EQUILIBRIUM SURFACE TENSION OF AQUEOUS SOLUTIONS OF NEKAL BX AND THE EFFECT OF SALTS*

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INTRODUCTION

The study of the surface tension of aqueous solutions of wetting agents is of great interest from several points of view and has received considerable attention in recent years.[1,2] Wetting agents are so highly capillary active that they may be expected to form unimolecular adsorption film with a completely close packing, even at low concentration; this makes it possible to apply Gibbs' adsorption equation for the evaluation of the molecular cross-section. Since the molecular cross-section of these substances can also be investigated by spreading on aqueous substrates[3,4] a comparative study can be made of the two methods for the determination of cross-section. The study would be of interest in correlating wetting power with surface tension, for it is known that wetting power is intimately connected with surface tension.[5] Moreover wetting agents may be expected to show the phenomenon of activated accumulation discovered in this laboratory[6,7,8] and also independently by McBain and co-workers.[9,10] Surface tension studies can be expected to throw light on the interpretation of this phenomenon.

EXPERIMENTAL

Purification of Nekal BX

The main impurity in commercial Nekal BX is sodium sulphate. To remove this, Nekal BX was shaken well with hot benzene using a mechanical shaker. The undissolved portion was allowed to settle down. The supernatant solution was decanted out and the benzene was distilled off. The residue was dried, powdered, heated in an oven at 110° C. for six hours and stored in a stoppered bottle in a desiccator over dehydrated calcium chloride.

Ash content of purified Nekal BX

A known weight of purified Nekal BX was ignited in a platinum crucible. The ash was treated with dilute sulphuric acid to convert it into the sulphate, and the excess of the acid was evaporated. The residue was ignited and weighed. The sodium content was found to correspond to 1·10 atoms of sodium per molecule of Nekal BX.

The osmotic coefficient of Nekal BX in aqueous solution at various concentrations

The osmotic coefficient was determined by the cryoscopic method and calculated using the formula

$$g = \frac{\theta}{\nu \lambda m},$$

where θ = depression of freezing point, $\nu = 2$, $\lambda = 1·85$ and m = molal concentration of Nekal BX. If we assume that aggregation of only anions occurs and that the cations are all osmotically active, the average number of anions per micelle can be calculated. The values are given in Table I.

TABLE I

Concentration of Nekal BX g in 100 grams of water	θ	g	Average No. of anions aggregated to form a micelle
4·0	0·252	0·53	14·7
1·0	0·091	0·74	2·1
0·4	0·046	0·98	1·1
0·20	0·024	1·02	1·0

Preparation of flat springs of quartz

The surface tension was measured by the ring method. The determination of maximum pull was made by using a new type of silica spring prepared in the following manner. Silica fibre drawn in the usual way was attached to the steel blade of a spatula by means of a gummed label. Sharp bends were then given to the fibre at the edges of the spatula by heating with an oxy-gas flame. The blade was manipulated so as to get the fibres parallel to each other after each bend. After the winding was over the label was burnt off when the spring easily slid out of the spatula as the blade had a taper both in its width and in its thickness.

The springs that got are found to be very satisfactory. They obey Hooke's law perfectly. If from a fibre of given length, a helical spring

and a flat spring having same width are prepared, the two springs would give practically the same sensitiveness, as can be seen from the following considerations:—

The extension of a flat spring takes place by the bending of the fibres. The amount of extension x_1 can be calculated by the formula

$$x_1 = \text{number of coils} \times \text{displacement due to bending of each coil.}$$

The displacement δ due to the bending of each coil can be calculated to a first approximation by considering it as equivalent to twice the displacement suffered by a horizontally cylindrical fibre fixed at one end when loaded at the other end. This is given by the equation,

$$\delta = \frac{2\,w\,d^3}{3\,Y\,A\,k^2},$$

where w = the load, d = width of the flat spring, Y = Young's modulus, A = cross-section of the fibre and k = radius of gyration[12].

