processes in bis(dicarbonyl-(pseudo)cyclopentadienylruthenium) systems. Cis/trans isomerization was shown to occur in both diastereomers (CC/AA)-**1a** and (CA/AC)-**1a**, and the ratio of the cis and trans configurations is dependent on the polarity of the solvent and the temperature.

Acknowledgment. The authors thank Dr. D. J. Stufkens for helpful discussions and G. Schoemaker and D. Heijdenrijk for technical assistance. Several NMR spectra have been obtained at the National SON HF NMR facility at Nijmegen, The Netherlands. Part of this work was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

Supplementary Material Available: Tables of fractional coordinates, all bond lengths and angles, anisotropic thermal parameters of the non-H atoms, isotropic thermal parameters of the H atoms, and an ORTEP drawing of *cis*-(CC/AA)-**1a** (9 pages); listings of structure factor amplitudes (25 pages). Ordering information is given on any current masthead page.

Counterion Affinity Orders in Aqueous Micellar Solutions of Sodium Decyl Phosphate and Sodium Dodecyl Sulfate Determined by Changes in ^{23}Na NMR Relaxation Rates: A Surprising Dependence on Head Group Charge

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Received September 14, 1992

Abstract: Changes in quadrupole relaxation rates of ^{23}Na on addition of the Cl^- salts of Na^+, K^+, Rb^+, Cs^+, TMA^+, and TEA^+ ions were used to determine the relative affinities of these cations for micelles composed of the decyl phosphate monoanion, DPH^- (pH 5.3), the decyl phosphate dianion, DP^{2-} (pH 12.6), and their 1:1 mixture (pH 7.8) at 35 °C. Similar experiments were run in sodium dodecyl sulfate (SDS) micelles at 35 and 60 °C for comparison. The affinity of alkali metal ions for decyl phosphate micelles clearly increases with cation size at all three pH's. The alkali metal cations show significantly less affinity than TMA^+ and TEA^+ for DPH^- micelles and than TMA^+ for SDS micelles. In DP^{2-} micelles, the affinity order of the alkali metals remains the same, but surprisingly, TMA^+ and TEA^+ fail to displace Na^+ from the micellar interface. The 1:1 mixture of DPH^- and DP^{2-} shows intermediate behavior. These changes in affinity order with head group charge can be interpreted qualitatively by assuming that alkali metal ions are hydrated at the surface of decyl phosphate micelles but that they interact much more strongly with divalent than monovalent phosphate head groups, perhaps by site binding to the dianionic phosphate head group through an intervening water molecule. These results are compared with affinity orders of monovalent cations in solutions of micelles, vesicles, polyelectrolytes, DNA, and ion-exchange resins.

Introduction

Supramolecular aggregates and assemblies such as association colloids, vesicles, biological membranes, monolayers, proteins, DNA, polyelectrolytes, and ion-exchange resins all share an important structural feature, an interfacial region of moderate polarity (similar to that of alcohol) juxtaposed to a highly polar aqueous region.[1-14] Association colloids are dynamic aggregates of surfactants such as micelles, microemulsions, and reversed micelles which form homogeneous solutions spontaneously in water and in water and oil mixtures. Unlike polyelectrolytes and proteins, association colloids, monolayers, and biomembranes also have a substantial nonpolar region adjacent to the interfacial region which is composed of aggregated hydrocarbon chains and any added oil.[1,2,6,9-11] Aggregates with charged surfaces bind counterions selectively, and their solution properties such as aggregate size and shape, phase stability, the binding of ions and molecules, and their effects on the rates and equilibria of chemical reactions are sensitive to counterion concentration and type.[1,2,10,12,15-19] The relationship between an affinity order for a set of counterions and a particular aggregate property provides information on the nature of the interaction of counterions in the interfacial region, e.g., whether the counterions associated with the interface remain hydrated or are partially dehydrated and site-bound to surfactant head groups.[14,20-23]

Aqueous solutions of ionic micelles composed of surfactants with hydrocarbon tails of 8-18 carbons attached to cationic or

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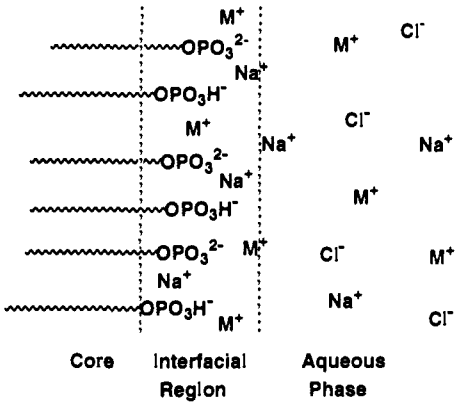

