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Conference Abstract

Ion Binding and Exchange by Ionized Monolayers as Related to their Surface Potential*

L. Ter-Minassian-Saraga

Université René Descartes, Paris, France

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Ionized monolayers at the surface of aqueous solutions form planar arrays of charged sites. When they are constituted by soap molecules they may be distributed uniformly over the surface. When they are formed by polyelectrolytes, the shape and structure of the polyions determine the real spacing between the charged sites and the real local charge density may be different from the average surface density of the monolayer.

The local charge density directs the distribution of the counter-ions as well as the value of the electric potential difference set up between the ionized system: monolayer or polyion — and the aqueous solution.

Stern[1] has assumed that non-electrostatic short-range interactions may lead to ion binding by the surfaces. From their study of the surface potential of ionized soap monolayers Bell *et al.*[2] have concluded that counterion binding may be mainly due to electrostatic interactions and increase with the surface density of the monolayer. In this type of work the surface potential is measured and from it the distribution of the counterions is deduced.

A very similar approach has been extensively used by those[3] studying colligative or transport properties of polyelectrolyte solutions or gels. In this type of work the electric potential between the charged plane of the polyion and the solution is deduced from measurements of the distribution of a neutral salt between the polyelectrolyte system and the aqueous phase (Donnan equilibrium). Finally it has been suggested[3] that the displacement of the equilibrium of an ionic reaction taking place at the boundary of the polyelectrolyte molecule may allow the determination of the electric potential at this boundary. The charging of a polymer molecule, either by neutralization of a polyacid or by quaternization of its amino groups has been studied[3]. The local or apparent pK of these reactions, which vary with the charge density, has been related to the calculated ionic distribution and electric potential.

In the present work both variations of the local electric potentials and displacement of equilibria of ionic reactions, namely ion exchange, are determined for the same ionized monolayers formed either by soap molecules or by polyelectrolytes. This was done in order to get a clearer picture of the type of ionic associations in these ionized systems.

METHODS

Ion exchange reactions[4–5]. — Ionized films of known surface concentrations are formed either by adsorbing or by spreading their molecules at the surfaces of aqueous solutions containing radioactive counterions: $PoCl_6^{2-}$ or $^{45}Ca^{2+}$. A Geiger counter, placed over the solutions, detects the intensity of radiation emitted by the atoms at and next to the surfaces. From this measurement and a suitable calibration, the surface density of the counterions exchanged or removed by the films from the underlying solution, is calculated. The amount of unexchanged counterions is deduced by substraction from the known total number of ionizing molecules or groups of the film.

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Surface potential measurements[6]. — The surface potential ΔV is measured by a differential device using two radioactive Am/Gold electrodoes located above two surfaces of aqueous solutions, one of them carrying a film. The measured electric potential difference is the surface potential of the monolayer and is equal to the difference between the outer potentials near the two aqueous surfaces.

RESULTS

Two ion exchange reactions have been studied:

$$PoCl_6^{2-} + XCl \rightleftarrows XPoCl_6^- + Cl^- \qquad (1)$$

$$\begin{aligned} &a)\ Ca^{2+} + YNa \rightleftarrows YCa^+ + Na^+ \\ &b)\ Ca^{2+} + YH \rightleftarrows YCa^+ + H^+ \end{aligned} \qquad (2)$$

In both cases a divalent ion displaces a monovalent one from a singly charged site. X is the cation of a cationic soap; Y is a carboxylate site of the polyelectrolyte molecule.

Reaction (1)

Reaction (1) has been studied with monolayers of three cationic soaps[4-6]: hexadecyltrimethylammonium bromide, hexadecylpyridinium chloride, dodecyltrimethylammonium bromide. It has been found that both the ion ecxhange equilibrium constant and the surface potential increase with the surface density of the ionized monolayer[4].

The partition coefficient K of the $PoCl_6^{2-}$ ion verifies the relation (1)[6]. It is equal to:

$$K = K_0\, e^{-ze\Delta V/kT}$$

where K_0 is a constant, k, T, z and e are the Boltzmann constant, the temperature, the charge number of the counterion and the electronic charge.

Reaction (2)

The ion exchangers are formed by spreading a polydiacid, the alternate copolymer of maleic acid hexadecylvinylether (HPA), at the surface of the substrates of various NaCl and $^{45}CaCl_2$ concentrations and pH.