$d = 2\,R$, where R is the radius of the spring whose diameter is equivalent to the width of flat spring.

$$A = \Pi r^2,$$

where r = radius of the cross-section of the fibre.

$$K^2 = \frac{r^2}{2}$$

$$\delta = \frac{32\,w\,R^3}{3\,Y\,\pi\,r^4}$$

Since the number of coils in the spring $= \dfrac{L}{4R}$, where L is the total length of the fibre,

$$x_1 = \frac{32\,w\,R^3}{3\,Y\,\pi\,r^4} \times \frac{L}{4\,R},$$

$$= \frac{8\,w\,R^2\,L}{3\,Y\,\pi\,r^4}.$$

For a helical spring of the total length L, radius R, the extension x_2 is given by the formula[12]

$$x_2 = \frac{2\,w\,R^2\,L}{n\,\pi\,r^4},$$

where n is the rigidity modulus.

Then,

$$\frac{x_1}{x_2} = \frac{4\,n}{3\,y}$$

For silica $n \simeq 3$ and $y \simeq 5$.

So,
$$\frac{4n}{3y} = \frac{4 \times 3}{3 \times 5} = \frac{12}{15} = 0 \cdot 8,$$

showing that the sensitivenesses of the two types of springs are of the same order.

Flat springs can easily be prepared in less than half an hour while several hours have to be spent in the preparation of the helical springs even when an automatic device is employed.[11]

It has to be pointed out, however, that if the springs are to be enclosed in narrow tubes as in sorption work it is preferable to use the helical springs since the latter are more compact for any given sensitiveness and capacity.

Flat springs were prepared out of ordinary glass fibre but were found to be totally unsatisfactory. Even with pyrex glass small flow effects were noticed, especially when the springs were subjected to high loads for long intervals of time. The quartz springs however showed no detectable flow effects.

The quartz spring used in the present work had a sensitiveness of $2 \cdot 7$ cm. per gram. The travelling microscope used had an accuracy of $0 \cdot 01$ mm.

Temperature control

The ordinary air and water thermostats were found to be unsuitable for the work since the stirring arrangements caused too much disturbance of the surface and of the spring. The following arrangement was employed to overcome this difficulty. The conical flasks containing the solutions were kept in a shallow circular pan which contained water kept at 30° C. $\pm 0 \cdot 1$. Water from an electrically maintained thermostat 30° C. $\pm 0 \cdot 1°$ C. was fed into the pan from four points symmetrically situated at the circumference of the pan. The level of the water in the pan was kept constant by pumping the excess of water back to the thermostat by means of a circulation pump. The suction tube for this purpose was kept at the centre of the pan. The chamber in which the experiment was tried was kept at 32° C. to 34° C. by keeping two heating mats in the chamber in suitable position in order to prevent the condensation of water on the sides of the flask containing the solution. The heating arrangement was also helpful in preventing a cooling of the water in the pan due to evaporation. Using this arrangement a constant temperature could be easily maintained for long periods without any special attention.

Determination of surface tension

The determination of equilibrium surface tension offers many difficulties. The method employed should be a static one, since the systems under consideration show surface aging. Of the static methods, the capillary rise method is defective on account of the friction effects that operate at the meniscus.[8] The sessile bubble and pendant drop methods are by far the best from this point of view though the technique has to be very elaborate to secure accurate results. The ring method is also found to be suitable for the purpose[13,14] and has been adopted in the present work. The corical flasks in which solutions were kept during the measurement of surface tension, were cleaned in the following manner:—

Flasks, whose rims had been ground, were treated with hot chromic acid mixture and then thoroughly cleaned with distilled water. They were next dried in an air oven at 140° to 150° C., cooled and again rinsed with distilled water taking care not to wet the outside of the flask. Surface-active impurities were thus eliminated. The flasks were once again dried and their necks were paraffinned on the outside to eliminate any creeping in of surface-active impurities from the thermostatic bath. It was observed that unless these precautions were taken for avoiding contamination from surface-active impurities the results could not be reproduced. Except during the measurement of surface tension the flasks were kept covered with ground glass plates placed over the ground rims. A fresh surface of the solution was generated by running down the solution into the flask at a uniform rate by means of a fifty c.c. pipette at a position just touching the centre of the bottom of the flask. This is similar in principle to the method adopted by Alexander.[15] The flasks containing the solution were arranged in a circle at the circumference of the thermostatic pan mounted on a table which could be either rotated, raised or lowered. The rotatory movement was helpful in bringing one solution after another beneath the spring with minimum disturbance of the surface. The vertical movement of the table could be made very gently by a worm-gear arrangement and was employed in measuring the maximum pull. Movement of the spring to measure this pull was not practicable owing to the vibrations produced.