Figure 1. A section of the interfacial region of a DPH^-/DP^{2-} mixed micelle. The locations of head groups and counterions are arbitrary.

anionic head groups are attractive model systems for the ion-binding properties of the much more complex systems of natural and synthetic liposomes and vesicles and biological membranes.[1,7,8] Ionic surfactants can be prepared in high purity, and they dissolve spontaneously in water to give optically transparent and thermodynamically stable solutions.[1] At surfactant concentrations in excess of the critical micelle concentration, or cmc, the hydrophobic effect drives the spontaneous formation of micelles.[11] In dilute aqueous solution, ionic micelles are usually approximately spherical aggregates of 50–150 surfactant monomers. Aggregation creates a liquidlike hydrocarbon core composed of surfactant tails separated from bulk water by an interfacial region composed primarily of surfactant head groups and their counterions (e.g., Figure 1). Counterions are "bound" primarily by the strong electrical field created by the head groups but also by specific interactions that depend upon head group and counterion type. Micellar properties such as the cmc and aggregation number must be determined under the experimental conditions because they are sensitive to surfactant chain length, head group structure, and counterion type.[1,10,15,24,25] Specific counterion effects on a variety of micellar properties generally follow a Hofmeister series;[24] i.e., for counterions of the same valence, the size of the effect increases with counterion size (crystal radius) and the ease of dehydration of the counterion.[16,25–28] However, specificity may also depend upon hydrogen-bonding interactions between hydrated counterions and head groups or the partial disruption of the hydration layers of the head groups and counterions, and the possibility that a fraction of the counterions are site-bound to surfactant head groups, e.g., contact ion pair formation, cannot be excluded.

A large fraction of the work published on specific counterion effects on the properties of association colloids has been carried out in micellar solutions using surfactants with monovalent head groups that are anionic, e.g., $-OSO_3^-$ with alkali metal, alkaline earth, or quaternary ammonium counterions, or cationic, e.g., $-NMe_3^+$ with halide, and other hydrophilic mono- and divalent organic and inorganic counterions.[2,12,15–19] Results are generally interpreted in terms of a pseudophase model in which the totality of the aggregates in solution is assumed to act as a separate phase.[1,15] A two-site model has been successfully applied to the distributions of counterions; i.e., they are assumed to be either "bound" to the micellar pseudophase or "free" in the aqueous phase.[2,15–17,29,30] The head group and counterion concentrations in the interfacial region of an ionic micelle are on the order of 3–5 M, which gives the micellar surface some of the properties of concentrated salt solutions.[2,26,31,32] Although the solution as a whole is electrically neutral, both the micellar and aqueous pseudophases carry a net charge because thermal forces distribute a fraction of the counterions radially into the aqueous phase.[2,15] The fraction of counterions bound, β, is typically in the range 0.6–0.9. For many counterions, β values are remarkably insensitive to surfactant and salt concentrations,[2,15–17] as are the fractions of counterions bound to polyelectrolytes and DNA,[4,5,33,34] and β is often treated as an empirical constant.[35]

The locations of head groups and distributions of counterions within the interfacial region cannot be determined precisely (Figure 1) because micelles are dynamic aggregates without precise dimensions and because the boundaries of the interfacial region depend to some extent on the components present in the aggregate. Univalent head groups and counterions are assumed to be hydrated, but their hydration shells may be disrupted.[36] "Free" water fills the remaining space and is probably in contact with one or two methylene groups adjacent to the head group and portions of the hydrocarbon tails that periodically protrude from the core into the interface.[31,37,38] Counterions are assumed to be free to move within the interfacial region and to exchange rapidly with counterions in the surrounding aqueous phase.[30–32]

We are currently exploring specific counterion effects on the properties of micelles composed of amphoteric surfactants as

Scheme I

$$Na_m^+ + M_w^+ \longleftrightarrow Na_w^+ + M_m^+$$

Scheme II

$$ROPO_3H_2 \underset{H^+}{\overset{H^+}{\rightleftharpoons}} ROPO_3H^{1-} \underset{H^+}{\overset{H^+}{\rightleftharpoons}} ROPO_3^{2-}$$

