Specific Counterion Effects in Surface and Colloid Chemistry. Ionized Monolayers

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Data are presented on the effect of various monovalent cations on the π-A and ΔV-A characteristics of charged insoluble monolayers. The following interaction sequences were established: R—COO⁻,   Li $>$ Na $>$ K $>$ tetramethylammonium $>$ tetraethylammonium; R—SO$_4^-$, Cs = Rb $>$ K $>$ Na $>$ Li; R—N (CH$_3$)$_3^+$, SCN $>$ $>$ I $>$ NO$_3$ $>$ Br $>$ Cl $>$ F; R—NH(CH$_3$)$_2^+$ and R—NH$_3^+$, Br $>$ Cl. The results thus parallel data on ion sequence effects reported in other branches of colloid and physical chemistry. They are discussed in the light of various hypotheses advanced to explain these effects.

The monolayer π-A curves were compared with those predicted from theoretically derived equations of state: agreement was generally poor.

INTRODUCTION

Specific counterion effects in colloid chemistry are well known under such names as the »Hofmeister« or »lyotropic« series[1]. The original work referred to the different ability of ions, with the same magnitude and sign of charge, to flocculate colloidal particles bearing a charge of opposite sign. More recently, investigations have been reported[2-5] of the effect of counterions on ionic surfactant aggregates, viz., micelles, but less studied have been specific counterion effects on long chain ionic surfactants in the form of charged monolayers. This is despite the fact that many investigations have been made into the properties of such monolayers at both the water/air and water/oil interface. The insoluble monolayer method has considerable advantages for studies of this type. The technique is simple, the factors affecting surface pressure, area (π-A) and surface potential, area (ΔV-A) characteristics have been extensively examined and documented, and it is a matter of extreme ease to control and/or vary the charge density at the interface.

The monolayers investigated in the study reported below were $C_{19}H_{39}$—COO⁻, R—SO$_4^-$, R—N(CH$_3$)$_3^+$, R—NH(CH$_3$)$_2^+$, R—NH$_4^\infty$, where R = $C_{22}H_{45}$.

EXPERIMENTAL

The arachidic acid[6], sodium docosyl sulfate and docosylammonium bromides were all high purity specimens and have been described[7]. Details of the Langmuir film balance have been presented elsewhere[8]. The alkali metal salts and hydroxides used were all of analytical grade as were the tetramethylammonium (TMA) and tetraethylammonium (TEA) bromide and hydroxide specimens.

RESULTS

We consider first monolayers of the C_{20} fatty acid, arachidic acid, spread on pH 12 subsolutions of a 0.01 M alkali metal or tetraalkylammonium (TAA) hydroxide. It is seen from Fig. 1 that there is a considerable difference in
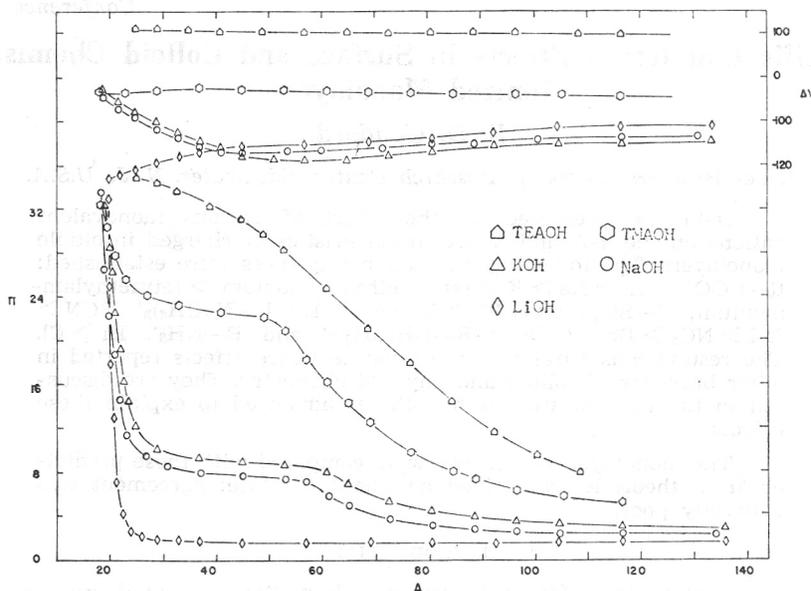