A Du Nouy ring fixed to a nichrome wire was flamed and attached to the spring which was suspended from a glass rod fixed to an iron stand. The spring had been previously calibrated. The knob of the hook of the spring was focussed through a travelling microscope and the corresponding reading was taken as the initial reading. The flask containing the solution whose surface had been freshly made, was brought underneath the ring. The ring was then completely dipped into the solution by pulling down the

nichrome wire with the fingers. On releasing the fingers the ring attached itself to the surface of the solution. The flask was then lowered and the position of the knob followed by adjusting the microscope until maximum pull was attained. It was possible to make this measurement without detaching the ring from the surface of the liquid. The values of the surface tension were obtained by applying the corrections indicated by Harkins and Jordan.[16] The following interpolation formula was derived from the data of Harkins and Jordan:

Surface tension $= 21 \cdot 6 + 117 \cdot 3 \,(M - 0 \cdot 2) + 23 \cdot 75 \,(M - 0 \cdot 2)^2$, where M is the maximum pull in grams. This holds for dilute aqueous solutions for Du Nouy ring $\left(\dfrac{R}{r} = 39 \cdot 0 \text{ and } R = 0 \cdot 636 \text{ cm.}\right)$ over a range of temperature 25° C. $\pm 15^\circ$ C. The measurements were continued until equilibrium values were got and there was no significant change for at least one week. It was found necessary to continue the observation for about a month in order to get the final values. The equilibrium surface tension of solutions of Nekal BX in water, in $0 \cdot 1$ N sodium chloride, in $0 \cdot 01$ N sodium chloride, $0 \cdot 01$ N hydrochloric acid and $0 \cdot 01$ N sodium sulphate with different concentrations of Nekal BX were determined. The results are given in Tables II and III and Fig. 1.

TABLE II

− log C.	C = Wt. of Nekal Bx in 100 c.c. of water	Equilibrium surface tension		
		Soln. in water at 30° C.	Soln. in 0·01 N NaCl at 30° C.	Soln. in 0·1 NaCl (23° ± 2° C.)
3·0000	0·0010	71·2	..	..
2·6021	0·0025	65·1	..	51·1
2·3010	0·0050	60·8	57·6	46·6
2·0000	0·0100	56·3	53·0	41·6
1·6021	0·0250	50·0	46·8	36·2
1·3010	0·0500	46·2	41·7	31·9
1·0000	0·1000	41·0	37·7	29·9
0·6979	0·2000	36·3	33·3	29·3
0·3979	0·4000	31·9	31·6	29·3
0·2218	0·6000	..	..	29·6
0·0969	0·8000	31·5	31·3	29·8

