THE SURFACE TENSIONS OF TERNARY SOLUTIONS. PART I. THE SURFACE TENSIONS OF AQUEOUS SOLUTIONS OF (a) SODIUM AND POTASSIUM CHLORIDES, (b) SODIUM CHLORIDE AND HYDROCHLORIC ACID.

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The addition of an electrolyte to water usually produces an increase in surface tension which is given by the relation

$$\gamma - \gamma_0 = km, \qquad . \qquad . \qquad . \qquad . \quad (1)$$

where γ and γ_0 are the surface tensions of the solution and of water respectively, k is a constant, and m is the number of moles of solute present per 1000 gms. of water. When two electrolytes are present the change in surface tension is usually taken as equal to the sum of the changes each would produce separately, and is given by

$$\gamma_{12} - \gamma_0 = k_1 m_1 + k_2 m_2, \qquad . \qquad . \qquad . \quad (2)$$

where γ_{12} is the surface tension of the solution and the subscripts 1 and 2 refer to the two solutes. This relation may be conveniently tested by keeping the concentration of one solute constant and varying that of the other. A plot of γ_{12} against m should give

$$\left(\frac{\partial \gamma_{12}}{\partial m_1}\right)_{m_2} = k_1 . \qquad . \qquad . \qquad . \qquad . \quad (3)$$

$$\left(\frac{\partial \gamma_{12}}{\partial m_2}\right)_{m_1} = k_2 . \qquad . \qquad . \qquad . \qquad . \quad (4)$$

These considerations are applied below to solutions of sodium and potassium chlorides and of hydrochloric acid and sodium chloride.

Experimental.

The surface tensions of the solutions were obtained by the maximum bubble pressure method, the apparatus used being similar to that of Brown [1] to which reference should be made for complete details. Dry air was stored under pressure in a reservoir over mercury and was allowed to pass slowly over phosphorus pentoxide, through a glass wool trap, through a finely adjustable valve and into the experimental cell (Fig. 1) at A, and thence via B to a large reservoir kept at constant temperature. C was connected with a reservoir of butyl phthalate, the level of which could be easily changed, thus giving a fine adjustment of the level of the liquid in the cell. The cell at A and B was also in communication with the limbs of a manometer containing butyl phthalate, by means of which the pressure required to force a single bubble through the surface of the liquid could be measured with a cathetometer placed at a suitable distance. Both cell and manometer were kept in a thermostat at $25°$ ($\pm$ 0·02). At

[1] *Phil. Mag.*, 1932, **13**, 578.

each measurement the jet was arranged to be just coincident with the surface of the liquid, and when the bubble had passed through the surface the contact was broken. Some difficulty was experienced in the cleaning of the cell and jet. Before each fresh solution was examined, it was washed out with hot chromic acid and then with a large quantity of water ; steam was then blown into it for about five minutes and finally it was dried by evacuation at 100°. The jet was made by drawing down a piece of quill tubing, breaking off at the constricted part and examining under a microscope until one satisfactory was obtained.

The surface tension was calculated from

$$\gamma = \frac{rg}{2}\left(h\rho - \frac{2}{3}r\rho_1\right) \quad . \quad (5)$$

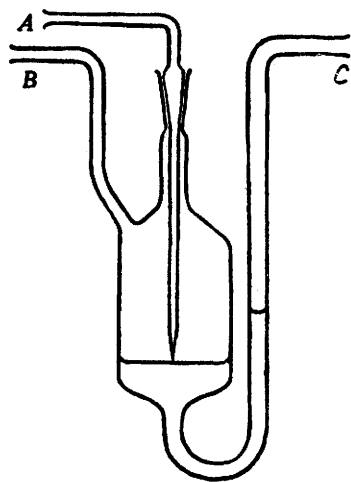where r is the radius of the jet = 0·0102 cm.

FIG. 1.

g = 981 cm./sec.^{2}
h = maximum bubble pressure in cm. butyl phthalate.
ρ = density of butyl phthalate at 25° = 1·0434 gms./c.c.
ρ_1 = density of liquid under observation, found by a Westphal balance.

The surface tension in dyne/cm. of pure water found in this way was 72·01 at 25°, and that of pure benzene at the same temperature 28·20. These values are in good agreement with those generally accepted.

Binary Solutions.