Fig. 1. π—A and $\triangle$V—A isotherms of arachidic acid on 0.01M alkali subsolutions at 25° C.

the π-A characteristics as the counterion is changed among the alkali metal ions, Li giving the most condensed monolayer, followed by Na and then K. A pronounced expansion occurs with TAA ions. These results imply that the electrical contribution[9] to the surface pressure is least for Li and thus that interaction with the COO⁻ group is strongest in this case. This is also supported by the increase in negative surface potential, in the sequence Li to Na to K, which is observed over most of the area range. In experiments not shown, predictions of the Davies[9] equation (based on the Gouy-Chapman model) of lower surface pressures and lower (negative) surface potentials with increased concentration of salt in the subsolution were confirmed. As will be discussed later, in one instance, viz., with TMA as counterion, reasonable agreement was obtained between the experimental π-A curve and that derived from the Davies equation. Furthermore, as predicted by the Gouy-Chapman model, a change of 59mV in surface potential was observed when the TMA concentration was increased from 0.01 to 0.1 M for monolayers in the expanded state.

The sequence of interaction with COO⁻ derived from the above π-A results is Li > Na > K > TMA > TEA. The $\triangle$V data indicate the same sequence for the alkali metal ions but not for the TAA ions. The much more positive $\triangle$V values obtained with the latter are connected with the different electrical characteristics of these ions and probably also with their larger size.

Turning to the docosyl sulfate monolayers, we see (Fig. 2) there are again large differences in monolayer characteristics as the monovalent counterion is changed. For the alkali metals the sequence of contraction is Li < Na < K < Rb = Cs, which is just the opposite of the fatty acid case. The surface potentials for the alkali metal ions again follow the sequence

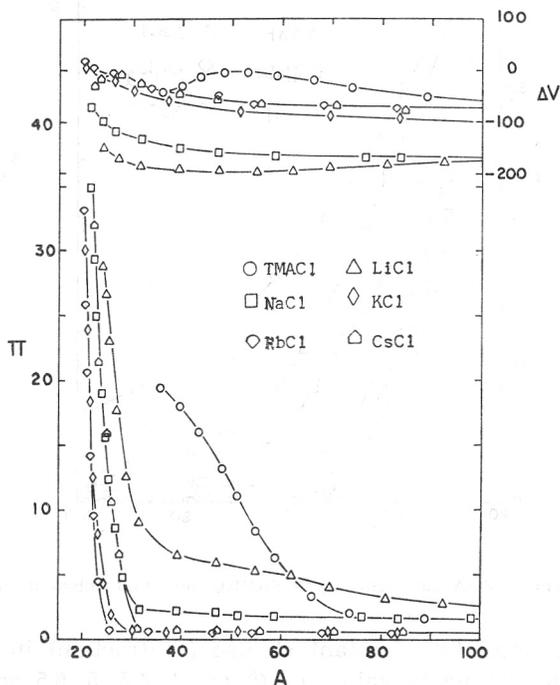Fig. 2. π—A and △V—A isotherms of docosyl sulfate on 0.0001M subsolutions at 25° C.

of the π-A curves. Earlier work[3] on the lowering of CMC of sodium lauryl sulfate by univalent cations had indicated stronger interaction of TAA ions than alkali metal ions with alkyl sulfate micelles. However the π-A data presented here do not allow TMA to be ranked unequivocally. We believe that counterion size effects, in the case of the TMA and Cs ion, account for the larger limiting areas observed with these two ions. See Fig. 2. Reduction in surface pressure and negative surface potential was again observed on increasing salt concentration in the subsolution, in qualitative conformity with the predictions of the electrical model.

