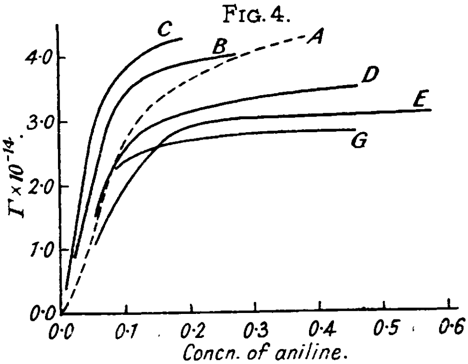


FIG. 4.



Effect of sodium chloride (Fig. 1) *and of aniline hydrochloride* (Fig. 2) *on the surface tensions* (γ) *and partial pressures of aniline* (p) *of aqueous aniline solutions. Effects of these salts on the relationship between surface-tension lowering* (F) *and partial pressure of aniline* (p) (Fig. 3). *Effects of salts on the relationship between surface adsorption of aniline* (Γ) *and concentration of aniline* (Fig. 4).

Solvents: *A*, H_2O; *B*, 1·00*M*-NaCl; *C*, 2·00*M*-NaCl; *D*, 0·50*M*-NH_2Ph,HCl; *E*, 1·00*M*-NH_2Ph,HCl; *G*, 1·00*M*-NaCl + 1·00*M*-NH_2Ph,HCl.

Results.—Individual experimental results are in Table II. Average values are represented by the continuous curves in Figs. 1 and 2. The broken curves give, for comparison, the results with aqueous solutions taken from the earlier paper. γ represents surface tension (in dynes/cm.), and p the partial vapour pressure of aniline (in mm.).

Considering, first, the action of sodium chloride (Fig. 1), it is clear that the truth of the statement that addition of this salt lowers the surface tension of an aniline solution depends upon the concentration of the latter, since the surface tension–concentration curves intersect. Worley's explanation of the action of sodium chloride is simply tested by plotting the surface-tension lowering, $\gamma_0 - \gamma = F$, against the partial pressure of aniline for each series; this elim-

TABLE II.

Surface Tensions and Partial Vapour Pressures of Solutions of Aniline.

(a) *In sodium chloride solutions.*

1·00*M*-NaCl.			2·00*M*-NaCl.		
Concn. of NH$_2$Ph.	γ.	p.	Concn. of NH$_2$Ph.	γ.	p.
0·000	74·4	0·000	0·000	76·2, 76·3	—
0·022	72·7, 72·7	—	0·055	65·5, 65·7	0·114
0·055	68·0, 67·9	0·084	0·074	61·7	0·148, 0·151
0·075	64·4, 64·2	0·115, 0·114	0·116	55·7, 55·7	0·230
0·111	59·5	0·163, 0·159	0·158	51·3	0·300, 0·300
0·179	53·1, 53·3	0·260	0·175	49·7	—
0·226	50·0, 50·3	0·306, 0·312	0·183	49·4	0·343
			0·185	49·0, 48·9, 48·8	0·344
0·250	48·7, 48·9	0·332, 0·332	0·191	48·4	0·354
0·275	—	0·364, 0·360	0·196	—	0·360, 0·356, 0·362
(satd.)			(satd.)		

(b) *In aniline hydrochloride solution.*

0·50*M*-NH$_2$Ph,HCl.			1·00*M*-NH$_2$Ph,HCl.		
0·000	69·6, 69·6, 69·7	—	0·000	67·1, 67·1	—
0·041	67·3	—	0·060	61·7	—
0·105	59·3, 59·7	0·099	0·121	56·6, 56·7	0·098, 0·102
0·162	55·2, 55·2	0·149, 0·147	0·218	50·5	—
0·257	50·1	0·218	0·271	48·3, 48·3	0·193, 0·193
0·290	—	0·248	0·317	—	0·223
0·356	46·5	0·285, 0·290	0·361	45·5, 45·8	—
0·418	44·6	0·320, 0·319	0·431	44·1	0·276
0·425	44·7, 44·4	—	0·478	43·3	0·293
0·465	—	0·347, 0·352	0·528	42·4	—
(satd.)			0·548	42·1, 42·3	—
			0·575	41·6, 41·6	—
			0·590	—	0·338, 0·345
			(satd.)		