TABLE III

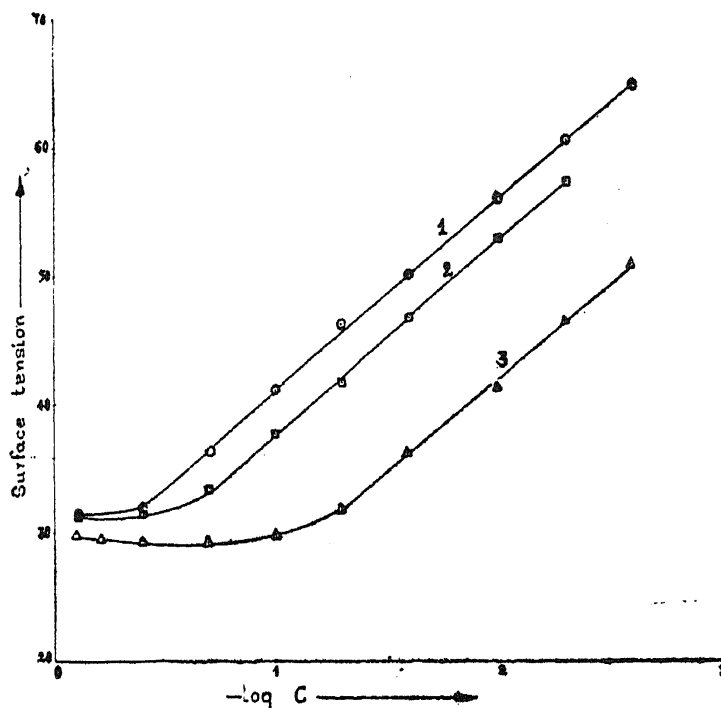| g. Nekal BX in 100 g. water	Equilibrium surface tension		
	Soln. 0·01 N BaCl$_2$	Soln. in 0·01 N Na$_2$SO$_4$	Soln. in 0·01 N HCl
0·005	..	55·0	49·4
0·010	38·3	49·4	43·4
0·025	32·5	43·5	38·8

FIG. 1

Curve 1. Surface tension of Nekal B × Solution in water
Curve 2.   „   „   „   in 0·01N—NaCl
Curve 3.   „   „   „   in 0·1N—NaCl

DISCUSSION

1. *Application of Gibbs' adsorption equation.*

(i) *The derivation of the usual form of Gibbs' adsorption equation.*—Gibbs derived[17] thermodynamically the important relation (for systems at constant temperature and pressure)

$$- d\sigma = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 + \Gamma_3 d\mu_3 + \ldots, \tag{1}$$

where σ is the surface tension of a solution, Γ is the Gibbs' adsorption excess and μ the chemical potential. The subscripts 1, 2, 3, etc., refer to different components present in the solution. For a two-component system the equation becomes

$$- d\sigma = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 \ldots \tag{2}$$

Therefore,

$$- \frac{d\sigma}{d\mu_2} = \Gamma_1 \frac{d\mu_1}{d\mu_2} + \Gamma_2. \tag{3}$$

But from the properties of partial molal quantities, we have,

$$N_1 d\mu_1 + N_2 d\mu_2 = 0, \tag{4}$$

where N_1 and N_2 are mole fractions of the two components. Combining 3 and 4, we get,

$$- \frac{d\sigma}{d\mu_2} = - \Gamma_1 \frac{N_2}{N_1} + \Gamma_2. \tag{5}$$

For any position of the dividing surface, if Γ_2 is positive, Γ_1 would be expected to be negative and would be proportional to Γ_2, so that one can put,

$$\Gamma_1 = - a\Gamma_2. \tag{6}$$

Combining (5) and (6), we get,

$$-\frac{d\sigma}{d\mu_2} = \Gamma_2 \left\{1 + a \frac{N_2}{N_1}\right\}. \tag{7}$$

It may be noted that a can be correlated with the relative dimensions of the two types of molecules, and is always positive.

Equation 7, which is perfectly general for two component systems can be further simplified for the particular case of dilute solutions. For if $N_1 >> N_2$ we get,

$$-\frac{d\sigma}{d\mu_2} = \Gamma_2. \tag{8}$$

Equation 8 represents the usual form in which Gibbs' adsorption equation is expressed and applies to all *dilute* solutions having two components, *irrespective of the position of the dividing surface.*

(ii) *Significance of the Gibbs' adsorption excess.*—Since equation (8) is true irrespective of the position of the dividing surface, one can put the dividing surface at the physical interface. Thus Γ_2 would give the amount of solute present in the adsorption layer in excess over what would have been present if there were no preferential adsorption of the solute. It may be pointed out that in *dilute solutions,* the quantities obtained by the moving bubble method[18] or by the highly exacting microtome technique[19] are identical with Γ_2.