With the long chain quaternary ammonium monolayer, $C_{22}H_{45}N(CH_3)_3^+$, major differences were found in the effect of the different monovalent anions on the π-A curves; these were again paralleled by the ΔV data. See Fig. 3. The interaction sequence is $SCN > I > NO_3 > Br > Cl > F$. With a swamping concentration of the least interacting anion (F) present, as little as 10^{-6} M added SCN led to a detectable effect on the π-A curve. This affords a method of estimating the specific interaction energy (ϕ) of the different ions with the $—N(CH_3)_3^+$ head group; the concentration of added counterion necessary

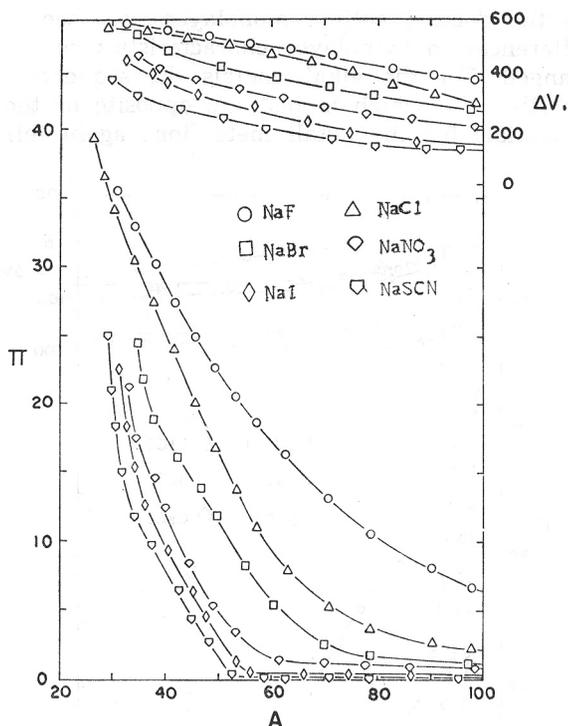Fig. 3. π—A and $\triangle$V—A isotherms of $C_{22}N(CH_3)_3^+$ on 0.01M subsolutions at 25° C.

to bring about a small but constant change (contraction) in the π-A curve was measured. The estimated values of ϕ are 1, 4.5, 5, 6.5 and 8 kT for Cl, Br, NO_3, I and SCN, respectively, the value of ϕ for Cl being arbitrarily set at 1kT. Davies[10] has calculated the specific interaction energy of F, Cl and I with an octadecyltrimethylammonium ion from monolayer viscosity measurements. The values obtained, *viz.*, 2.1, 3.0 and 3.9 kT, respectively, are considerably lower than those given above.

For $C_{22}H_{45}NH(CH_3)_2^+$ and $C_{22}H_{45}NH_3^+$ monolayers the interaction sequence Br $>$ Cl was established. See Fig. 4.

DISCUSSION

Application of Equations of State to π-A Data

Various equations of state have been derived for ionized monolayers. These have been based on a molecular model approach, for example by Davies[9] or on thermodynamic reasoning, for example by Fowkes[11] and Lucassen-Reynders[12]. Since there are virtually no data on activity coefficients in the surface, it has been customary, in applying the thermodynamic equations, to assume ideal behavior. Doing this we found that the thermodynamic equations seriously overestimate the surface pressure of both the arachidic acid[6] and docosyl sulfate[7] monolayers spread on alkali metal subsolutions;
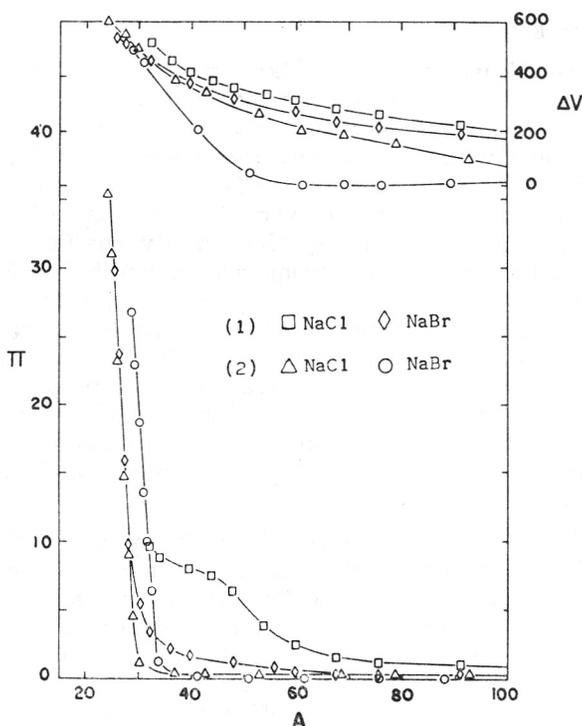
Fig. 4. π—A and $\triangle$V—A isotherms of (1) $C_{22}H_{45}NH(CH_3)_2^+$ and (2) $C_{22}H_{45}NH_3^+$ on **0.1M** NaCl and NaBr solutions **0.001M** in HCl at 25⁰ C.

