# *Effect of Ionization on the Behavior of Insoluble Monolayers*

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(Received March 23, 1959)

It has been observed experimentally that an insoluble monolayer of electrolyte is more condensed on an aqueous subphase of higher concentration of salt while it is more expanded on that of lower concentration. Such an effect of salt on the behavior of ionized monolayer was first elucidated by Davies[1] in the light of the theory of electric double layer, which was based on the Gouy-Chapman's theory of diffuse double layer developed by Derjaguin and Landau[2] and Verwey and Overbeek[3]. Investigations on ionized monolayers have been carried out further along this line[4,5].

In the present paper the authors will show that the same results can be derived from a simpler thermodynamic consideration as well as from the electrostatic theory. The present theory is not only more intuitive and tractable but also is a more general approximation, although it assumes an uncertified model.

An insoluble monolayer may be supposed to be a two-dimensional solution in a surface phase, in which the monolayer substance behaves as a solute, apart from its non-polar side chains. It exerts a surface pressure for maintaining thermodynamic equilibrium with the bulk phase. Thus, for an electrolyte monolayer it may be assumed that its ionized groups are dissolved uniformly in a "surface phase" with a definite thickness, $\delta$, and ions of salt in the aqueous subphase are distributed between the surface and bulk phases, counter ions being concentrated in the surface phase and co-ions being repelled from there into the bulk phase. The distribution of ions between the two phases will be first evaluated by an analogy to the membrane equilibrium and then by an improved approximation. The difference in ionic concentrations between the two phases resulting from the ionization of monolayer contributes to both surface pressure and potential. These contributions will be calculated by means of a thermodynamic procedure.

Consider a uni-univalent type of salt and a monolayer substance whose molecule dissociates into an insoluble cation carrying $i$-univalent ionized groups and $i$ univalent anions common with those of the salt. The ionized groups of the monolayer are assumed to be uniformly distributed in the surface phase. Since the surface phase can not be defined from the present theory alone, its thickness, $\delta$, must be assigned so as to cover the effective thickness of the diffuse double layer, as seen later.

## Membrane Equilibrium for Ionized Monolayer

In the present model it is assumed that the boundary between the surface and bulk phases behaves like a semipermeable membrane in osmotic equilibrium and, to the first approximation, the distribution of diffusible ions between these phases is governed by conditions similar to those in Donnan's membrane equilibrium in colloidal solution[6]. That is, electrochemical potentials of each diffusible ion in both phases are put equal. In the expression of the electrochemical potential functions, activities may be substituted by concentrations, unless they are very high.

Let the concentrations of cation and anion of salt be $\bar{n}_+$ and $\bar{n}_-$ (ions per cm$^3$) in the surface phase, respectively, and those of both ions equally $n$ in the bulk phase. If the electrostatic potential of diffusible ions in the surface phase relative to that in the bulk phase is $\psi_D$, conditions for equilibrium are given by

$$\begin{aligned} \boldsymbol{k}T\ln\bar{n}_+ + \boldsymbol{e}\psi_D &= \boldsymbol{k}T\ln n \\ \boldsymbol{k}T\ln\bar{n}_- - \boldsymbol{e}\psi_D &= \boldsymbol{k}T\ln n \end{aligned} \qquad (1)$$

where $\boldsymbol{e}$ is the elementary charge, $\boldsymbol{k}$ the

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[1] J. T. Davies, *Proc. Roy. Soc.*, **A208**, 224 (1951).

[2] B. Derjaguin and L. Landau, *Acta Physicochim.*, **14**, 633 (1941).

[3] E. J. W. Verwey and J. Th. G. Overbeek, "Theory of the Stability of Lyophobic Colloids", Elsevier, Publishing Co., Inc., New York (1948).

[4] K. Hamaguchi and T. Isemura, This Bulletin, **28**, 9 (1955).

[5] J. N. Phillips and E. Rideal, *Proc. Roy. Soc.*, **A232**, 159 (1955).

[6] F. G. Donnan and E. A. Guggenheim, *Z. physik. Chem.*, **A162**, 346 (1932).