(c) *In* 1·00M-*sodium chloride* + 1·00M-*aniline hydrochloride solution.*

0·000	65·0, 65·2, 65·0	—	0·260	44·8	0·218
0·028	61·9, 61·7	—	0·343	42·5 42·5	0·272
0·055	58·2, 57·9	—	0·395	41·2, 41·5	0·288 (?)
0·083	54·8	0·083, 0·082	0·418	41·1, 41·0	0·313
			0·434	40·7, 40·6	—
0·094	53·7, 53·9	—	0·436	40·4	0·325, 0·321
			0·465	—	0·335, 0·339
0·127	51·5	0·123, 0·121	(satd.)		
0·201	47·1, 47·3	0·178, 0·179			

inates the initial effect of the salt in raising the surface tension of water. The result is shown in Fig. 3. The curves for water and for sodium chloride solutions (*A*, *B*, *C*) have similar shapes but diverge considerably at higher concentrations. The explanation cannot therefore apply exactly, and a reason for the divergence is suggested later.

To a first approximation, aniline hydrochloride, which has a salting-in effect upon the base, acts in a symmetrically opposite sense to sodium chloride : it extends the surface-tension and vapour-pressure curves over a larger concentration range (Fig. 2). There are important differences, however. The surface-tension curves *A*, *D*, and *E* do not intersect, so this salt always lowers the surface tension of aniline solutions. The vapour-pressure curves differ in that the maximum value for saturated solutions of aniline is not constant, as with sodium chloride, but diminishes with increasing hydrochloride concentration (see p. 1665). Furthermore, when the *F*–*p* curve is compared with that for water, there is a greater difference than with sodium chloride. In Fig. 3, for simplicity, only the curve for 1·00*M*-hydrochloride (*E*) is shown.

Salting-out Effects.—Data such as those given in Table IIa have been used in two different ways for calculating the hydration numbers of salts. Both assume that the water molecules attached to the ions are prevented from filling their rôle as solvent : one method then directly calculates the decrease in solvent power revealed in the salting-out effect; the other infers the decrease in solvent power by comparing the changes in surface tension produced when a surface-active solute is added first to water and secondly to the salt solution. It has been considered (*e.g.*, Freundlich and Schnell, *Z. physikal. Chem.*, 1928, **133**, 151) that the two methods give concordant results. Reference to Fig. **3** shows that for sodium chloride the relationship between F and p varies slightly, but definitely, with salt concentration; it therefore follows that the two methods will give similar, but cannot give identical, hydration numbers.

The large salting-in effect of aniline hydrochloride is probably specific, for such an effect is commonly noticed when an organic acid or base is dissolved in a solution of its salt (see, *e.g.*, Randall and Failey, *Chem. Rev.*, 1927, **4**, 300; Bennett, Brooks, and Glasstone, J., 1935, 1823). The effect suggests that there is some attraction between the aniline and its hydrochloride (presumably the anilinium ion). Evidence for an attraction is furnished by the supposed existence of compounds such as $(NH_2Ph)_2,HCl$ (Thonus, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 553; Mandal, *Ber.*, 1920, **53**, 2216). It is possible that such compounds arise mesomerically (by the operation of resonance forces), somewhat as follows :

$$C_6H_5{\cdot}\overset{\oplus}{N}H_2{-}H \quad NH_2{\cdot}C_6H_5 \rightleftarrows C_6H_5{\cdot}NH_2 \quad H{-}\overset{\oplus}{N}H_2{\cdot}C_6H_5$$

and if this is true, a tendency for aniline molecules and anilinium ions to attract one another in solution may arise similarly.