DPH_2 DPH^{1-} DP^{2-}

Table I. Critical Micelle Concentrations[a] of Decyl Phosphate Micelles at Several pH's and at 0 and 0.5 M Added NaCl

system	pH	cmc, 0 M NaCl	cmc, 0.5 M NaCl
DPH^-[b]	5.2	0.027	0.0083
DPH^-/DP^{2-}[c]	7.9	0.048	0.015
DP^{2-}[d]	12.3[c]	0.126	0.056

[a] In units of moles per liter. [b] 50 °C; ref 39. [c] 25 °C. [d] Each solution contained enough NaOH to neutralize DPH_2 and to make the final pH 12.3.

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(35) β values for surfactants with very hydrophilic counterions such as H^+, HO^-, and F^- are sensitive to surfactant and salt concentrations. These systems have been successfully treated quantitatively by using β as a variable or by applying the Poisson–Boltzmann equation with an additional term for specific counterion effects.[2]
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simple models for the ion-binding properties of phospholipid head groups commonly found at the surfaces of biological membranes. Initial studies show that the specific counterion effects on the apparent pK_a of an indicator bound to micelles of the decyl phosphate monoanion and sodium dodecyl sulfate (SDS) follow a Hofmeister series, $Cs^+ > Rb^+ > K^+ > Na^+$, but added Li^+ precipitates decyl phosphate.[23,39] However, affinity orders for cation binding to vesicles,[12,23] phosphate polymers,[40] and DNA[34] show different orders, indicating significant differences in the balance of forces responsible for counterion binding in these aggregates and assemblies.

Affinity orders reflect the selectivity of an interface toward different counterions compared to a reference ion under the same experimental conditions. Scheme I illustrates, using a two-site ion-exchange model, the exchange of Na^+ with another monovalent cation, M^+, between the micellar surface, m, and the bulk aqueous phase, w. The ion-exchange model has been used to successfully treat specific counterion effects, both qualitatively and quantitatively, on a wide range of chemical reactions and indicator equilibria in micellar solutions[2] and the competitive binding of cations at the surface of DNA.[34] Quantitative differences in affinity are often expressed by using an empirical ion-exchange constant for the reaction in Scheme I. The ion-exchange model has also been successfully applied to counterion competition between monovalent and divalent counterions in micellar[41] and DNA[34] solutions. However, no information is available on specific counterion binding to micelles with divalent head groups, and we decided to explore the specific counterion-binding properties of micelles of the sodium salts of the decyl phosphate monoanion, the decyl phosphate dianion, and their 1:1 mixtures. Competitive counterion binding to SDS micelles was studied for comparison because sodium dodecyl sulfate is the salt of a strong acid and, unlike the decyl phosphate monoanion, cannot interact specifically via intermolecular hydrogen bonds with adjacent water molecules or phosphate head groups.

The physical and chemical properties of alkyl phosphates in both monomer and micellar forms in aqueous solution are strongly affected by the state of ionization of the phosphate group and therefore solution pH (Scheme II). The cmc's of decyl phosphates decrease dramatically with increasing protonation (Table I). In strong acid, decyl dihydrogen phosphate is soluble in significant quantities only at elevated temperatures.[42] The Krafft points for alkyl phosphate dianions[43] are considerably higher than those for the monoanions.[44] Aggregation numbers of sodium octyl phosphates estimated by small-angle neutron scattering at 30 °C vary from over 100 for the monoanion to less than 10 for the dianion.[45] Degrees of ionization, $\alpha = [X_w]/[D_n]$, for $R = C_{12}H_{23}$ to $C_{16}H_{33}$ dianions decrease slightly from 0.35 to 0.28 and are numerically similar to those of the sodium alkyl sulfates of equivalent chain length.[43] Chachaty and co-workers[46] have used a variety of ESR and NMR techniques to estimate micelle size, shape, degree of counterion binding, and internal chain mobility of alkyl phosphate monoanion micelles. Ruzza et al. have studied the effect of decyl phosphate monoanion micelles on the acid hydrolysis of dioxolanes.[47]