this was also found to be the case with the Gouy-Davies equation. This equation, however, fits the TMA/fatty acid monolayer[6] data reasonably well, but the thermodynamic equations still yield values of π that are too high. The situation improves for the still more expanded TEA fatty acid monolayers, but even here, the fits were found to be poor.

For the long chain quaternary ammonium $C_{22}H_{45}N(CH_3)_3^+$ monolayers, the equations all lead to serious overestimates of the pressure, except in the case of the F subsolutions[7]. However, in no case was the fit adequate.

The inability of equations of state, based on ideality in the surface, to describe the behavior of charged monolayers is understandable in the light of the results on counterion sequence effects reported here since these effects are major. It becomes clear that, to be applicable, such equations would have to include terms which account for specific ion-counterion interaction forces, or, in thermodynamically derived equations, to include surface activity coefficients which, *a priori*, would not be expected to be unity. Since non-ideality and ion sequence effects are encountered in aqueous solutions[13] similar effects are to be expected in their surface layers which can be considered as two-dimensional aqueous solutions. This area constitutes a logical one for future theoretical and experimental research on ionized mono-layers.

Ion Sequence Effects

The sequence of interaction of alkali metal ions with monolayers of docosyl sulfate is virtually the same as that known as the Hofmeister series for flocculation of negatively charged colloids, *viz.*, Cs, Rb, K, Na, Li, effectiveness increasing with reduced *hydrated* ionic radius. This sequence has also been reported (in some cases partially) for interaction with octadecyl sulfate[14] and dodecyl sulfate[15] monolayers, the lowering of CMC[3] and solubility of alkyl sulfates in water, for the activity coefficients of toluene-[16] and alkane-sulfonates[17] and other strong acid anions[13,18], and for the interactions with strong acid ion exchange resins[19,20]. The above sequence is the opposite of that found for interactions with ionized fatty acid monolayers[6,21], where interaction increased with reduced *crystallographic* radius. Other data implying similar sequences for the interaction of cations with carboxylate ions come from measurements of the solubility of soaps in water, activity coefficients of alkali metal carboxylates[13,16], and interaction with carboxylate ion exchange resins[22] and their swelling[23]. A similar ion sequence has been reported for polyphosphates[24].

For the $C_{22}H_{45}N(CH_3)_3^+$ monolayers the order of interaction with anions is $SCN > I > NO_3 > Br > Cl > F$. This, with minor exceptions, corresponds to the order of interaction reported for various charged colloids, of CMC lowering of quaternary ammonium surfactants[2] and their interfacial potentials[25], of decreasing interaction of halide ions with strong base ion exchangers[26-28] and of increased activity coefficients of TAA halides[29,30]. In the latter case Diamond[31] attributes the effect to the large size of TAA cations and the ordered water structure around them in solution. If the counterion is also large, *e. g.* I^-, the water tends to minimize the disturbance to itself by forcing ion and counterion into the same cavity. This leads to a negative deviation of the activity coefficient and this mechanism seems plausible to explain the results obtained with DCTAB monolayers.