The results obtained for binary solutions containing sodium chloride, potassium chloride and hydrochloric acid are given in Table I. The final column gives the value of the constant, k, calculated from equation (1). The surface tensions of hydrochloric acid solutions decrease with increasing concentration, while those of sodium and potassium chlorides increase.

TABLE I.—SURFACE TENSIONS OF BINARY SOLUTIONS.

	m.	h.	γ.	$\Delta\gamma$.	k.
Sodium Chloride Solutions	1·021	14·15	73·84	1·75	1·73
	2·080	14·48	75·59	3·58	1·72
	3·197	14·84	77·44	5·43	1·70
	4·360	15·22	79·43	7·42	1·70
	5·608	15·62	81·54	9·53	1·70
Potassium Chloride Solutions	1·000	14·12	73·68	1·67	1·67
	2·010	14·43	75·34	3·33	1·65
	3·051	14·70	76·73	4·72	1·55
	4·015	14·96	78·14	6·13	1·53
Hydrochloric Acid Solutions.	1·00	13·77	71·87	—0·14	—0·14
	3·00	13·73	71·64	—0·37	—0·12
	5·00	13·68	71·43	—0·58	—0·11

Ternary Solutions.

(*a*) **Aqueous Solutions of Sodium Chloride and Potassium Chloride.**— The mixtures were made up by weight from B.D.H. AR. chemicals and pure water of surface tension $72 \cdot 01$ dynes/cm. The surface tensions measured are given in Table II. together with the molal concentrations of the salts. The fifth and sixth columns give $(\gamma_{12} - \gamma_0)$ observed, and calculated from (2). The agreement is good, but there is a discrepancy which is greater than the experimental error.

TABLE II.—Solutions of Sodium and Potassium Chlorides.

m_1.	m_2.	h.	γ_{12}.	$\Delta\gamma_{12}$ obs.	$\Delta\gamma_{12}$ calc.
$1 \cdot 01$	$1 \cdot 05$	$14 \cdot 435$	$75 \cdot 35$	$3 \cdot 34$	$3 \cdot 55$
$1 \cdot 01$	$2 \cdot 07$	$14 \cdot 735$	$76 \cdot 91$	$4 \cdot 90$	$5 \cdot 24$
$1 \cdot 01$	$3 \cdot 09$	$15 \cdot 015$	$78 \cdot 37$	$6 \cdot 36$	$6 \cdot 51$
$1 \cdot 01$	$4 \cdot 12$	$15 \cdot 24$	$79 \cdot 54$	$7 \cdot 53$	$8 \cdot 09$
$2 \cdot 02$	$1 \cdot 00$	$14 \cdot 725$	$76 \cdot 86$	$4 \cdot 85$	$5 \cdot 15$
$2 \cdot 02$	$2 \cdot 01$	$14 \cdot 98$	$78 \cdot 46$	$6 \cdot 45$	$6 \cdot 81$
$2 \cdot 02$	$3 \cdot 00$	$15 \cdot 26$	$79 \cdot 97$	$7 \cdot 96$	$8 \cdot 03$
$3 \cdot 01$	$1 \cdot 01$	$15 \cdot 05$	$78 \cdot 55$	$6 \cdot 54$	$6 \cdot 80$
$3 \cdot 01$	$2 \cdot 01$	$15 \cdot 39$	$80 \cdot 15$	$8 \cdot 34$	$8 \cdot 44$
$3 \cdot 00$	$3 \cdot 00$	$15 \cdot 62$	$81 \cdot 54$	$9 \cdot 53$	$9 \cdot 67$
$4 \cdot 02$	$1 \cdot 00$	$15 \cdot 38$	$80 \cdot 30$	$8 \cdot 29$	$8 \cdot 50$
$4 \cdot 02$	$2 \cdot 01$	$15 \cdot 72$	$82 \cdot 08$	$10 \cdot 07$	$10 \cdot 17$

Plots of γ_{12} against m for constant sodium chloride concentration and increasing potassium chloride, and for constant potassium chloride and increasing sodium chloride gave a series of nearly parallel straight lines. According to equations (3) and (4) a series of parallel straight lines should be obtained on both graphs, of slope k_2 and k_1. The slopes (k'_1 and k'_2) for the various mixtures are given in Table III. ; these values should be compared with those given in Table I. for sodium and potassium chloride alone. The curves for the mixtures with one component constant appear

TABLE III.—Solutions of Sodium and Potassium Chlorides.