We decided to monitor the selectivity of decyl phosphate micelles toward different cations by ^{23}Na relaxation NMR for several reasons. ^{23}Na NMR has been used extensively to probe the ion-binding properties of association colloids, proteins, membranes, and polyelectrolytes[3,48,49] and DNA.[34] ^{23}Na is a quadrupolar ion of high natural abundance and substantial receptivity which permits working over a wide concentration range.[50] The interaction of the ^{23}Na nucleus' quadrupole moment with fluctuating electric field gradients is sensitive to its microenvironment, and comparisons of the longitudinal, T_1, and transverse, T_2, relaxation times show that the extreme narrowing condition applies in micellar solutions.[29,30,51] In principle, a two-site model can be applied to the distribution of counterions because the exchange rate of ^{23}Na between the micellar surface and the bulk solution is rapid compared to relaxation. The observed relaxation rate, R_{obs}, is then expressed as the weighted sum of the relaxations in each phase:[29,30]

$$R_{obs} = X_w R_w + X_m R_m \quad (1)$$

where subscripts w and m indicate the fraction, X, of Na^+ ions relaxing at their characteristic rates in the water and micellar phases, respectively. Most of the experiments were carried out at 35 °C, to ensure that the decyl phosphate monoanion remained in solution at high salt concentrations. Experiments in SDS were carried out at 35 and 60 °C because temperature effects on competitive counterion binding by SDS have not been explored. We only report qualitative affinity orders at this time because current counterion competition models cannot account for changes in affinity orders and because the high salt and surfactant concentrations and the complexity of our system preclude estimation of ion-exchange constants at this time (see below).

Experimental Section

Materials. Decyl dihydrogen phosphate, $C_{10}H_{21}OPO_3H_2$ (DPH_2), was prepared by mixing reagent grade decyl alcohol (0.1 mol, 19.1 mL) with reagent grade phosphorus oxychloride (0.1 mol, 9.32 mL), with vigorous stirring for 1 h under aspirator vacuum to remove HCl(g), and then heated at 50 °C for 5 h.[52] The reaction was quenched by adding the mixture dropwise to excess cold H_2O, and the resultant mixture was then stirred for 5 h at 30 °C. The product was extracted with Et_2O several times. The combined extracts were dried with anhydrous $MgSO_4$, and Et_2O was removed on a rotoevaporator to give a white solid, which was recrystallized repeatedly from hexane; mp 48 °C (lit.[44] 48 °C). Anal. Found: C, 50.19; P, 13.01. Calcd: 50.36%; P, 13.01. The ^{31}P NMR spectrum of an aqueous solution of DPH_2 and 2 equiv of NaOH contained a single signal, $\delta = 1.33$ ppm, with 85% H_3PO_4 as an external standard showing the absence of di- and tridecyl phosphate impurities. Commercial sodium dodecyl sulfate, SDS (BDH, specially purified), was purified previously, and a plot of its surface tension versus SDS concentration was without minimum.[53] All SDS solutions were freshly prepared to avoid hydrolysis. Reagent grade inorganic salts MCl (=NaCl, KCl, LiCl, CsCl) were vacuum-dried and used without further purification. NaOH solutions used for neutralizing DPH_2 were Fisher standardized concentrates. Reagent grade tetramethylammonium chloride ((TMA)Cl) and tetraethylammonium chloride ((TEA)Cl) were recrystallized twice from $EtOH/Et_2O$ and vacuum-dried for 2 days. Reagent grade guanidine and *N*-methylguanidine hydrochlorides were vacuum-dried for 2 days. All solutions were prepared from house distilled water which was passed over activated carbon and ion-exchange resin and then redistilled.

Methods. The cmc's of decyl phosphate were determined at 25 ± 0.1 °C and at various pH's by a literature fluorimetry method[54] using a Perkin-Elmer fluorescence spectrophotometer, Model MPF-3L, and 8-anilino-1-naphthalenesulfonate (ANS), 5×10^{-5} M, as a probe. Solutions for ^{23}Na T_1 experiments were prepared in 1-mL volumetric flasks from aliquots of 0.5 M DPH_2 and 2.5 M NaOH (to set the pH) and microliter aliquots of MCl stock solutions.[55] Solution pH was measured on samples