Boltzmann constant and $T$ the absolute temperature. Furthermore, it is assumed that the surface phase remains electrically neutral, i. e.

$$\bar{n}_+ + \frac{i\Gamma_M}{\delta} = \bar{n}_- \tag{2}$$

where $\Gamma_M$ (ions per cm$^2$) is the surface concentration of non-diffusible cations, each with $i$ univalent ionized groups, in the surface phase. From Eqs. 1 and 2 the equilibrium concentrations of diffusible ions are obtained as

$$\begin{aligned} \bar{n}_+ &= \frac{1}{2}\left\{-\frac{i\Gamma_M}{\delta}+\sqrt{\left(\frac{i\Gamma_M}{\delta}\right)^2+4n^2}\right\} \\ \bar{n}_- &= \frac{1}{2}\left\{\frac{i\Gamma_M}{\delta}+\sqrt{\left(\frac{i\Gamma_M}{\delta}\right)^2+4n^2}\right\} \end{aligned} \tag{3}$$

They can also be written as

$$\begin{aligned} \bar{n}_+ &= n\exp\left(-e\psi_D/kT\right) \\ \bar{n}_- &= n\exp\left(e\psi_D/kT\right) \end{aligned} \tag{4}$$

where

$$i\Gamma_M = 2n\delta\sinh\frac{e\psi_D}{kT} \tag{5}$$

The surface excesses of diffusible ions may be defined as

$$\begin{aligned} \Gamma_+ &= \delta(\bar{n}_+ - n) \\ \Gamma_- &= \delta(\bar{n}_- - n) \end{aligned} \tag{6}$$

and the surface concentration of the ionized group is

$$i\Gamma_M = 1/A \tag{7}$$

where $A$ is the area per ionized group.

In order to determine the thickness of the surface phase, $\delta$, and the potential of ionized groups of monolayer, $\psi_M$, one must take account of the results of the theory of diffuse double layer. According to the theory, concentrations of diffusible ions at the depth, $x$, below the surface, where the electrostatic potential is $\psi$, are given by

$$\begin{aligned} n_+ &= n\exp\left(-e\psi/kT\right) \\ n_- &= n\exp\left(e\psi/kT\right) \end{aligned} \tag{8}$$

where $n$ is the concentration of each ion or salt far away from the surface. Their surface excesses may be defined by

$$\begin{aligned} \Gamma_+ &= \int_0^\infty (n_+ - n)\,\mathrm{d}x \\ \Gamma_- &= \int_0^\infty (n_- - n)\,\mathrm{d}x \end{aligned} \tag{9}$$

which lead to

$$\begin{aligned} \Gamma_+ &= \frac{2n}{\kappa}\left\{\exp\left(-\frac{e\psi_G}{2kT}\right)-1\right\} \\ \Gamma_- &= \frac{2n}{\kappa}\left\{\exp\left(\frac{e\psi_G}{2kT}\right)-1\right\} \end{aligned} \tag{10}$$

Here $\psi_G$ is the potential at the surface, $x=0$, and $\kappa$ is the Debye-Hückel parameter

$$\kappa^2 = \frac{8\pi n e^2}{\varepsilon kT} \tag{11}$$

$\varepsilon$ being the dielectric constant. As for the distribution of diffusible ions, the present treatment corresponds to an averaged procedure of the theory of diffuse double layer. Thus, equating Eq. 6 to Eq. 10, it follows that

$$\delta = 2/\kappa \tag{12}$$

and

$$\psi_D = \psi_G/2 \tag{13}$$

The electrostatic potential of ionized groups of monolayer, $\psi_M$, should be equal to the Gouy potential, $\psi_G$. Hence, it is twice as high as the electrostatic potential of diffusible ions, or the membrane potential, $\psi_D$.

$$\psi_M = 2\psi_D \tag{14}$$

It may be assumed generally in the treatment of ionized monolayers based on the present model of surface phase that the thickness of surface phase is given by $2/\kappa$ and the electrostatic potential of ionized groups is twice as high as that of diffusible ions.

### Improved Approximation for the Distribution of Ions

The distribution of diffusible ions obtained in the previous section has been derived from a simple assumption that the surface phase is electrically neutral. In this section one will develop an approximate method when this assumption is removed.

When the surface and bulk phases are distinguished from each other, the electrostatic potential, $\psi$, of diffusible ions follows the Poisson equations

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\frac{4\pi e}{\varepsilon}\left(\frac{i\Gamma_M}{\delta}+n_+-n_-\right)$$

$$\text{for } x \leq \delta \text{ (surface phase)} \tag{15}$$

$$= -\frac{4\pi e}{\varepsilon}(n_+ - n_-)$$

$$\text{for } x \geq \delta \text{ (bulk phase)} \tag{16}$$

where $\delta = 2/\kappa$, and their concentrations are given by equations formally identical with

Eq. 8. Eqs. 8 and 15 imply that the surface phase is not always electrically neutral.