(iii) *Nekal BX and type III curve.*—With pure Nekal BX solutions, neglecting activity coefficients, if the Gibbs' adsorption equation is applied, a unique behaviour is noticed. The adsorption increases with concentration, attains a constant value of $1 \cdot 60 \times 10^{14}$ moles. per sq. cm. and then abruptly falls to zero at a concentration of $0 \cdot 4$ per cent. Nekal BX. This corresponds to type III of McBain.[1] But the curve is very unique in one respect namely that the fall from maximum adsorption to zero adsorption is extremely steep.

Type III curve, as applied to Nekal BX, presents a paradox in the chemistry of surfaces as can be seen from the following considerations:—

(*a*) Gibbs' equation in the simplified form can be applied to this system as we are dealing with a dilute solution having a single solute. The Γ values give directly the amounts present in the surface layer.

(b) Whereas adsorption should increase with increase of concentration. it is found abruptly to fall to zero at a particular concentration.

(c) If it is to be assumed that the fall is due to micelle formation, the micelles being assumed to be surface-inactive, the question yet remains as to why the surface tension of the solution is so low when compared with that of water.

(d) The paradox cannot be attributed to any want of equilibrium since in each case ample time was allowed for equilibrium while the attainment of equilibrium was almost immediate at higher concentrations.

(e) Surface-active impurities have been avoided in measuring the surface tension, by taking the precautions detailed in the appropriate section.

(f) The microtome method as applied to analogous cause of lauryl sulphonic acid shows a positive adsorption in the region in which Gibbs' equation predicts a zero or a negative adsorption. (Such experiments however have not been carried out with Nekal BX.)

(g) The type of the curve remains unaltered even when the osmotic coefficients are taken into account while applying Gibbs' equation.

Attempts to explain this anomaly have been made by McBain[1] and by Alexander. McBain considers this problem in all its aspects and concludes that the Gibbs' adsorption equation itself is a limiting law. But it is not at all clear why it should be a limiting law. Alexander[2] seems to be right in his arguments in discarding the explanation of McBain, but his own explanation given to account for the curve is also unsatisfactory. Alexander considers that the whole complication is due to micelle formation. In applying the Gibbs' equation he considers the Gibbs' adsorption excess as made up of two parts: Γ_s (of single molecules) and Γ_m (of micelles). Then,

$$- d\sigma = \Gamma_w \, d\mu_w + \Gamma_s \, d\mu_s + \Gamma_m \, d\mu_m \tag{1}$$

Placing the dividing surface so as $\Gamma_w = 0$ (and this is allowable in dilute solutions), we get,

$$- d\sigma = \Gamma_s^w \, d\mu_s + \Gamma_m^w \, d\mu_m \tag{2}$$

If the single molecules and micelles are in equilibrium,

$$\mu_s = \mu_m \tag{3}$$

whence

$$- d\sigma = \Gamma_s^w \, d\mu_s + \Gamma_w^m \, d\mu_s \tag{4}$$

But

$$d\mu_s = RT \, d \ln c_s f_s \tag{5}$$

where $c_s f_s$ is the activity of single molecules.

Combining 4 and 5,

$$-\frac{d\sigma}{dc} = RT\ (\Gamma_s^w + \Gamma_m^w)\ \frac{d\ c_s\,f_s}{dc} \cdot \frac{1}{c_s\,f_s}$$

Since $\frac{d\sigma}{dc} = 0$ [at higher concentrations], ($c =$ total concentration of the solute)

either

$$\Gamma_s^w + \Gamma_m^w = 0 \tag{6}$$

or

$$\frac{d\ c_s\,f_s}{dc} = 0 \tag{7}$$

or

$$c_s\,f_s = \infty. \tag{8}$$

[Alexander puts the condition in equation (8) as $c_s\,f_s$ being equal to zero; but this is obviously a slip.]

Alexander considers that the condition in equation (7) is satisfied and not the others in order to explain the paradox.