$m_2 = 1$.			$m_2 = 2$.			$m_2 = 3$.		
m_1.	$\Delta\gamma$.	k'_1.	m_1.	$\Delta\gamma$.	k'_1.	m_1.	$\Delta\gamma$.	k'_1.
1	$1 \cdot 67$	$1 \cdot 67$	1	$1 \cdot 81$	$1 \cdot 81$	1	$1 \cdot 64$	$1 \cdot 64$
2	$3 \cdot 18$	$1 \cdot 59$	2	$3 \cdot 36$	$1 \cdot 68$	2	$3 \cdot 24$	$1 \cdot 62$
3	$4 \cdot 87$	$1 \cdot 62$	3	$5 \cdot 05$	$1 \cdot 68$	3	$4 \cdot 81$	$1 \cdot 61$
4	$6 \cdot 62$	$1 \cdot 65$	4	$6 \cdot 98$	$1 \cdot 75$		Mean	$1 \cdot 62$
	Mean	$1 \cdot 63$		Mean	$1 \cdot 73$			

$m_1 = 1$.			$m_1 = 2$.			$m_1 = 3$.		
m_2.	$\Delta\gamma$.	k'_2.	m_2.	$\Delta\gamma$.	k'_2.	m_2.	$\Delta\gamma$.	k'_2.
1	$1 \cdot 61$	$1 \cdot 61$	1	$1 \cdot 41$	$1 \cdot 41$	1	$1 \cdot 44$	$1 \cdot 44$
2	$3 \cdot 17$	$1 \cdot 59$	2	$3 \cdot 01$	$1 \cdot 50$	2	$3 \cdot 04$	$1 \cdot 52$
3	$4 \cdot 63$	$1 \cdot 54$	3	$4 \cdot 52$	$1 \cdot 51$	3	$4 \cdot 43$	$1 \cdot 48$
	Mean	$1 \cdot 57$		Mean	$1 \cdot 50$		Mean	$1 \cdot 48$

TABLE   IV.—SOLUTIONS OF SODIUM CHLORIDE AND HYDROCHLORIC ACID.

m_1.	m_2.	h.	γ_{12}.	$\Delta\gamma_{12}$.	$\Delta\gamma_{12}$ calc. from (2).	$\Delta\gamma_{12}$ calc. from (6).
0·99	1·0	14·01	73·12	1·11	1·63	1·13
1·98	1·0	14·22	74·23	2·22	3·27	2·28
2·95	1·0	14·45	75·42	3·41	4·87	3·40
3·98	1·0	14·69	76·68	4·67	6·63	4·64
4·96	1·0	14·86	77·57	5·56	8·29	5·81
1·06	2·0	13·96	72·86	0·85	1·64	0·89
2·00	2·0	14·14	73·78	1·77	3·16	1·75
3·01	2·0	14·31	74·68	2·67	4·84	2·72
4·00	2·0	14·47	75·54	3·53	6·55	3·83
1·00	3·0	13·91	72·59	0·58	1·44	0·57
2·01	3·0	14·07	73·43	1·42	3·10	1·36
3·02	3·0	14·23	74·28	2·27	4·76	2·12
0·99	4·0	13·88	72·43	0·42	1·29	0·30
1·99	4·0	14·02	73·15	1·14	2·95	0·96
1·00	5·0	13·84	72·26	0·25	1·24	0·12
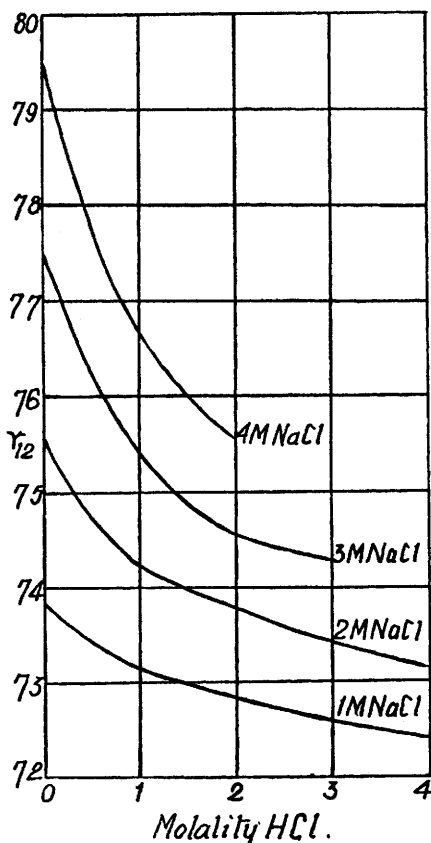
FIG. 2.—Plot of Molality HCl — γ_{12} for NaCl — HCl mixtures.

to be slightly less steep than those with one component alone, although in one case they are equally steep (NaCl in 2MKCl). The contribution of each solute to the surface tension is thus a little less than it would have been in a separate solution.