In order to solve the Poisson-Boltzmann equations, Eqs. 15 and 16 with Eqs. 8, it will be assumed that the surface phase deviates slightly from being electroneutral. In such a case the "$\lambda$-method", which was devised for solving the problem of polyelectrolyte solution⁷⁾, might be applied to the present equations. Then a quantity $\lambda$ is defined as

$$\frac{i\Gamma_M}{\delta}+n_+-n_-=\frac{i\Gamma_M}{\delta}\lambda \tag{17}$$

$$\lambda \ll 1 \tag{18}$$

Evidently, the problem is reduced to that of the membrane equilibrium, if $\lambda=0$. From Eqs. 8 and 17, it follows that

$$\sinh\frac{e\psi}{kT}=\frac{i\Gamma_M}{2n\delta}(1-\lambda) \tag{19}$$

Expanding $e\psi/kT$ in a series of $\lambda$ using Eq. 19 and ignoring the terms higher than $\lambda$, one obtains

$$\frac{e\psi}{kT}=\ln\frac{i\Gamma_M+\sqrt{(i\Gamma_M)^2+4(n\delta)^2}}{2n\delta}-\frac{i\Gamma_M\lambda}{\sqrt{(i\Gamma_M)^2+4(n\delta)^2}} \tag{20}$$

and

$$\lambda=\frac{\sqrt{(i\Gamma_M)^2+4(n\delta)^2}}{i\Gamma_M}\left[-\frac{e\psi}{kT}+\ln\frac{i\Gamma_M+\sqrt{(i\Gamma_M)^2+4(n\delta)^2}}{2n\delta}\right] \tag{21}$$

Then, instead of Eq. 15, one has a linear equation

$$\frac{d^2\lambda}{dx^2}=\chi^2\lambda \tag{22}$$

or

$$\frac{d^2\psi}{dx^2}=\chi^2(\psi-\psi_D) \tag{23}$$

where

$$\chi^2=\frac{4\pi e^2}{\varepsilon kT}\sqrt{\left(\frac{i\Gamma_M}{\delta}\right)^2+4n^2} \tag{24}$$

and

$$\frac{e\psi_D}{kT}=\ln\frac{i\Gamma_M+\sqrt{(i\Gamma_M)^2+4(n\delta)^2}}{2n\delta} \tag{5a}$$

The most general boundary conditions for Eqs. 15 and 16 are given by

$$(d\psi/dx)_{x=0}=0 \tag{25}$$

$$\psi \text{ and } d\psi/dx : \text{continuous at } x=\delta \tag{26}$$

and

$$\psi_{x=\infty}=(d\psi/dx)_{x=\infty}=0 \tag{27}$$

Under these conditions one can obtain solutions which correspond to those derivd by Lifson⁸⁾ and Nagasawa and Kagawa⁹⁾ for the polyelectrolyte solution. For the sake of simplicity, however, a simpler condition

$$\psi_{x=0}=0 \tag{26a}$$

is chosen here instead of the second condition (26). This means that $\psi=0$ and $n_+=n_-=n$ in the bulk phase ($x\geq\delta$). Thus the surface phase ($x\leq\delta$) may be treated separately. The solutions of Eqs. 22 and 23 are found to be

$$\lambda=\frac{\sqrt{(i\Gamma_M)^2+4(n\delta)^2}}{i\Gamma_M}\frac{e\psi_D}{kT}\frac{\cosh\chi x}{\cosh\chi\delta} \tag{28}$$

and

$$\psi=\psi_D\left(1-\frac{\cosh\chi x}{\cosh\chi\delta}\right) \tag{29}$$

respectively.

