

An Equation for the Surface Pressure of Long Chain Electrolytes Taking Interionic and Van der Waals Attractions into Consideration

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Starting from an equation similar to that proposed by Volmer and Frumkin for the surface pressure of neutral long chain molecules, an equation has been derived for the surface pressure of long chain electrolytes at oil/water interface taking electrostatic repulsion and interionic attraction into consideration. The equation may be written as follows

$$\pi = 2n_0 kT \ln \left(\frac{A}{A-A_0} \right) + \left(\exp^{(A-A_0)a/A} - 1 \right) n_0 kT \ln \left(\frac{A}{A-A_0} \right) + \frac{n_0 kT}{2} \ln f$$

where $n = \frac{1}{A}$ represents the number of long chain ions adsorbed per unit area of the interface, f their mean activity coefficient and $A_0 = \frac{1}{n_0}$, the other terms have their usual significance. Experimental evidence available in the literature has been cited in support of this equation.

It has also been pointed out that the view that at oil/water interface cohesive pressure due to the attraction of the CH_2 groups in the chains is absent may not always be correct. At low substrate concentration, many of the CH_2 groups of the long chains may lie in the aqueous part of the oil/water interface and there they can attract one another and give rise to cohesive pressure. Experimental evidence available in the literature has been cited in support of this theory of the author. Accepting Chattoraj and Chatterjee's equation for cohesive pressure $\pi_s = \frac{a_s}{A^2}$, the following approximate equation has been proposed for the oil/water interface :

$$\left(\pi + \frac{a_s}{A^2} \right) = 2n_0 kT \ln \left(\frac{A}{A-A_0} \right) + \left(\frac{A-A_0}{A} \right) n_0 kT \ln \left(\frac{A}{A-A_0} \right) + \frac{n_0 kT}{2} \ln f$$

Similarly the equation for air/water interface may be written as follows :

$$\left(\pi + \frac{a_s}{A^2} \right) = 2n_0 kT \ln \left(\frac{A}{A-A_0} \right) + \left(\frac{A-A_0}{A} \right) n_0 kT \ln \left(\frac{A}{A-A_0} \right) + \frac{n_0 kT}{2} \ln f$$

It has been concluded that the existence of cohesive pressure at oil/water interface will create conditions favourable for the Langmuir isotherm to hold good in the case of adsorption of long chain electrolytes.

It has been reported in a previous paper¹ that on the basis of Langmuir's theory of adsorption the surface pressure exerted by adsorbed long chain neutral molecules at the oil/water interface may be represented by the following equation²

$$\pi_0 = n_0 kT \ln (1 + K_1 C_1) = n_0 kT \ln \left(\frac{A}{A-A_0} \right) \quad \dots \quad (1)$$

1. B. N. Ghosh, *J. Indian Chem. Soc.*, 1965, **43**, 19.

2. Similar equations were deduced by Volmer, *Z. Physikal. Chem.*, 1925, **116**, 253 and by Frumkin, *Ibid*, 1925, **116**, 468.

where n_0 and n represent respectively the number of long chain molecules adsorbed per unit area at the saturation level and at the concentration C_1 , K_1 is a constant, $A_0 = \frac{1}{n_0}$ and $A = \frac{1}{n}$; k and T have their usual significance. $K_1 C_1$ has been shown to be equal to $\frac{A_0}{A - A_0}$.

Starting from equation (1) it has been shown that for uni-univalent long chain strong electrolytes adsorbed at oil/water interface, the surface pressure should be represented by the following equation ;

$$\pi = 2\pi_0 + \left(\frac{A - A_0}{A}\right) \pi_0 \quad \dots \quad \dots \quad (2)$$

$$= 2n_0 kT \ln \left(\frac{A}{A - A_0}\right) + \left(\frac{A - A_0}{A}\right) n_0 kT \ln \left(\frac{A}{A - A_0}\right) \quad (2a)$$

The aforesaid equations have been deduced on the assumption that the observed pressure is contributed by the adsorbed long chain ions and their counter ions, each ionic species contributing the same pressure π_0 and that an extra pressure due to electrostatic repulsion is contributed by the adsorbed long chain ions only and not by their counter ions. The extra pressure due to electrostatic repulsion is represented by the expression : $\frac{A - A_0}{A} n_0 kT \ln \left(\frac{A}{A - A_0}\right)$.