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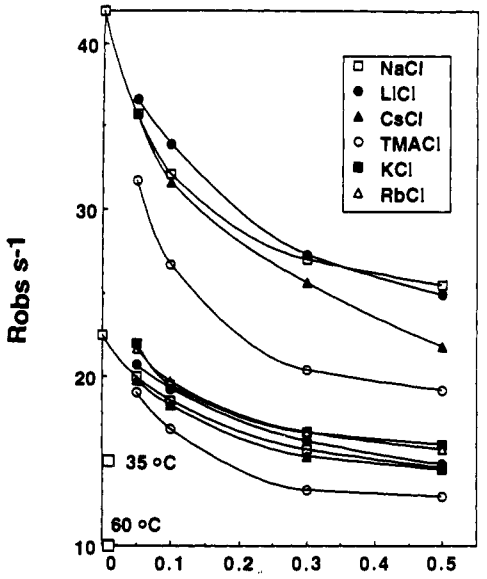

Figure 2. Effect of added salts, MCl, on R_{obs} for ^{23}Na at 35 °C (upper curves) and 60 °C (lower curves) in 0.18 M solutions of SDS. Single points (large open squares) are values of R_{obs} for ^{23}Na in aqueous 0.01 M NaCl at 35 and 60 °C.

of the same solutions used in the NMR experiments with a Corning Model 130 pH meter fitted with a Ross semimicro pH electrode, Model 81-03, calibrated at pH 7.00 and 10.00 using standard buffers at 35 °C. ^{23}Na spin–lattice relaxation times, T_1, were measured on a Varian VXR-200 at 52.9 Hz by the inversion-recovery Fourier transform method, with a 180°–t–90° pulse sequence[29,30,51,56] at 35 ± 0.2 and 60 ± 0.2 °C. Duplicate and sometimes triplicate determinations of T_1 on independently prepared solutions agreed to better than ±5%. ^{31}P chemical shifts, δ ± 0.2 ppm, with 85% H_3PO_4 as the reference, were measured on the same Varian VXR-200 spectrophotometer at 80.98 MHz at ambient temperature. Samples were placed in a 5-mm coaxial NMR tube with the internal tube containing D_2O as a lock. Surfactant solutions were prepared in 1-mL volumetric flasks by adding microliter aliquots of concentrated salt solutions ([MCl] = 2.5 M) to stock solutions of SDS or DPH_2 and aliquots of standardized NaOH solutions to set the pH.

Results

Experiments in SDS. A plot of R_{obs} against 1/[SDS] at 35 °C (Figure S1 and Table S1 provided in the supplementary material) gave a sharp intersection point at 8.5×10^{-3} M for the cmc in good agreement with literature values of 8.65×10^{-3} M at 40 °C determined by conductivity[57] and of 8.7×10^{-3} M at 25 °C by determined ^{23}Na NMR.[30] At high [SDS] (≥0.05 M), R_{obs} curves upward from the line, consistent with literature results.[30] Figure 2 (data in supplementary Table S2) shows the effect of added salts, MCl, on ^{23}Na relaxation rates, R_{obs} (s^{-1}) ($1/T_1$), in aqueous 0.18 M SDS solutions at 35 and 60 °C. Added KCl and RbCl precipitate dodecyl sulfate at 35 °C, but at 60 °C, above their Krafft points,[58] transparent solutions are formed. The higher relaxation rate for ^{23}Na in SDS and other anionic micelles than in water is attributed to asymmetric field gradients or partial disruption of the Na^+ hydration shell in the interfacial region.[3,36]

As [MCl] increases, values for R_{obs} approach R_w for ^{23}Na in water: 15 and 10 s^{-1} at 35 and 60 °C. These values increase only 4% up to 0.5 M NaCl and are in good agreement with literature

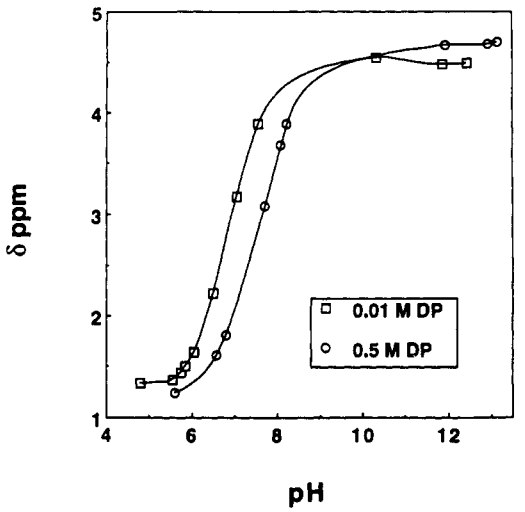

Figure 3. ^{31}P chemical shift vs pH titration curves at ambient temperature for aqueous, monomeric 0.01 M DP at constant total Na^+, [Na_T] = [NaOH] + [NaCl] = 0.05 M, and for micellar 0.5 M DP in 0.5 M NaCl.