The fact that the maximum pressure of aniline at saturation was diminished by the presence of hydrochloride (*e.g.*, from 0·360 to 0·342 mm. by 1·00M-salt) suggested that this salt dissolved in the non-aqueous phase. Quantitative analysis of conjugate phases confirmed this, and enabled the distribution ratio to be determined. The results are shown in Table III. The distribution ratio varies with, and shows no simple dependence upon, concentration. The results agree satisfactorily with those of Sidgwick, Pickford, and Wilsdon (J., 1911, **99**, 1216), obtained in a different manner.

TABLE III.

Distribution of aniline hydrochloride between the aqueous and the aniline phase at 20·0°.

Aqueous phase.		Aniline phase.		Distribution ratio (water/aniline).
Concn. of free NH_2Ph.	Concn. of NH_2Ph,HCl.	Concn. of NH_2Ph,HCl.	*d.*	
0·461	0·458	0·123	1·026	3·72
0·532	0·804	0·451	1·035	1·78
0·555	0·879	0·558	1·037	1·58

The results for the series of solutions containing both sodium chloride and aniline hydrochloride are represented by curves G in Fig. 2. The F–p curve (not shown in Fig. **3**) closely resembles that for 1·00M-hydrochloride alone. In the presence of 1·00M-sodium chloride and 1·00M-aniline hydrochloride the partial pressure of aniline above the saturated solution (0·337 mm.) is lower than it is in the presence of the hydrochloride alone (0·342 mm.). This is evidence that sodium chloride increases the concentration of hydrochloride in the non-aqueous phase, and therefore exerts a salting-out effect upon it (cf. p. 1668).

Hydrolysis of Aniline Hydrochloride.—It might be thought that the aniline liberated by hydrolysis of the hydrochloride would affect the surface-tension measurements. However, the dissociation constant of the base being $4{\cdot}0 \times 10^{-10}$, the concentration of free aniline in a M-solution of the salt is only about 0·005M; this would cause a barely perceptible change in surface tension; for solutions containing added aniline the change would be imperceptible. In any case this effect can be neglected without prejudice to the thermodynamic argument.

Surface Adsorptions.—In order to interpret the data now obtained, it is necessary to evaluate the surface adsorptions of aniline. This was done for the aqueous solutions studied earlier (*loc. cit.*) by use of the Gibbs adsorption equation in the simple form applicable to two-component systems, *viz.*,

$$\Gamma = -\,(1/kT) \,.\, d\gamma/d \log_e p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(k is the Boltzmann constant, and Γ the adsorption expressed as molecules per sq. cm.; the vapour pressure of aniline, p, is taken as proportional to its activity.) The systems considered now, however, consist of at least three components, so the simple equation is not valid. The rigid treatment of three-component systems involves more complicated equations (*e.g.*, Butler and Lees, J., 1932, 2097; Belton, *Trans. Faraday Soc.*, 1935, **31**, 1413, 1648), whose usefulness is restricted by lack of data.

Nevertheless, it may be shown that, for the systems studied here, the use of equation (1) involves no considerable error. For three-component systems the general form of the Gibbs isotherm can be written

$$d\gamma = -\,\Gamma_2 d\mu_2 - \Gamma_3 d\mu_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where μ_2 and μ_3 are the chemical potentials of two of the components (aniline and salt respectively in this case), and Γ_2 and Γ_3 their adsorptions measured with respect to the third component (water). Again, taking the partial vapour pressure of aniline as proportional to its activity, and letting the concentration of the salt be c and its mean ion activity coefficient f, we have

$$d\gamma = -\Gamma_2 kT \,.\, d\log_e p - 2\Gamma_3 kT \,.\, d\log_e fc.$$

In each series c is constant, so that

$$-d\gamma = \Gamma_2 kT \,.\, d\log_e p + 2\Gamma_3 kT \,.\, d\log_e f, \text{ and}$$

$$-\frac{1}{kT}\left(\frac{\partial\gamma}{\partial\log_e p}\right)_c = \Gamma_2 + 2\Gamma_3\left(\frac{\partial\log_e f}{\partial\log_e p}\right)_c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