Variations and inversions in ion sequences, as reported above, have been known for many years, and several attempts have been made to ratioanalyze the inversion in sequence of the alkali metal ions in their interaction with strong acid anions *versus* weak acid anions. Robinson, Harned and Stokes[13,32] proposed that the former sequence is normal and is related to the size of the hydrated cation; on the other hand, the sequence for weak anions is ascribed to »local hydrolysis« caused by the high field strength around small cations, such as lithium. This leads to a cation sequence which is related to the size of the unhydrated ion. Teunissen and deJong[1,19,33] have proposed that the relative polarizability of water and the anion governs the cation sequence, and listed the polarizability order as $PO_4^{3-} > COO^- > H_2O > SO_4^{2-}$. Gurney[34] formulated a hypothesis which divided ions into »order-producing« (small ions *e. g.*, Li, and anions of weak acids) and »order-destroying« (large ions, *e. g.*, Cs, Br); in solution, ions of like ordering attract, those of opposite ordering repel each other. A more generalized hypothesis is due to Eisenman[35] who proposes that cation selectivity is governed solely by the field strength around the anion. Although each of the above hypotheses has merit we believe that improved knowledge of the properties of positive and negative ions in an aqueous environment, which classification includes monolayer-, micelle-, resin-, colloid-, polyelectrolyte- counterion systems, awaits more

fundamental knowledge of the relative and absolute role of factors such as electrostatic attraction, specificity of ionic interaction, ion hydration and water structure[4]. It should be mentioned in the latter regard that a comprehensive treatment of ion sequence effects, based on current knowledge and views of water structure and ion solvation[36,37], has recently been advanced by Erlander[38,39].

We consider finally the effect of TAA ions. Since an ionized arachidic acid monolayer spread on a TMA subsolution approximately obeyed the Davies equation one could conclude that this ion is one for which specific interaction with the carboxylate ion is at a minimum. On the other hand, we believe that the appreciable expansion effects encountered with the TEA ion, together with the high value of ΔV measured with this ion, are connected with its large size and incipient surface activity. As regards interaction with alkyl sulfates, work based on CMC data of lauryl sulfate[3] has indicated that TAA ions react more strongly with the alkyl sulfate ion than do alkali metal ions and that interaction increases with increased size of the TAA ion. Recently, this subject has been reviewed extensively by Mukerjee, Mysels and Kapauan[4] who show that a series of TAA ions fall on a different line from the alkali metal line in a plot of CMC *versus* counterion size. These results run parallel to results on ion binding by ion exchange resins[40]. The increased interaction with size of the TAA may indicate increased participation of the alkyl groups of the TAA groups in structure-enforced bonding[31], but this cannot explain the opposite effect noticed in the interaction of TAA with carboxylate resins[41] (or fatty acid monolayers[6]). In this connection it is of interest that, by criteria of monolayer contraction, the results in the present paper do not indicate the association of the TMA ion with an alkyl sulfate monolayer to be particularly strong. At monolayer areas > 60 A^2/molecule the TMA curves lie between those of Li and Na ions. These results thus appear to be in good agreement with activity coefficient data on methane- and ethane-sulfonates[17].

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IZVOD

Specifični efekti protuiona u površinskoj i koloidnoj kemiji. Ionizirani monoslojevi

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Izneseni su podaci o efektima različitih monovalentnih kationa na π-A (površinski tlak—površina) i ΔV—A (površinski potencijal—površina) funkcije za nabijene, netopljive monoslojeve. Utvrđeni su slijedeći nizovi za jačinu interakcije: za RCOO⁻: Li > Na > K > tetrametilamonium > tetraetilamonium; za R—SO₄⁻: Cs = Rb > K > Na > Li; za R—N(CH₃)₃⁺: SCN > I > NO₃ > Br > Cl > F; za R—NH(CH₃)₂⁺ i za R—NH₃⁺: Br > Cl. Ovi rezultati odgovaraju efektima koji su opisani za druge sisteme u koloidnoj i fizikalnoj kemiji. U diskusiji rada iznesene su teorije koje tumače efekte ionskih nizova s time da se kvantitativno slaganje između teorija (odnosno hipoteza) i eksperimentalnih podataka može očekivati samo na osnovi novih fundamentalnih saznanja o elektrostatskim privlačenjima, specifičnoj ionskoj interakciji, ionskoj hidrataciji i strukturi vode.

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