results.[56,59] R_{obs} decreases with added NaCl owing to the fact that virtually all added Na^+ remains in the aqueous pseudophase because the fraction of counterions bound is insensitive to the ionic strength. At 0.18 M SDS, added salt reduces the cmc but cannot increase the micelle concentration significantly because, even at 0 M NaCl, less than 5% of SDS is in monomer form. Other added cations reduce R_{obs} by displacing Na^+ from the micelle surface into the aqueous pseudophase (Scheme I). At 35 °C, the selectivity order for displacing ^{23}Na is $TMA^+ > Cs^+ > Li^+$, which is typical of selectivity orders in SDS for these ions.[23,25,56,60] At 60 °C, the effects of the alkali metal cations on R_{obs} are essentially the same, but TMA^+ is still the most effective at displacing ^{23}Na. These results are similar to the modest effects of alkali metal and TMA^+ ions on the cmc of dodecyl sulfate micelles[25] and on chemical reactivity[61,62] but are markedly different from alkali metal ion effects on micelle growth.[58]

Experiments in DP. Figure 3 (data in supplementary Table S3) shows the effect of increasing pH at ambient temperature on the ^{31}P chemical shift of aqueous, monomeric 0.01 M DP at constant Na^+ concentration, [Na_T] = 0.05 M, and of aqueous, micellar 0.5 M DP in 0.5 M NaCl. The apparent pK_a's estimated from the titration curves are 7.6 for micellized DPH^- and 6.92 for the DPH^- monomer,[63] which is close to that of the butyl phosphate monoanion, pK_a = 6.84.[64] This 0.7 unit micellar-induced increase in the pK_a of DPH^- is typical of the approximately 1–2 pK_a unit anionic-micellar-induced decreases in the pK_a's of bound indicators.[16]

Figure 4 (data in supplementary Table S4) shows the effect of added salts on R_{obs} for ^{23}Na in 0.25 M solutions of decyl phosphate (DP) at 35 °C at three different solution pH's. These three operational pH's were selected on the basis of the titration curve for micellized DPH^- in Figure 3: at pH 5.3 (curves A), decyl phosphate is in its monoanion form, DPH^-; at pH 7.8 (curves B), near the pK_a of DP, the DHP^-:DP^{2-} ratio is approximately 1:1; and at pH 12.6 (curves C), DP is completely in its dianion form, DP^{2-}. Added alkaline earth chlorides,[63] LiCl, guanidine hydrochloride (pK_a = 12.6[65]), and *N*-methylguanidine hydro-

(55) The fluidities of the DP solutions in the presence and absence of added MCl were about the same and similar to that of water. Estimates of ^{31}P line widths of 0.25 M DP^{2-} in 0.5 M MCl solutions were about the same, indicating the absence of specific counterion effects on micelle growth at the highest MCl concentrations studied.

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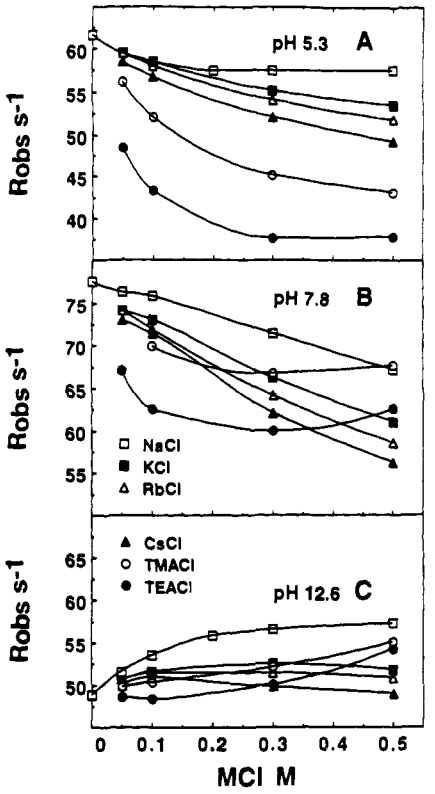