To justify the use of equation (1) it is only necessary to show that the last term in (3) is negligible here: Γ_3 will certainly not be large for sodium chloride, and in all series $(\partial\log_e f/\partial\log_e p)_c$ will almost certainly be very small. In effect, this term represents the change in the activity coefficient of the salt brought about by the addition of aniline. Since the aniline is always at very low concentration (the mol.-fraction not exceeding 0·01 and generally being much less), the change should be negligible. Several investigations of the activity of an electrolyte in a mixed solvent have shown that the activity coefficient–mol.-fraction curve tends to become parallel with the composition axis at low concentrations of the organic liquid (*e.g.*, Scatchard, *J. Amer. Chem. Soc.*, 1927, **49**, 217; Åkerlöf, *ibid.*, 1930, **52**, 2359; but cf. Hamilton and Butler, *Proc. Roy. Soc.*, 1932, *A*, **138**, 450). In any case it seems unlikely that aniline molecules at such a low bulk concentration would have any considerable specific interaction with sodium or chloride ions; with anilinium ions some slight interaction is admittedly probable. The use of equation (1) is therefore tolerably justified, especially for the solutions containing sodium chloride.

On the basis of this equation, adsorptions of aniline have been worked out, either graphically by plotting surface tension against log p and taking tangents, or by an equivalent calculation (Schofield and Rideal, *Proc. Roy. Soc.*, 1925, *A*, **109**, 66, 71). The resulting values are very sensitive to slight irregularities in the data; they were therefore plotted against aniline concentrations, and a smooth curve drawn between the points; curves so obtained are reproduced in Fig. 4, and adsorptions taken from these curves are given in Table IV, the corresponding values for the series of solutions containing both salts being included (section c). Since the last system is one of four components, use of equation (1) for calculating adsorptions is less justifiable, but the results will probably be of the correct order of magnitude.

TABLE IV.

Surface Adsorptions (interpolated at Round Concentrations) for Solutions of Aniline.

(a) *In sodium chloride solution.*

Concn. of NH_2Ph.	1·00*M*-NaCl. $\Gamma \times 10^{-14}$.	2·00*M*-NaCl. $\Gamma \times 10^{-14}$.
0·000	0·0	0·0
0·015	0·4	0·7
0·030	1·0	1·7
0·050	2·0	2·8
0·075	3·1	3·5
0·100	3·4$_5$	3·8$_5$
0·125	3·6$_5$	4·0$_0$
0·150	3·7$_5$	4·1$_5$
0·175	—	4·2$_0$
0·196 (satd.)	—	4·2$_4$
0·200	3·9$_0$	—
0·230	3·9$_5$	—
0·275 (satd.)	4·0$_0$	—

(b) *In aniline hydrochloride solution.*

Concn. of NH_2Ph.	0·50*M*-NH_2Ph,HCl. $\Gamma \times 10^{-14}$.	1·00*M*-NH_2Ph,HCl. $\Gamma \times 10^{-14}$.
0·000	0·0	0·0
0·030	0·7	0·7
0·060	1·8	1·2
0·100	2·6	2·1$_5$
0·150	2·9$_5$	2·7$_0$
0·200	3·1$_0$	2·9$_0$
0·250	3·2$_5$	—
0·275	—	3·0$_0$
0·325	3·3$_5$	—
0·350	—	3·0$_5$
0·400	3·4$_5$	—
0·425	—	3·0$_5$
0·465 (satd.)	3·4$_7$	—
0·500	—	3·1$_0$
0·585 (satd.)	—	3·1$_0$

(c) *In* 1·00*M-sodium chloride* + 1·00*M-aniline hydrochloride solution.*

Concn. of NH_2Ph	0·000	0·030	0·060	0·100	0·150	0·200	0·250	0·300	0·390	0·465 (satd.)
$\Gamma \times 10^{-14}$………	0·0	0·8	1·8$_5$	2·4$_0$	2·6$_5$	2·7$_0$	2·7$_5$	2·7$_5$	2·8$_0$	2·8$_2$

DISCUSSION.