(b) **Aqueous Solutions of Sodium Chloride and Hydrochloric Acid.** — The solutions were made up by weight from pure chemicals and the same water as before. The strength of the hydrochloric acid was verified by standardisation. Table IV. gives the molal concentrations of sodium chloride (m_1) and hydrochloric acid (m_2) and the corresponding surface tension. The fifth and sixth columns give the surface tension increments observed and calculated from (2). Comparison of these shows that the simple additive relation is only very approximate and that the discrepancies are much greater than those obtained for solutions of sodium and potassium chlorides. The plot of γ_{12} against m_1 (m_2 constant) gives a series of straight lines, but they are not parallel as would be expected from (3) ; the plot of γ_{12} against m_2 (m_1 constant) gives a series of curves again showing no agreement with (4) (Fig. 2). Examination of the data showed

that γ_{12} could be represented by the relation

$$\gamma_{12} - \gamma_0 = k_1 m_1 + k_2 m_2 + k_3 m_1 m_2^{\frac{1}{2}} \qquad . \qquad . \qquad . \quad (6)$$

in which k_3 is an empirical constant equal to -0.5. The values of $\Delta\gamma_{12}$ so calculated are given in the final column of Table IV. The agreement with the observed values is very good—a difference of one in the first place represents an error in the surface tension of one in seven hundred. The slopes of the curves for γ_{12} against m_1 (m_2 constant) and γ_{12} against m_2 (m_1 constant) are thus given by

$$\left(\frac{\partial\gamma_{12}}{\partial m_1}\right)_{m_2} = k_1 + k_3 m_2^{\frac{1}{2}} \qquad \left(\frac{\partial\gamma_{12}}{\partial m_2}\right)_{m_1} = k_2 + \tfrac{1}{2}k_3 m_1 m_2^{-\frac{1}{2}} . \quad (7)$$

Application of the Gibbs Equation.

The values of $(\partial\gamma_{12}/\partial m_1)_{m_2}$ and $(\partial\gamma_{12}/\partial m_2)_{m_1}$, which are calculable from (2) and from (6), may also be derived from the Gibbs equation, according to which

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 - \Gamma_3 d\mu_3, \qquad . \qquad . \qquad . \quad (8)$$

where Γ_1, Γ_2, Γ_3 are the surface concentrations of the components and μ_1, μ_2, μ_3 their chemical potentials. If the surface is chosen so that $\Gamma_3 = 0$, then

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2$$
$$= -\Gamma_1 2RT\, d\log f_1 m_1 - \Gamma_2 2RT\, d\log f_2 m_2, \qquad . \qquad . \quad (9)$$

where f_1 and f_2 are the appropriate activity coefficients of the solutes. If the concentration of one is kept constant and the other varied, then this may be written

$$-\frac{1}{2RT}\left(\frac{\partial\gamma_{12}}{\partial m_1}\right)_{m_2} = \Gamma_1\left(\frac{1}{m_1} + \left(\frac{\partial\log f_1}{\partial m_1}\right)_{m_2}\right) + \Gamma_2\left(\frac{\partial\log f_2}{\partial m_1}\right)_{m_2} \quad (10$$

$$-\frac{1}{2RT}\left(\frac{\partial\gamma_{12}}{\partial m_2}\right)_{m_1} = \Gamma_2\left(\frac{1}{m_2} + \left(\frac{\partial\log f_2}{\partial m_2}\right)_{m_1}\right) + \Gamma_1\left(\frac{\partial\log f_1}{\partial m_2}\right)_{m_1} \quad (11)$$

For only one solute (subscript $_0$)

$$-\frac{1}{2RT}\frac{d\gamma}{dm} = -\frac{k}{2RT} = {}_0\Gamma\left(\frac{1}{m} + \frac{d\log f}{dm}\right). \qquad . \qquad . \quad (12)$$

Equations (3) and (4) and consequently (2) are thus special cases of a more general equation. A complete solution of equations (10) and (11) requires a knowledge of the variations of the activity coefficient of each component of the system, data not usually available. In certain cases, as below, approximations may be made and the adsorptions calculated.