After this, one will be concerned with the mean concentrations and the mean potential of ions in the surface phase. By a simple averaging procedure or by Gauss's theorem of electrostatics, the mean value of $\lambda$ is calculated to be

$$\langle\lambda\rangle=\frac{\sqrt{(i\Gamma_M)^2+4(n\delta)^2}}{i\Gamma_M}\frac{e\psi_D}{kT}\frac{\tanh\chi\delta}{\chi\delta} \tag{30}$$

The mean concentrations of cation and anion in the surface phase are then represented by

$$\begin{aligned}\langle n_+\rangle&=\frac{1}{2}\left\{-\frac{i\Gamma_M}{\delta}+\sqrt{\left(\frac{i\Gamma_M}{\delta}\right)^2+4n^2}\right\}\times\left\{1+\frac{i\Gamma_M\langle\lambda\rangle}{\sqrt{(i\Gamma_M)^2+4(n\delta)^2}}\right\}\\ \langle n_-\rangle&=\frac{1}{2}\left\{\frac{i\Gamma_M}{\delta}+\sqrt{\left(\frac{i\Gamma_M}{\delta}\right)^2+4n^2}\right\}\times\left\{1-\frac{i\Gamma_M\langle\lambda\rangle}{\sqrt{(i\Gamma_M)^2+4(n\delta)^2}}\right\}\end{aligned} \tag{31}$$

respectively, and their surface excesses are defined by

$$\begin{aligned}\Gamma_+&=\delta(\langle n_+\rangle-n)\\ \Gamma_-&=\delta(\langle n_-\rangle-n)\end{aligned} \tag{32}$$

respectively. The mean electric potential of diffusible ions in the surface phase is given by

$$\langle\psi\rangle=\psi_D\left(1-\frac{\tanh\chi\delta}{\chi\delta}\right) \tag{33}$$

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7) F. Oosawa, N. Imai and I. Kagawa, *J. Polymer Sci.*, **13**, 93 (1953).

8) S. Lifson, *J. Chem. Phys.*, **27**, 700 (1957).

9) M. Nagasawa and I. Kagawa, This Bulletin, **31**, 961 (1958).

The potential of ionized groups of monolayer is assumed to be defined by

$$\psi_M = 2\langle\psi\rangle \tag{34}$$

as described before. Then one has

$$\langle n_+\rangle/n = n/\langle n_-\rangle = \exp\left(-e\psi_M/2\boldsymbol{k}T\right) \tag{35}$$

### Contribution of Ionization to Surface Pressure and Potential

When a monolayer is ionized and charged positively, diffusible ions in aqueous subphase become distributed between the surface and the bulk phase, as given by Eq. 3 or 31, and the electrostatic potential of the monolayer becomes higher than that of the diffusible ions in the bulk phase by the amount $\psi_M$, as given by Eq. 14 or 34. The thermodynamic equilibrium is established by accompanying the decrease in surface free energy, i. e. the increase of surface pressure. The relationship between the increment of surface pressure and the ionic concentrations will be described by an equation such as the Gibbs absorption isotherm. At a constant surface concentration of monolayer, the surface pressure, $\Pi_i$, due to the ionization of monolayer can be expressed by

$$\mathrm{d}\Pi_i = \boldsymbol{k}T(\Gamma_+ + \Gamma_-)\,\mathrm{d}\ln n + i\Gamma_M \mathrm{d}(e\psi_M) \tag{36}$$

In the following formula one will carry out the integration of Eq. 36 in the case of the $\lambda$-approximation, since the results from the treatment of membrane equilibrium can be derived as a limiting case. Inserting Eqs. 31 and 32 into Eq. 36 and neglecting the terms higher than $\lambda$, it may be written as

$$\mathrm{d}\Pi_i = \boldsymbol{k}T\left\{-2n\delta + \sqrt{(i\Gamma_M)^2 + 4(n\delta)^2} - \frac{(i\Gamma_M)^2\langle\lambda\rangle}{\sqrt{(i\Gamma_M)^2 + 4(n\delta)^2}}\right\}\mathrm{d}\ln n + i\Gamma_M \mathrm{d}(e\psi_M) \tag{37}$$

Integration leads to

$$\Pi_i = 2\boldsymbol{k}T\left\{-2n\delta + \sqrt{(i\Gamma_M)^2 + 4(n\delta)^2} - \frac{(i\Gamma_M)^2\langle\lambda\rangle}{\sqrt{(i\Gamma_M)^2 + 4(n\delta)^2}}\right\} - \boldsymbol{k}T(i\Gamma_M)^2\int_\infty^n \frac{\langle\lambda\rangle}{\sqrt{(i\Gamma_M)^2 + 4(n\delta)^2}}\frac{\mathrm{d}n}{n} \tag{38}$$

provided that the integration constant is chosen so as to be $\Pi_i = 0$ at the infinite salt concentration. If the last term with a complicated integral is ignored, it follows that

$$\Pi_i = 2\boldsymbol{k}T(\Gamma_+ + \Gamma_-) \tag{39}$$

$$= 2\boldsymbol{k}T\delta(\langle n_+\rangle + \langle n_-\rangle - 2n) \tag{40}$$