In the earlier work it was shown that, as the bulk concentration rises towards saturation, a complete unimolecular film of aniline molecules ($4{\cdot}2_7 \times 10^{14}$/cm.^{2}) is gradually built up at the surface. Considering, first, the effect of sodium chloride, it is seen (Fig. 4; *A, B, C*) that, although the limiting maximum adsorption is not notably affected by the presence of the salt, the concentration at which this limiting adsorption is approached is greatly lowered as a result of the salting-out effect. This point has sometimes been overlooked.

Secondly, with regard to the divergence between the *F–p* curves for the aqueous and the sodium chloride series (Fig. 3; *A, B, C*), the values of *F* for the latter show a positive divergence, *i.e.*, the surface tensions are *lower* than would correspond to an exact agreement with Worley's interpretation. This might be expected if the salt, which is negatively adsorbed in pure aqueous solution, were less (negatively) adsorbed when there is a film of orientated aniline molecules upon the surface. It can be shown that this is not unlikely. The negative adsorption of a salt such as sodium chloride is probably due chiefly to the hydration of its ions, which cannot reach the surface without expenditure of the energy needed to strip them of their hydrating molecules. Moreover, in so far as cations are generally more hydrated than anions—and in particular, sodium more than chloride (see Glasstone, "Electrochemistry of Solutions," p. 46)—the latter will have less difficulty in approaching the surface. At the surface of a sodium chloride solution there will thus tend to be a potential difference, which will be negative compared with that at a pure water surface. Frumkin's measurements (*Z. physikal. Chem.*, 1924, **109**, 38) show that the potential is — 4 millivolts for the 2·00*M*-solution. At the surface of an aniline solution, on the other hand, Frumkin, Donde, and Kulvarskaja (*ibid.*, 1926, **123**, 321) found a strongly positive potential—about 140 millivolts for surfaces with a complete film of adsorbed molecules. This potential is no doubt due to interaction between the orientated aniline molecules and the underlying water surface, and, being in an opposite sense to that for the pure salt solution, will oppose the state of affairs existing there and tend to decrease the negative adsorption of the salt. The matter may be considered from a different aspect. A sodium ion, in order to reach the surface of its aqueous solution, must become partly dehydrated; but, when there is a film of aniline molecules on the surface, it may penetrate to the film, *i.e.*, to the surface of the region occupied by water molecules, by exchanging some of its water of hydration for the aniline molecules already suitably orientated, a process which would certainly require the expenditure of far less energy. The same factor may operate to a less extent with the chloride ion also. Since in the present work all adsorptions are calculated with respect to the *water*, this behaviour would appear as a decrease in the negative adsorption of sodium chloride.

That such a decrease actually occurs may be demonstrated from the results. If μ_2 is kept constant, equation (2) may be rewritten

$$-(\partial\gamma/\partial\mu_3)_{\mu_2} = \Gamma_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

It is valid in the present instance to replace the condition of constant chemical potential by one of constant partial vapour pressure. If, as before, the activity coefficient of the salt is assumed to be unaffected by the presence of the small concentration of aniline, equation (4) may be used in the form

$$-(1/2kT)(\partial\gamma/\partial \log_e fc)_p = \Gamma_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Therefore, by plotting surface tension against the logarithm of the activity of the salt (under conditions of constant partial pressure of aniline), an estimate of the salt adsorption can be made. The values so calculated are shown in Table V; *e.g.*, with the 2·00*M*-salt solution, the adsorption changes from — $0{\cdot}4 \times 10^{14}$ for the solution containing no aniline to about — $0{\cdot}15 \times 10^{14}$ for a sufficiently concentrated aniline solution to have an almost complete surface film. A similar conclusion is reached for the 1·00*M*-solution.