An attempt has been made to introduce correction for the interionic attraction by writing equation (2a) in the following form

$$\pi = 2n_0 kT \ln \left(\frac{A}{A - A_0}\right) + n_0 kT f \left(\frac{A - A_0}{A}\right) \ln \left(\frac{A}{A - A_0}\right) \quad \dots \quad (3)$$

where f denotes the mean activity coefficient of the ions. Such a procedure may be justified only when $K_1 C_1 \ll 1$ and not otherwise. It appears that a relatively more satisfactory correction for the interionic attraction may be introduced in the following way.

For ideal neutral long chain molecules only equation (1) should hold. When the long chain molecules assume, say, a positive charge, an ion atmosphere is formed round each of them and so π , will be reduced to $\pi^+ = n_0 kT \ln (1 + K_1 C_1 f)$ where f is the mean activity coefficient of the ions. For ionic strength up to 0.1 maintained by using, say NaCl, when $K_1 C_1$ varies within certain limits, the value of $(1 + K_1 C_1 f)$ for a given value of $K_1 C_1$ does not differ much from $(1 + K_1 C_1) / \sqrt{f}$. Therefore, within these limits one may write $\pi^+ = n_0 kT \ln (1 + K_1 C_1 f) = n_0 kT \ln (1 + K_1 C_1) / \sqrt{f}$. If $K_1 C_1$ is reduced below 0.6, the difference between $(1 + K_1 C_1 f)$ and $(1 + K_1 C_1) / \sqrt{f}$ becomes appreciable. The effect of this difference on the observed pressure can be compensated to a considerable extent by putting a load on the expression for pressure due to electrostatic repulsion and writing it in the form,

$$n_0 kT \left(\exp^{(A - A_0)a/A} - 1 \right) \ln \left(\frac{A}{A - A_0} \right), \text{ where } a = (1 - 0.12(f)^{\frac{1}{2}})$$

With these adjustments the expression for the observed pressure may be written as follows :

$$\pi = 2 n_0 kT \ln \left(\frac{A}{A - A_0} \right) + \left(\exp^{(A - A_0)a/A} - 1 \right) n_0 kT \ln \left(\frac{A}{A - A_0} \right) + \frac{n_0 kT}{2} \ln f \quad (4)$$

Taking the size of the ions into consideration at 25° we have for a uni-univalent electrolyte,

$$-\log f = \frac{0.505 \sqrt{C}}{1 + B_a \sqrt{C}}$$

Putting $n_0 = \frac{1}{A_0}$ and $B_a' = 0.7$ and substituting the value of $\log f$ in equation (4) we get for $A_0 = 40(\text{\AA})^3$

$$\pi = \frac{2kT}{A_0} \ln \left(\frac{A}{A - A_0} \right) + \frac{kT}{A_0} \left(\exp^{(A - A_0)a/A} - 1 \right) \ln \left(\frac{A}{A - A_0} \right) - \frac{0.58 \sqrt{C}}{1 + 0.7 \sqrt{C}} \quad (4a)$$

It has been shown in a previous paper³ that an equation very similar to (4a) agree well with the experimental data. Although equations (4) and (4a) have been derived from a consideration of adsorption, at the oil/water interface, of soluble long chain electrolytes, yet they should be applicable to (almost) insoluble long chain electrolytes spread as monolayers at oil/water interface.