In the approximation of membrane equilibrium, $\langle\lambda\rangle = 0$, Eq. 40 reduces to

$$\Pi_i = 2\boldsymbol{k}T\delta(\bar{n}_+ + \bar{n}_- - 2n) \tag{41}$$

Eqs. 40 and 41 represent a colligative nature of surface pressure at a low surface concentration of monolayer. Eqs. 40 and 41 can be rewritten by the use of measurable quantities as

$$\Pi_i = 2\boldsymbol{k}T\left\{-\frac{4n}{\kappa} + \sqrt{\frac{1}{A^2} + \left(\frac{4n}{\kappa}\right)^2} - \frac{1}{A^2}\frac{\langle\lambda\rangle}{\sqrt{\frac{1}{A^2} + \left(\frac{4n}{\kappa}\right)^2}}\right\} \tag{42}$$

and

$$\Pi_i = 2\boldsymbol{k}T\left\{-\frac{4n}{\kappa} + \sqrt{\frac{1}{A^2} + \left(\frac{4n}{\kappa}\right)^2}\right\} \tag{43}$$

respectively, and by the use of the electrostatic potential of monolayer the above two equation become as follows:

$$\Pi_i = 4n\delta\boldsymbol{k}T\left(\cosh\frac{e\psi_M}{2\boldsymbol{k}T} - 1\right) \tag{44}$$

Eq. 44 in the case of $\langle\lambda\rangle = 0$ is in complete agreement with the equation derived from the theory of diffuse double layer

$$\Pi_i = \frac{8n\boldsymbol{k}T}{\kappa}\left(\cosh\frac{e\psi_G}{2\boldsymbol{k}T} - 1\right) \tag{45}$$

which should be expected if Eqs. 12—14 hold.

The situation that the same results follow both from the treatments of membrane equilibrium and of diffuse double layer has also been noticed in the theory of polyelectrolyte solution[9,10]. Further, it would be more plausible to assume that $\delta = 2/\kappa$, although it had always been assumed that $\delta = 1/\kappa$[11].

If the surface pressure of unionized monolayer is $\Pi_0$, the observed surface pressure of ionized monolayer can be expressed by

$$\Pi = \Pi_0 + \Pi_i \tag{46}$$

Thus, the surface pressure of ionized

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[10] J. J. Hermans and J. Th. G. Overbeek, *Rec. trav. chim.*, **67**, 761 (1948); G. E. Kimball, M. Cutler and H. Samelson, *J. Phys. Chem.*, **56**, 57 (1952); P. J. Flory, "Principles of Polymer Chemistry", Cornell Univ. Press, Ithaca, N. Y. (1953), p. 854 ff.

[11] J. F. Danielli, *Biochem. J.*, **35**, 470 (1941); J. T. Davies and E. K. Rideal, *J. Colloid Sci.*, **3**, 313 (1948); J. F. Danielli and J. T. Davies, *Adv. Enzymol.*, **11**, 35 (1951); J. J. Betts and B. A. Pethica, *Trans. Faraday Soc.*, **52**, 1581 (1956).

TABLE I

$T=293°\text{K}$, $\varepsilon=80$

1) *Octadecyltrimethylammonium chloride on* NaCl

$A=85\ \text{A}^2$ per long chain ion

| $n$ mol./l. | $\delta$ A | $\Pi_i$ (Eq. 43) | $\Pi$ dyn./cm. | $\Pi_0$ | $\phi_D$ mV. | $\bar{n}_+$ mol./l. | $\bar{n}_-$ |
|---|---|---|---|---|---|---|---|
| 0.033 | 33.6 | 8.46 | 5.8 | −2.66 | 72.4 | 0.00188 | 0.583 |
| 0.10 | 19.3 | 7.80 | 5.3 | −2.50 | 62.0 | 0.00853 | 1.17 |
| 0.50 | 8.62 | 6.18 | 3.8 | −2.38 | 42.4 | 0.0935 | 2.69 |
| 2.0 | 4.32 | 4.28 | 2.7 | −1.58 | 27.2 | 0.676 | 5.88 |