Regarding the data for solutions containing aniline hydrochloride, it is seen that the adsorption of aniline (Fig. 4, curves *D, E*; Table IVb) shows an important difference here.

TABLE V.

The Effect of Aniline on the Estimated Surface Adsorptions of Salts.

Salt solution.	$\Gamma \times 10^{-14}$. In absence of aniline.	$\Gamma \times 10^{-14}$. In presence of adsorbed aniline.
1·00*M*-NaCl	−0·3	−0·05
2·00*M*-NaCl	−0·4	−0·15
0·50*M*-NH_2Ph,HCl	0·4	0·5
1·00*M*-NH_2Ph,HCl	0·8	$0{\cdot}7_5$
1·00*M*-NaCl + 1·00*M*-NH_2Ph,HCl	(1·2)	—

Instead of reaching a maximum value of about $4{\cdot}2 \times 10^{14}$, as for aqueous and sodium chloride solutions, the maxima are smaller, $\Gamma \times 10^{-14}$ being 3·5 and 3·1 respectively for 0·50*M*- and 1·00*M*-hydrochloride solutions. This is because aniline hydrochloride, unlike sodium chloride, is itself positively adsorbed at the surface. The anilinium ion, which is but little if at all hydrated (Remy and Reisener, *Z. physikal. Chem.*, 1927, **126**, 161; Remy, *Trans. Faraday Soc.*, 1927, **23**, 386), will have no cause for avoiding the surface; and, being largely hydrocarbon, it will tend to go into the surface and become orientated there. Estimates of the amounts adsorbed can be reached by following the same procedure as for sodium chloride. In the absence of data regarding the activity coefficients of aniline salts, those of Scatchard and Prentiss (*J. Amer. Chem. Soc.*, 1932, **54**, 2702) for ammonium chloride were taken as an approximation. The adsorptions found cannot be considered accurate, but will probably be of the right order (Table V). Since it is the anilinium ions that are actually in the surface, and since these are larger than chloride ions, the adsorptions can be considered as referring simply to the cations. To find the total adsorption, the values for the anilinium ions should be added to those for the aniline molecules. When this is done, the number of molecules + ions found ($3{\cdot}9$—$4{\cdot}0 \times 10^{14}$ per sq. cm.) differs little from that found for the other solutions discussed ($4{\cdot}0$—$4{\cdot}3 \times 10^{14}$). The slight difference, if significant, may indicate that anilinium ions occupy rather more space than do aniline molecules; in view of the like charges on the ions, this is not improbable.

Finally, the adsorptions found for the solutions containing both sodium chloride and aniline hydrochloride, though less reliable, clearly show that an even smaller maximum value of about $2{\cdot}8 \times 10^{14}$ is reached at saturation (Fig. 4, *G*; Table IVc). This unexpected result probably arises becauses sodium chloride exerts a salting-out effect on the hydrochloride also (see above) and enhances its adsorption. It is evident that the hydrochloride lowers the surface tension of a sodium chloride solution more than that of pure water; when water dissolves 1 mol. of aniline hydrochloride per litre, the surface tension falls from 72·75 to 67·1, whereas, if 1 mol. of sodium chloride per litre is also present, the fall is from 74·4 to 65·0. A very rough estimate of the aniline hydrochloride adsorbed from this mixed solution leads to a value of about $1{\cdot}2 \times 10^{14}$. Added to the $2{\cdot}8 \times 10^{14}$ molecules/cm.^{2} for the aniline alone, this again leads to a total adsorption of approximately $4{\cdot}0 \times 10^{14}$.

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