The defect in the treatment of Alexander can be easily appreciated if one replaces equation (4) by its equivalent equation

$$-\ d\sigma = (\Gamma_s^w + \Gamma_m^w)\ d\mu_m \tag{9}$$

which, proceeding on lines similar to those adopted by Alexander, leads to the final conclusion

$$\frac{d\ c_m\,f_m}{dc} = 0.$$

It is not clear how this conclusion can be experimentally justified.

The defect in Alexander's argument appears to be in that it overlooks the important fact that Gibbs' treatment is thermodynamically rigorous and does not depend on any particular constitution of the solution. *Micelle formation is therefore a supernumerary phenomenon from the point of view of the application of Gibbs' adsorption equation.* As long as there is equilibrium between the micelles and the single molecules, it is unnecessary to separate either the activity or the Gibbs' adsorption excess of the single and polymer molecules. [Such a separation is tantamount to assuming single and polymer molecules as separate components; it would on the same lines be necessary to further increase the number of components taking into account the different polymers of water, the different hydrates of the solute, etc.] If the treatment is modified so as to remove this defect, the phenomenon of $\frac{d\sigma}{dc}$ becoming zero at higher concentrations, remains unexplained.

(iv) *Cross-section of Nekal BX molecule.*—If one can assume that Gibbs' adsorption equation can be successfully applied at concentration below that at which Γ becomes zero, one can show that the saturation of the surface occurs at a concentration of about 0·003 per cent. and the Γ remains constant at higher concentrations up to 0·4 per cent. of Nekal BX. The Γ corresponding to saturation $= 1·60 \times 10^{14}$ molecules per sq. cm. $\therefore$ Cross-section $= 62·5$ sq. Å. The cross-section from surface film measurements[3] works out to be 53 sq. Å. The lower value in the latter case is probably due to the fact that barium chloride solution was used as the substrate.

It is of interest to note that the value of cross-section of Nekal BX at the surface of 0·01 N sodium chloride solution is almost the same (62·6 sq. Å) as that at the surface of water. But the cross-section got by calculating from the data obtained by working with Nekal BX solutions in 0·1 N sodium chloride works out to be 64·8 sq. Å, a value which is markedly higher. This result is rather surprising since addition of salts may normally be expected to reduce the electrostatic repulsion and consequently decrease the effective cross-section; but, the opposite has been found to be the case. This is presumably connected with the facts that (*a*) concentrations and not activities have been used in applying the Gibbs' equation and (*b*) with Nekal BX in 0·1 N sodium chloride, there is a three-component system.

2. *The theory of Cassie and Palmer*

Cassie and Palmer[20] have given an interesting theory for explaining the effect of salts on soluble, ionised monolayers and have brought in support of their theory, the data obtained by Powney and Addison.[21] An examination of the data on Nekal BX solutions (Tables II and III) shows that a divalent cation like the barium ion has much more effect than the univalent cation on the negatively charged monolayer. This observation is qualitatively in conformity with their theory.

A quantitative application however has given a different result. The values of λ^2 calculated according to equations (16·0) and (16·1) of Cassie and Palmer are given in Table IV. The results show that the value of λ^2 shows large variations unlike the corresponding values calculated from the data obtained by Powney and Addison. This shows that the theory of Cassie and Palmer is not valid in the present case. The disagreement is probably due to the wrong assumption made by Cassie and Palmer, that the surface pressure is a single valued function of Γ. That Γ need not be a single valued function of surface pressure is obvious from the work on the spreading of stearic acid on various substrates.[25] It is to be noted however, that this assumption is somewhat justifiable at high surface pressures

(for since the surface is closely packed the Γ values would not very much change with surface pressure). It is of interest to note in this connection that the data in Table IV tend to agree with the theory of Cassie and Palmer in the region of high surface pressure. The data of Powney and Addison, which are cited by Cassie and Palmer, also correspond to the same region. It is to be noted that H^+ ions bring about a much larger lowering of surface tension than Na^+ ions at an equivalent concentration. Though this is contrary to the simple considerations of Cassie and Palmer, it can be correlated with the well-known higher adsorbability of H^+ ions.[26] A quantitative examination of the effect of Ba^{++} ions has not been attempted since the theory breaks down even with $1:1$ electrolytes.