$\Pi_0=-3.5$ (Davies)

2) *Copoly-1 : 3 : 1-(L-lysine, L-phenylalanine, L-glutamic acid) on* KCl *in* 0.005 N HCl

$n=n_{\text{HCl}}+n_{\text{KCl}}$

$A=20\times5\ \text{A}^2$ per ionized group (L-lysyl residue)

| $n$ mol./l. | $\delta$ A | $\Pi_i$ (Eq. 43) | $\Pi$ dyn./cm. | $\Pi_0$ | $\phi_D$ mV. | $\bar{n}_+$ mol./l. | $\bar{n}_-$ |
|---|---|---|---|---|---|---|---|
| 0.040 | 30.5 | 6.90 | 0.65 | −6.25 | 64.5 | 0.00347 | 0.581 |
| 0.075 | 22.3 | 6.56 | 0.55 | −6.11 | 57.4 | 0.00817 | 0.780 |
| 0.135 | 16.6 | 6·16 | 0.30 | −5.86 | 50.4 | 0.0189 | 1.033 |
| 0.405 | 9.59 | 5.12 | 0.05 | −5.07 | 37.8 | 0·0915 | 1.843 |

$\Pi_0=-5.8$ (Hamaguchi and Isemura)

monolayer is higher at lower salt concentration, and, conversely, it is lower at higher salt concentration. At sufficiently high salt concentrations, $\Pi_i=0$ and, accordingly, $\Pi=\Pi_0$. (A polyelectrolyte monolayer exerts an additional surface pressure due to the elastic deformation of polymer chains on ionization, but the inference mentioned here remains unaltered.)

The surface potential of ionized monolayer measured experimentally has the form[1,12]

$$\Delta V=\frac{4\pi\mu}{A}+\phi_M \tag{47}$$

where $\mu$ is the surface moment per ionized group. At sufficiently high salt concentrations, $\phi_M=0$ and, accordingly, $\Delta V=4\pi\mu/A$. At low salt concentrations,

$$\left(\frac{\partial\Delta V}{\partial\ln n}\right)_{i\Gamma_M\text{ or }A}=\left(\frac{\partial\phi_M}{\partial\ln n}\right)_{i\Gamma_M\text{ or }A}=-\frac{Tk}{e} \tag{48}$$

as already found by Crisp[13].

## Comparison with Experiments

The results obtained above from either treatment for ionized monolayers, the approximation of membrane equilibrium or the $\lambda$-method, can be readily examined with experimental data, by comparing the values of $\Pi_0$ and $\mu$ at various salt concentrations, which can be evaluated by subtracting the calculated values of $\Pi_i$ and $\phi_M$ from the observed values of $\Pi$ and $\Delta V$, respectively. If the treatments were valid, the $\Pi_0$ and $\mu$ values should be independent of salt concentration. One has applied the procedure to the available data on surface pressure of two typically different monolayers, i. e. those of octadecyltrimethylammonium chloride*[,1] and of copoly-1 : 3 : 1-(L-lysine, L-phenylalanine, L-glutamic acid)**[,4].

For the approximation of membrane equilibrium, using Eq. 43 for $\Pi_i$, the results as shown in Table I are obtained. It can be seen that the $\Pi_0$ values are not independent of salt concentration. Further, all these values are found to be negative. The negative $\Pi_0$ values imply that the corresponding unionized monolayers would contract in themselves rather than spread on aqueous surfaces. Davies' suggestion that the ionized monolayers would be condensed into "islands" or micelles is not valid, since the ionized monolayers do not contract but only form condensed films on strong salt solutions. This inconsistency may be ascribed to an overestimate of $\Pi_i$ values. The too high contribution of ionization to monolayer properties

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[12] J. H. Schulman and A. H. Hughes, *Proc. Roy. Soc.*, **A138**, 430 (1932).

[13] D. J. Crisp, Research, "Surface Chemistry", Butterworths Scientific Publications, London (1949), p. 65.

* For this monolayer, a constant value of $\mu$ was noticed by Davies[1]. However, the $\mu$ value appears to be insensitive to salt concentration.

** If the deformation of polymer chains on ionization is taken into account, the $\Pi_0$ values would be lower than those in Table I, in which this contribution is not involved.

comes from the distribution of counter ions being too much concentrated in the surface phase and of co-ions being too much repelled from there. Indeed, the present approximation sometimes leads to concentration of counter ions in the surface phase being more than ten times as high as that in the bulk phase.