Equation (4a) has been subjected to test using the data on spread films of $C_{18}H_{37}SO_4Na$ and $C_{18}H_{37}N(CH_3)_3Cl$ at oil/water interface obtained by Phillips and Rideal⁴. The following equations of Davies have also been used for a comparative study.

$$\pi = \frac{kT}{A - A_0} + 6.1 \sqrt{C} \left[\cosh^{-1} \left(\frac{134}{A \sqrt{C}} \right) - 1 \right] \quad (5)$$

When $A \sqrt{C} < 38$ the aforesaid equation has been used in the form

$$\pi = \frac{kT}{A - A_0} - 6.1 C - \frac{2kTA_0}{A(A - A_0)} \quad \dots \quad \dots \quad (5a)$$

Explanatory notes on the data recorded in the tables 1 and 2. In the tables 1 and 2 are recorded the data obtained by Phillips and Rideal⁴. π_g and π_d represent the values of surface pressure calculated from the equations (4a) of Ghosh and (5) of Davies respectively. For calculating π_g and π_d , A_0 has been taken as $41(\text{\AA})^3$ and $30(\text{\AA})^3$ respectively. In equation (4a), f , in the factor, a , has been calculated from the Debye—Hückel limiting equation ; $-\log f = 0.505 \sqrt{C}$. In column 8 of the tables the values of $(\pi_g - \pi_s)$ have been recorded where π_s represent the cohesive pressure. The minus sign usually placed before it has been omitted. It is generally accepted that at oil/water interface $\pi_s = 0$ because in the oil the CH_2 groups of one chain do not attract the CH_2 groups of the neighbouring chains. This theory is valid only when all the CH_2 groups in the absorbed long chain ions are in the oil. If some of them are in the aqueous side of the interface, then the parts of the long chains

3. B. N. Ghosh, *Jour. Indian Chem. Soc.*, 1968, **45**, 258.

4. J. N. Phillips and E. Rideal, *Proc. Roy. Soc.*, 1955, **A232**, 159.

containing them in the aqueous side can attract one another and produce cohesive pressure. This point has been discussed in detail later on.

Davies⁵ has proposed the expression $\pi_s = \frac{400 m}{A^2}$ where m is the effective number of CH_2 groups in the long chain. On the basis of Van der Waals theory of attraction Chatteraj and Chatterjee⁶ have proposed the equation $\pi_s = \frac{a_s}{A^2}$ where a_s is a constant for a given thickness of the interface. Both Davies and Chatteraj have pointed out that below $A=110 \text{ \AA}^2$ deviations from the aforesaid equations become perceptible. In this paper π_s has been calculated using Chatteraj's equation. The difference between the observed and the calculated values of surface pressure is plotted against $\frac{1}{A^2}$, the straight line that fits the plot best is drawn and a_s is found from its slope. In table I for $\text{C}_{18}\text{H}_{37}\text{SO}_4\text{Na}$ at substrate concentration 0.01 M, $a_s=2.8 \times 10^4$. For $\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_3^+\text{Cl}^-$ in table II at substrate concentration 1 M $a_s=1.3 \times 10^4$.

TABLE I

Con.	Film Area (\AA^2) ^a	Values of π (dynes/cm) observed for films of $\text{C}_{18}\text{H}_{37}\text{SO}_4\text{Na}$ on			π_d in dynes/cm	π_s in dynes/cm	$(\pi_g - \pi_s)$ in dynes/cm
		NaCl	HCl	LiCl			
1.00M	200	3.8	4.1	4.9	3.3	3.6	
	150	5.4	5.7	6.5	5.4	6.0	
	100	9.0	9.8	10.5	10.9	10.8	
	80	12.4	14.4	14.0	13.9	14.8	
0.1M	200	4.9	—	5.9	4.9	5.5	
	150	6.6	—	7.8	7.1	7.7	
	100	10.5	—	12.0	12.2	12.6	
	80	14.0	—	16.0	16.6	16.6	
0.01M	200	5.7	5.0	5.3	5.3	6.3	5.6
	150	7.3	6.8	7.0	8.2	8.6	7.4
	100	10.6	11.6	11.0	13.6	13.5	10.7
	80	13.8	15.0	14.7	17.8	17.5	13.1