(a) Aqueous Solutions of Sodium and Potassium Chlorides.

It may be assumed for this system that $(\partial\log f_1/\partial m_1)_{m_2} = d\log f_1/dm_1$. Combining (10) and (12), and (11) and (12) and putting k_1 for the slope in the mixed solution, we have

$$-\frac{k'_1}{2RT} = -\frac{\Gamma_1}{{}_0\Gamma_1}\cdot\frac{k_1}{2RT} + \Gamma_2\left(\frac{\partial\log f_2}{\partial m_1}\right)_{m_2} \qquad . \qquad . \quad (13)$$

$$-\frac{k'_2}{2RT} = -\frac{\Gamma_2}{{}_0\Gamma_2}\cdot\frac{k_2}{2RT} + \Gamma_1\left(\frac{\partial\log f_1}{\partial m_2}\right)_{m_1} \qquad . \qquad . \quad (14)$$

For the lower concentrations the $\partial \log f/\partial m$ terms are small and may be neglected.   Hence

$$\Gamma_1 = \frac{k'_1}{k_1}{}_0\Gamma_1 . \qquad . \qquad . \qquad . \qquad . \quad (15)$$

Even for $5M$ solutions the error introduced is only a few per cent. Similarly.

$$\Gamma_2 = \frac{k'_2}{k_2}{}_0\Gamma_2. \qquad . \qquad . \qquad . \qquad . \quad (16)$$

The approximate values of Γ_1 and Γ_2 calculated in this way are given in Table V.   The sum $\Gamma_1 + \Gamma_2$ gives the total negative adsorption at the surface.   The values of ${}_0\Gamma_1 + {}_0\Gamma_2$ for separate solutions, given for comparison, have been calculated from (12), the values of $d \log f/dm$ being obtained from the empirical equations of Harned.[2]

It appears that for this system each solute is hardly affected by the presence of the other, and that each is adsorbed to the same extent in the mixed solution as it would be in a separate solution.   If the layer of water at the surface is assumed to be unimolecular, its thickness, δ, is given by $1000 \ (\Gamma_1 + \Gamma_2)/(m_1 + m_2)$.   These values are given in the final column of Table V. and the result, as for separate solutions of sodium and potassium chlorides, is about the diameter of a water molecule, with a tendency to become less at higher concentrations, probably due to a change in orientation.

TABLE V.—SOLUTIONS OF SODIUM AND POTASSIUM CHLORIDES.

m_1.	m_2.	Γ_1.	Γ_2.	$\Gamma_1 + \Gamma_2$.	${}_0\Gamma_1 + {}_0\Gamma_2$.	$\delta(A°)$.
1	1	0·39	0·35	0·74	0·79	3·7
1	2	0·41	0·65	1·06	1·10	3·5
1	3	0·38	0·89	1·27	1·29	3·2
1	4	0·38	1·07	1·45	1·46	2·9
2	1	0·60	0·34	0·94	1·01	3·1
2	2	0·63	0·63	1·26	1·32	3·1
2	3	0·59	0·85	1·44	1·51	2·9
3	1	0·78	0·34	1·12	1·19	2·8
3	2	0·82	0·62	1·44	1·50	2·9
3	3	0·77	0·83	1·60	1·69	2·7
4	1	0·92	0·34	1·26	1·34	2·5
4	2	0·97	0·62	1·59	1·64	2·6

Γ in moles/sq. cm. $\times 10^{10}$.

(b) Aqueous Solutions of Sodium Chloride and Hydrochloric Acid.

For this system $\partial \log f_2/\partial m_1$ may be computed, but not $\partial \log f_1/\partial m_2$. In order, then, to calculate either Γ_1 or Γ_2 the other must be known. Now it appears that the relative values of the terms in (10), calculated below, are such that changes in Γ_2 may be neglected.   It may thus be assumed that $\Gamma_2 = {}_0\Gamma_2$ and Γ_1 calculated.   A very large change in Γ_2 would be required to produce only a small error in Γ_1 calculated in this way.   Further it must be assumed that $d \log f/dm$ is the same in both mixed and separate solutions ; this will introduce a small error.

[2] *J. Amer. Chem. Soc.*, 1920, **42**, 1808 ; 1922, **44**, 252.