It can be expected that this difficulty will be partly avoided by removing the assumption of the electroneutral surface phase. The $\lambda$-approximation has led to the surface pressure due to ionization given by Eq. 42, which is lower than that obtained by the approximation of membrane equilibrium, Eq. 43, by the amount

$$\frac{kT}{A}\ln\left[\frac{1/A+\sqrt{(1/A)^2+(4n/\kappa)^2}}{-1/A+\sqrt{(1/A)^2+(4n/\kappa)^2}}\right]\times\frac{\kappa}{2\chi}\tanh\frac{2\chi}{\kappa}$$

To confirm this, the data for the monolayer of octadecyltrimethylammonium chloride has been treated by Eq. 42 in a manner as previously. The results are shown in Table II. It can be seen that the $\Pi_0$ values are independent of salt concentration and are always positive. Thus, the inconsistency which was encountered previously in the method of membrane equilibrium is not revealed in the $\lambda$-approximation.

TABLE II

*Octadecyltrimethylammonium chloride on* NaCl, $T=293°\text{K}$, $\varepsilon=80$

$A=85\ \text{A}^2$ per long chain ion

| $n$ mol./l. | $\Pi_i$ (Eq. 42) dyn./cm. | $\Pi$ | $\Pi_0$ | $\langle\lambda\rangle$ |
|---|---|---|---|---|
| 0.033 | 3.87 | 5.8 | 1.93 | 0.487 |
| 0.100 | 2.99 | 5.3 | 2.31 | 0.509 |
| 0.50 | 1.40 | 3.8 | 2.40 | 0.539 |
| 2.0 | 0.34 | 2.7 | 2.36 | 0.523 |

The advantage of the $\lambda$-method is, however, only superficial. When the surface concentration of monolayer is not low enough, the last term of an integral in Eq. 38, which can not be easily estimated, becomes significant. Moreover, it is found from Table II that all the $\langle\lambda\rangle$ values are about 0.5 and incompatible with the fundamental assumption, Eq. 18. It may, therefore, be stated that the $\lambda$-method, as well as the approximation of membrane equilibrium, can not explain completely the effect of ionization on the typically expanded monolayer of octadecyltrimethylammonium chloride. The method is also found to be insufficient to elucidate consistently the ionization behavior of the condensed monolayer of copoly-1:3:1-(L-lysine, L-phenylalanine, L-glutamic acid).

The main purpose of the theory consists in a description of the experimental fact that an ionized monolayer is more condensed on concentrated salt solutions and is more expanded on dilute solutions. The present theory has, however, given explanations of only a part of the observations that higher salt concentrations reduce surface pressure of an ionized monolayer more than lower salt concentrations do. Generally, an ionized monolayer has an area where the reversal of surface pressure occurs, which is independent of salt concentration but dependent on salt species[5]: at the area larger than this, the surface pressure is lower at higher salt concentrations and at the smaller area it is reversed. Hence, the present theory concerns only the region of large area. It seems likely that for a comprehensive interpretation of the behavior of ionized monolayers the assumption of uniformly distributed ionized groups in the surface phase should be modified and penetration of ions into the surface phase, finite dimension of ions, association effect and other individual characteristics of ions should be taken into account.

## Summary

The effect of salt on ionized monolayers is treated with a model of "surface phase", in which ionized groups of monolayers are dissolved uniformly. To obtain the distribution of diffusible ions between the surface and bulk phases, the method of membrane equilibrium and the $\lambda$-approximation are employed. The former method is a special case of the latter. The contribution of ionization to surface pressure is calculated thermodynamically. The results derived from the former method are found to be in complete agreement with those derived from the theory of diffuse double layer, if the thickness of surface phase is chosen as $2/\kappa$ and the electric potential of ionized groups is twice as high as the membrane potential. On examining two typically different monolayers, the former method reveals some contradiction, although it explains experimental data qualitively. The latter method, which is more general, can overcome the difficulty and gives reasonable values for surface pressure of an expanded monolayer. It is

found, however, that even the $\lambda$-approximation is still unsatisfactory to describe the behavior of ionized monolayers in the range of area with which they are ordinarily concerned.

A part of the expense for this work was defrayed by the Ministry of Education, to which the authors' thanks are due.

*Faculty of Science*
*and*
*Institute for Protein Research*
*Osaka University*
*Osaka*