TABLE II

Con.	Film area in (\AA^2) ^a	Values of π (dynes/cm) observed for films of $\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_3^+\text{Cl}^-$ on			π_d in dynes/cm	π_g in dynes/cm	$(\pi_g - \pi_s)$ in dynes/cm
		NaCl	HCl	NaNO_3			
1.0M	200	3.7	3.1	3.9	3.3	3.6	3.3
	150	5.5	4.7	5.6	5.4	6.0	5.4
	100	9.7	8.9	9.7	10.9	10.8	9.5
	80	13.7	12.3	13.2	13.9	14.8	12.8
0.1M	200	4.0	3.7	4.1	4.9	5.5	
	150	5.7	5.4	5.6	7.1	7.7	
	100	10.0	9.3	9.5	12.2	12.6	
	80	13.7	12.5	12.7	16.6	16.6	

5. J. T. Davies, *Interfacial Phenomena* by Davies and Rideal, Academic Press, New York, 1961, 230.

6. D. K. Chatteraj and A. K. Chatterjee, *J. Colloid and Interface. Sci.*, 1966, **21**, 159.

DISCUSSION

It will be noticed from the data recorded in Table I that, for a fixed value of A , the value of π increases as the substrate concentration decreases from $1M$ to $0.1M$. With further decrease in concentration from $0.1M$ to $0.01M$ of a substrate, say NaCl , the values of π do not increase appreciably, while with LiCl as substrate they decrease slightly. According to the existing theory one would expect that, at a fixed value of A , as the substrate concentration diminishes progressively the electrostatic repulsion due to the charged heads of the adsorbed long chain ions should increase and so π should increase. The apparently anomalous result at substrate concentration $0.01M$ may be reconciled with the theory on the basis of the following consideration.

As the substrate concentration diminishes the thickness of the electrical double layer increases. Suppose a plane AB separates the oil from water, then at substrate concentrations $1M$, $0.1M$ and $0.01M$, the approximate thickness of the double layers, below the plane AB , i.e., in the aqueous side, will be 3\AA , 10\AA and 31\AA respectively. Since the interface as a whole is electrically neutral it must be thick enough to contain a long chain ion and the double layer. With $\text{C}_{18}\text{H}_{37}\text{SO}_4\text{Na}$ as the long chain electrolyte, when the thickness of the double layer is only 3\AA , all the CH_2 groups in the chain will lie in the oil above the plane AB and there they do not attract one another. The charged heads of the long chain ions will lie below the plane AB , with their centres at a distance of about 3\AA from it and give rise to electrostatic repulsion. As the substrate concentration decreases from $1M$ to $0.1M$ the thickness of the double layer increases from 3\AA to 10\AA approximately. For a fixed value of A , as the thickness of the double layer increases the electrostatic repulsion tends to increase and this is counteracted by the system by a suitable adjustment of the distance of the charged heads of the long chain ions from the plane AB . The centres of the charged heads of some of them will lie at a distance of 3\AA from AB , but those of others will lie in different layers whose distances from AB will be increasingly greater within the allowed limits of thickness of 10\AA of the double layer. Some of the CH_2 groups of each of the long chain ions whose heads lie at a distance greater than 3\AA will thus be transferred from the oil to the aqueous side of the plane AB and there they will attract one another and give rise to cohesive pressure. The adsorption of long chain ions in several layers with their heads at different distances from the plane AB has been suggested and depicted in a previous paper⁸. For a thickness of the double layer of the order of 10\AA , the CH_2 groups in the aqueous part of the interface will be few in number. So the cohesive pressure they will produce will be small and this will not appreciably affect the pressure due to electrostatic repulsion. Therefore, an increase in the value of π of almost the usual order will be observed.

At a substrate concentration of $0.01M$ the thickness of the double layer will be about 31\AA . With this increase in the thickness of the double layer the freedom of distribution of the charged heads of the long chain ions in different layer increases and consequently their distances from the plane AB increase consistent with the restrictions imposed by a double layer thickness of 31\AA . The number of CH_2 groups

transferred by the long chain ions from the oil to the aqueous side of the interface will in this case be much greater than that when the thickness of the double layer is 10\AA . Therefore, the attraction for one another of those parts of the chains which are in water will be much greater. Consequently the electrostatic repulsion due to the charged heads will be much reduced and there will hardly be any rise in π due to change of substrate concentration from $0.1M$ to $0.01M$.