Equation (10) may now be written (using (7) and (12))

$$-\frac{1}{2RT}(k_1 + k_3 m_2^{\frac{1}{2}}) = -\frac{k_1}{2RT} \cdot \frac{\Gamma_1}{{}_0\Gamma_1} + \Gamma_2\left(\frac{\partial \log f_2}{\partial m_1}\right)_{m_2},$$

or

$$1 + \frac{k_3 m_2^{\frac{1}{2}}}{k_1} + \Gamma_2 \frac{2RT}{k_1} \cdot \left(\frac{\partial \log f_2}{\partial m_1}\right)_{m_2} = \frac{\Gamma_1}{{}_0\Gamma_1}. \qquad . \qquad (18)$$

The values of k_1 (taken as 1·7) and k_3 are known, Γ_2 is put equal to ${}_0\Gamma_2$ calculated from the data in Table I. The values of $(\partial \log f_2/\partial m_1)_{m_2}$ were calculated from the data of Hawkins [3] who found for mixtures of sodium chloride and hydrochloric acid up to total concentrations of $6M$

$$\log f = -\frac{0 \cdot 354\sqrt{2C_T}}{1 + A\sqrt{2C_T}} + B(2C_1) + B'(2C_T - 2C_1) - \log (1 - 0 \cdot 002 wm_T),$$

where C_T is the total molar concentration, C_1 the molar acid concentration, and A, B and B' are determined constants. The values of $\Gamma_1/{}_0\Gamma_1$ calculated in this way are given in Table VI. The term involving Γ_2 is quite small throughout.

TABLE VI.—SOLUTIONS OF SODIUM CHLORIDE AND HYDROCHLORIC ACID.

m_1.	m_2.	Γ_2.	$\left(\dfrac{\partial \log f_2}{\partial m_1}\right)_{m_2}$.	$\dfrac{\Gamma_1}{{}_0\Gamma_1}$.	${}_0\delta$.	δ_{12}.
1	1	$2 \cdot 44 \times 10^{-12}$	0·0646	0·72	4·1	3·0
2	1	$2 \cdot 44 \times 10^{-12}$	0·0697	0·72	3·2	2·3
3	1	$2 \cdot 44 \times 10^{-12}$	0·0689	0·72	2·7	1·9
4	1	$2 \cdot 44 \times 10^{-12}$	0·0662	0·72	2·4	1·7
5	1	$2 \cdot 44 \times 10^{-12}$	0·0627	0·72	2·1	1·5
1	2	$3 \cdot 48 \times 10^{-12}$	0·0755	0·60	4·1	2·4
2	2	$3 \cdot 48 \times 10^{-12}$	0·0745	0·60	3·2	1·9
3	2	$3 \cdot 48 \times 10^{-12}$	0·0714	0·60	2·7	1·6
4	2	$3 \cdot 48 \times 10^{-12}$	0·0679	0·60	2·4	1·4
1	3	$3 \cdot 86 \times 10^{-12}$	0·0799	0·51	4·1	2·1
2	3	$3 \cdot 86 \times 10^{-12}$	0·0769	0·51	3·2	1·6
3	3	$3 \cdot 86 \times 10^{-12}$	0·0728	0·51	2·7	1·4
1	4	$4 \cdot 25 \times 10^{-12}$	0·0826	0·44	4·1	1·8
2	4	$4 \cdot 25 \times 10^{-12}$	0·0783	0·44	3·2	1·4
1	5	$4 \cdot 14 \times 10^{-12}$	0·0838	0·37	4·1	1·5

The thickness of the adsorbed water layer, assuming it to be unimolecular, is given under ${}_0\delta$ for the corresponding pure sodium chloride solution, and in the last column under δ_{12} for the mixtures ($\delta = 1000\Gamma/m$). The effect of the addition of hydrochloric acid is to reduce the thickness of this layer. The increased adsorption of HCl molecules seems to displace water molecules from the surface. An increase in the concentration of sodium chloride reduces the thickness of the water layer, but HCl is more effective than NaCl.

Summary.

The surface tensions of aqueous solutions of sodium and potassium chlorides, and of sodium chloride and hydrochloric acid, have been measured. The variation of the surface tension with the concentration of each component is discussed, and the surface adsorption of water calculated by means of the Gibbs equation.

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[3] *J. Amer. Chem. Soc.*, 1932, **54,** 4480.