In the absence of $CaCl_2$, the surface potential ΔV of the HPA films of a given density is decreased by the neutralization of the carboxylic groups. This curve, $\Delta V = f(pH)$, is obtained by the surface titration of the film. The increase of the ionic strength (NaCl concentration) of the aqueous subsolution does not change the ΔV. It is inferred, from these experiments, that although dissociation of carboxylic groups takes place, the counterions, mostly Na^+, form ion pairs with the carboxylate sites. The degree of dissociation — or neutralization — is calculated using the expression:

$$\alpha = \frac{\Delta V(pH) - \Delta V(2.7)}{\Delta V(10) - \Delta V(2.7)} \qquad (4)$$

The difference $[\Delta V(10) - \Delta V(2.7)]$ is equal to that found by Goddard[7] from titration curves of stearic acid monolayers. Strauss[8] has shown that for pH values lower than 10, only the first ionization of the maleic acid residue ocurrs. Then, it is assumed that the degree of neutralization α is equal to zero at $pH = 2.7$ and to 1 at $pH = 10$.

Values of α have been deduced at low and high average surface densities of HPA films. They are not different, showing that the ionization depends on the local intersite distance determined by the structure of the copolymer HPA.

Applying the equation of Henderson-Hasselbach, we calculate the variation of the apparent equilibrium constant of the first ionization of HPA with the degree of neutralization α of the film:

$$pK_{app} = pH + \log\frac{1-\alpha}{\alpha} = pK_1^0 + \frac{\Delta G^{el}}{RT} \qquad (5)$$

where K_{app} and K_1^0 are the equilibrium constants at $\alpha \neq 0$ and $\alpha = 0$ respectively and ΔG is the free enthalpy of the dissociation constant of one carboxyl group. We find also that

$$pK_{app} = \text{const} - \frac{e \, \Delta \, V(\alpha)}{2.3 \, kT} \qquad (6)$$

Comparing (5) and (6) it follows that the free enthalpy of ionization is given by the relation:

$$\Delta \, G^{el} = \text{const} - N_A \, e \, \Delta \, V \qquad (7)$$

where N_A is Avogadro's number. It follows that the variations of the partial free enthalpy of neutralization may be deduced from the variations of the surface potential. Furthermore our results show that $\Delta \, G^{el}$ is a linear function of α: see eqs. (7) and (4).

Exchange Ca/Na

When $CaCl_2$ is added to the aqueous substrate, Ca^{2+} ions displace H^+ or Na^+ counterions of the HPA film according to the relation (2). This reaction has been studied at pH 6 and 8 for:

— various concentrations of $CaCl_2$, pH of substrate and NaCl concentrations — at a given concentration of $CaCl_2$ and NaCl, as a function of pH.

The surface potentials of the HPA films have been measured under the same conditions as the ion exchange (2).

It has been found that at pH = 8 where $\alpha = 1$:

- the replacement of one Na by one Ca increases the surface potential which becomes more positive;
- the increase in pH increases the amount of Ca/Na exchange;
- Ca^{2+} is displaced by Na^+.

All these findings seem to verify the following law of mass action:

$$K_{app} = \frac{a_{Na} \, \Theta}{a_{Ca} \, (\alpha - \Theta)} = A_{exp} \left[- \frac{e \, \Delta \, V(\Theta, \alpha)}{kT} \right]$$

where Θ is the fraction of carboxylate groups occupied by Ca^{2+} ions, A is a constant and a_{Na}, a_{Ca} are the ionic activities in the solution.

As in the case of the neutralization reaction, the free enthalpy of the ion exchange varies with the degree of exchange Θ and of charging of surface α. It may be related to the corresponding variation of the surface potential which translates the variation of the electrostatic free enthalpy of the counterion — site pair.

CONCLUSION AND BIOLOGICAL IMPLICATIONS

The study of the surface potential of ionized films as well as of the counterion exchange by these systems has led us to the conclusion that most or the counterions form ion pairs with the charged sites of the films.

The results obtained for the exchanges $PoCl_6^{2-}/Cl^-$ and Ca^{2+}/Na^+ indicate that a divalent counterion may form an ion pair with a singly charged site and reverse the charge of the last one. The electrostatic free enthalpy associated with this process is responsible for the variation of the apparent equilibrium constant of ion exchange with the degree of exchange. In particular the Ca/Na ion exchange leads to an increase in the absolute value of the surface potential.

According to recent studies[9-11] the binding of Ca ions to nerve cell membranes may bring about an increase in their interfacial potential in a way, which we believe, may be explained by our results.

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