For the reasons stated above, the cohesive pressure at substrate concentration $1M$ will be absent and the values of π observed in the case of $C_{18}H_{37}SO_4Na$ monolayers should agree with those calculated from the equations (4a) or (5) as is actually found to be the case. At substrate concentration $0.1M$ the cohesive pressure is very small and hence the agreement between the observed and the calculated values of π at a given value of A is fairly satisfactory. At substrate concentration $0.01M$ the cohesive pressure π_s for the reasons stated above is quite appreciable and this is reflected in the relatively large difference between the observed and the calculated values of π for a given value of A . The values of π for different values of A has been calculated using the expression $\pi_s = \frac{a_s}{A^2}$. The value of $a_s = 2.8 \times 10^4$ has been found in the way discussed already. Knowing π_g and π_s , their difference ($\pi_g - \pi$) has been recorded in column 8 of table I. It will be noticed that these are well within the range of the observed values of π . For example the values of π with $NaCl$ as substrate agree well with the corresponding values of ($\pi_g - \pi_s$),

From the data recorded in table II, it will be noticed that for values of $A = 80 (\text{\AA})^2$ and $100 (\text{\AA})^2$ respectively, the observed values of π are lower than the calculated values at substrate concentration, $1M$. This is to be attributed to the fact that the three CH_3 groups attached to the N atom forming the head of the $C_{18}H_{37}N(CH_3)_3^+$ ion cannot be removed from water to oil even at a substrate concentration of $1M$. This is a consequence of the constitution of the ion. In the aqueous side of the interface, therefore, appreciable cohesive pressure will be generated due to the mutual attraction of the CH_3 groups of the charged heads and this will lower the electrostatic repulsion which is already small because of the high ionic strength $1M$. The values of π_s has been calculated taking $a_s = 1.3 \times 10^4$ and the calculated values of ($\pi_g - \pi_s$) agree well with the observed values of π , for example, when $NaNO_3$ is the substrate.

For a fixed value of A , the observed values of π increase only slightly as the substrate concentration decreases from $1M$ to $0.1M$. The reason is that as the substrate concentration is lowered the double layer thickness increases from 3\AA to 10\AA , some CH_3 groups are transferred from the oil to the aqueous side of the interface and these, with the three CH_3 groups per ion already present, generate sufficient cohesive pressure to neutralise the rise in pressure due to increased electrostatic repulsion following the dilution of the substrate.

From the discussion recorded above it may be concluded that at a substrate

concentration of $0.01M$ or lower the cohesive pressure exerted by long chain ions like $C_{18}H_{37}SO_4$ will be quite appreciable even at oil/water interface. In the case of long chain quaternary ammonium compounds the cohesive pressure at oil/water interface cannot be completely eliminated even at a substrate concentration of $1M$.

Therefore, the following approximate equation, obtained by dropping the load from the expression of pressure due to electrostatic repulsion in equation (4a) and introducing the expression for cohesive pressure, may be proposed for the oil/water interface.

$$\left(\pi + \frac{a_s}{A^2}\right) = \frac{2kT}{A_0} \left(1 + \frac{A - A_0}{2A}\right) \ln \left(\frac{A}{A - A_0}\right) - \frac{0.58(kT/A_0) \sqrt{C}}{1 + Ba' \sqrt{C}}$$

where a_s is a constant at a given thickness of the interface.

The corresponding equation for air/water interface may be written as follows

$$\left(\pi + \frac{a_s}{A^2}\right) = \frac{2kT}{A_0} \left(1 + \frac{A - A_0}{2A}\right) \ln \left(\frac{A}{A - A_0}\right) - \frac{0.58(kT/A_0) \sqrt{C}}{1 + Ba' \sqrt{C}}$$

where a_s is a constant for a given thickness of the interface.

It may also be pointed out that at low ionic strength the existence of cohesive force at oil/water interface will tend to neutralise the electrostatic repulsion of the charged heads of the adsorbed long chain ions and thereby extend the range of application of the Langmuir adsorption isotherm up to a fairly high concentration of a long chain electrolyte.

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