The effect of salts on the equilibrium surface tension can be qualitatively interpreted in the following way. The equilibrium surface tension is governed mainly by the equilibrium concentration of the Nekal BX in the surface layer. The latter is determined by the rate of entry of the ions into the layer and the rate of escape of the ions into the bulk. The entry is checked by the electrical potential barrier due to the ionised monolayer.[8] The rate of escape into the bulk however would be comparatively unaffected by the electrical potential barrier. Addition of salt would increase the ionic strength of the solution and thereby lower the height of the potential barrier. This would increase the rate of entry of Nekal BX into the surface but would not affect the rate of escape into the bulk. The surface concentration would therefore get increased and the surface tension would get lowered. Ba^{++} ions could be expected to be much more effective than Na^+ ions since the former may directly attach themselves to the monolayer and reduce the electrical charge. The behaviour of sodium sulphate is of interest in this connection. Sodium sulphate is more effective than sodium chloride in reducing the surface tension at equivalent concentrations. This is presumably due to the fact that sodium sulphate solution has a higher ionic strength than sodium chloride solution of an equivalent concentration. It may be pointed out that the theory of Cassie and Palmer cannot account for this behaviour of sodium sulphate.

According to the theory of Cassie and Palmer,

$$\lambda^2 = \gamma_1 \cdot S_1 [S_1 + C_1] = \gamma_2 \cdot S_2 [S_2 + C_2],$$

where S_1 and S_2 are the concentrations of the surface-active electrolytes, C_1 and C_2 are the concentrations of the salt, and γ_1 and γ_2 are the activity coefficients of the corresponding solutions having the same surface tension. The values of λ^2 calculated from our data are given in Table IV and a survey of the table shows, as has been already pointed out, that the data tend to agree with their theory only at lowest surface tensions.

TABLE IV

Surface tension	Concentration of wetting agent in molarity*	Concentration of NaCl in molarity	Logarithm of activity coefficient	$\lambda^2 \times 10^8$
57·6	$2\cdot53 \times 10^{-4}$	0·00	$\bar{1}\cdot992$	6
	$1\cdot59 \times 10^{-4}$	0·01	$\bar{1}\cdot950$	145
53·0	$5\cdot54 \times 10^{-4}$	0·00	$\bar{1}\cdot988$	30
	$3\cdot19 \times 10^{-4}$	0·01	$\bar{1}\cdot949$	292
51·1	$7\cdot47 \times 10^{-4}$	0·00	$\bar{1}\cdot986$	54
	$4\cdot20 \times 10^{-4}$	0·01	$\bar{1}\cdot949$	388
	$7\cdot96 \times 10^{-5}$	0·10	$\bar{1}\cdot842$	554
46·6	$1\cdot59 \times 10^{-3}$	0·00	$\bar{1}\cdot980$	241
	$7\cdot96 \times 10^{-4}$	0·01	$\bar{1}\cdot948$	763
	$1\cdot59 \times 10^{-4}$	0·10	$\bar{1}\cdot842$	1106
41·6	$2\cdot84 \times 10^{-3}$	0·00	$\bar{1}\cdot973$	758
	$1\cdot59 \times 10^{-3}$	0·01	$\bar{1}\cdot946$	1629
	$3\cdot19 \times 10^{-4}$	0·10	$\bar{1}\cdot842$	2221
36·2	$6\cdot37 \times 10^{-3}$	0·00	$\bar{1}\cdot960$	3701
	$3\cdot92 \times 10^{-3}$	0·01	$\bar{1}\cdot941$	4756
	$7\cdot96 \times 10^{-4}$	0·10	$\bar{1}\cdot841$	5564

* Taken from the graph in Fig. 2.

3. Application of Szyszkowski's equation

For relating the surface tension of a solution with the concentration of the solute Szyszkowski[22] suggested empirically the equation

$$\frac{\sigma_0 - \sigma}{\sigma_0} = B \log \left(\frac{c}{A} + 1\right) \tag{1}$$

where σ_0 and σ are the surface tensions of solvent and solution respectively. C is the concentration of the solute and A and B are constants. An examination of the Bond and Puls' treatment[23] of Szyszkowski's equation has shown that the latter can be justified on the basis of the Gibbs' adsorption equation and the Langmuir theory of adsorption. The following formal derivation can be given for Szyszkowski's equation :—

Number of molecules per sq. cm. in the surface layer in dilute solutions

$$= - \frac{1}{kT} \frac{d\sigma}{d \ln c} \tag{2}$$

Fraction of the total surface covered

$$= - \frac{1}{kT} \cdot \frac{d\sigma}{d \ln c} \, \sigma, \tag{3}$$

where a is the cross-section of the solute molecule.

V_1 = rate of escape of molecules into the bulk

$$= - \frac{1}{kT} \cdot \frac{d\sigma}{d \ln c} \cdot K_1$$

V_2 = rate of arrival of molecules into the surface

$$= K_2 c \left\{ 1 + \frac{1}{kT} \cdot \frac{d\sigma}{d \ln c} \, a \right\}$$

where K_1 and K_2 are constants.

At equilibrium $V_1 = V_2$. $\tag{4}$

Solving the differential equation corresponding to equation (4), we get,

$$\frac{\sigma_0 - \sigma}{\sigma_0} = \frac{kT}{a \sigma_0} \ln \left(1 + \frac{K_2}{K_1} \, a \, c \right) \tag{5}$$

which is of same form as equation (1). Comparing (1) and (5), we get,

$$B = \frac{kT}{a \sigma_0} \text{ and } A = \frac{K_1}{K_{2a}} \cdot$$

It is easily seen that B is a function of a and therefore is constant for different members of the homologous series. A, however, would be proportional to K_1 and would therefore increase with decrease in chain length. This is again in agreement with Szyszkowski's observation.

Other merits of the equation are

(a) at low concentrations the solute can be shown to behave as a perfect gaseous film;

(b) at high concentrations the equation reduces itself to that of Milner[24] which is found to be in agreement with experimental results; and

(c) at the highest concentrations a limiting area is indicated.

An application of the equation to Nekal BX solutions shows that the equation is applicable up to 0·4 per cent. Nekal BX and then it breaks

down completely; this is because the Gibbs' adsorption equation itself does not apply beyond that concentration. (It is to be noted however that even the lowest concentrations of Nekal BX employed in the present investigation correspond to the formation of a practically complete unimolecular layer.)

4. *Micelle formation*

If the horizontal portion of the $\sigma - (-\log C)$ curves is interpreted as due to micelle formation, the concentration at which the micelle formation occurs may be taken as 0·4 per cent. in the case of pure Nekal BX solutions, and 0·27 per cent. in the case of Nekal BX solutions in 0·01 N-N:.Cl.

SUMMARY

A simple technique has been described for the preparation of flat springs of quartz fibre. The new type of springs are found to be very satisfactory for the measurement of surface tension by the ring method.

A method for measuring the equilibrium surface tension of solutions (which show surface aging) has been described. Full details are given of the arrangement for adequate temperature control and for the prevention of contamination of solutions by surface-active impurities.

The equilibrium surface tension of Nekal BX solutions of various concentrations in water and in salt solutions, has been determined.

Application of Gibbs' equation to Nekal BX solutions has been discussed. Nekal BX solutions of concentrations above 0·4 per cent. have shown either no adsorption or negative adsorption, which cannot be explained on the basis of Gibbs' equation and the phenomenon therefore remains a paradox.

The arguments put forward by McBain and by Alexander to explain the type III curve have been shown to be untenable.

The cross-section of the Nekal BX molecule has been calculated on different substrates, *viz.*, water, 0·01 N and 0·1 N sodium chloride.

Applicability of Cassie and Palmer's theory to unimolecular adsorption layers formed by Nekal BX solutions has been discussed.

A formal derivation of the empirical equation of Szyszkowski has been given by combining Gibbs' equation and Langmuir's theory of adsorption and its application to Nekal BX solutions has been discussed.

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