Figure 4. Effect of added salts, MCl, on R_{obs} for ^{23}Na in 0.25 M solutions of decyl phosphate micelles at 35 °C: curves A, at pH 5.3; curves B, at pH 7.8, curves C, at pH 12.3. Symbols for the different salts are the same for all three sets of curves.

chloride (pK_a = 13.4[65]), all precipitate decyl phosphate from solution, and their precipitates do not redissolve even on heating to the boiling point of water. Table I lists the cmc's of DP at several pH's and NaCl concentrations.[63] The cmc's were obtained by extrapolation or interpolation from log cmc versus log [Na_T] (subscript T indicates the total [Na^+]) plots, which were linear at all pH's except the plot at pH 12.3, which curves downward. Values for cmc's of DP are not very temperature sensitive and agree with literature values.[44,66]

The effects of added MCl on R_{obs} in 0.25 M solutions of the decyl phosphate monoanion (Figure 4A) are similar to those in Figure 1 for 0.18 M SDS solutions, but the appearance of the curves in Figure 4A is dramatically different from those in Figure 4B,C. The most striking features of the results are (a) that values for R_{obs} in Figure 4B,C for added TEA^+ and TMA^+ actually cross over those of the alkali metal cations and approach the value for added Na^+ at high MCl concentrations in Figure 4B,C and (b) that the affinity order for the alkali cations remains the same despite the marked changes in the shapes of the R_{obs} profiles. The simplest interpretation of these results is that alkali cations, but not quaternary ammonium ions, undergo stronger interactions at micellar interfaces in the presence of divalent DP^{2-} than in the presence of monovalent DPH^- head groups (see Discussion).

In the absence of added MCl, R_{obs} values for ^{23}Na are respectively 62, 78, and 48 s^{-1} for DPH^-, DPH^-/DP^{2-} (1:1), and DP^{2-} (Figure 4, [MCl] = 0). The higher value of R_{obs} in DPH^- micelles than in water is consistent with the results in SDS micelles. The marked increase in R_{obs} on going from micelles of DPH^- to the 1:1 mixture containing DP^{2-} is probably caused by an increase in the fraction of Na^+ bound to the micellar interface as with DP^{2-} micelles (see below) and perhaps an increase in the disruption of the hydration shell of ^{23}Na. The lower value for DP^{2-} micelles at pH 12.6 is probably caused by the high concentration of ^{23}Na in the aqueous phase because only about 50% of the surfactant is in micellar form, cmc = 0.13. (Table I). Thus, R_{obs} for completely micellized DP^{2-} should probably be at least twice this value.

At pH 5.3 (Figure 4A), added MCl reduces R_{obs} and the selectivity order is unambiguous: $TEA^+ > TMA^+ > Cs^+ > Rb^+ > K^+ > Na^+$ (with the alkali metal cations following a Hofmeister series). The similarity of the results in DPH^- and SDS indicates that the proton on the phosphate group has little effect on the affinity order. The quaternary ammonium ions are the most effective at reducing R_{obs}, probably because they interact both electrostatically and hydrophobically with the micellar surface. However, unlike the results for SDS, R_{obs} for ^{23}Na appears to be approaching a plateau well above its value in water (15 s^{-1} at 35 °C), which indicates that R_m for micellized ^{23}Na may increase with added salts.

The presence of DP^{2-} in the micelles at pH 7.8 (Figure 4B) changes the selectivity order dramatically at high [MCl]. Added TMA^+ and TEA^+ decrease R_{obs} at low concentrations but have little effect at higher concentrations. Apparently, quaternary ammonium ions displace loosely bound Na^+ just as they do in DPH^- micelles, but they cannot displace Na^+ ions that are more tightly associated with the DP^{2-} head groups. Added alkali metal cations, however, can displace both lossely and tightly bound Na^+ ions because they also interact more strongly with DP^{2-} than with DPH^-.

At pH 12.6 (Figure 4C), added NaCl actually increases R_{obs}. The cmc of DP^{2-} in the absence of added salt is about 50% of the total DP concentration (Table I). Thus, added salts will decrease the cmc significantly and increase the quantity of micellar-bound ^{23}Na. R_{obs} should be greater for DP^{2-} than DPH^- micelles because the total quantity of bound Na^+ is substantially higher. Experimental estimates of the degrees of ionization, $\alpha = [X_w]/[D_n]$, of DPH^- and DP^{2-} micelles are numerically about the same, $\alpha \approx 0.3$.[44] This means that the ratio of counterions to head groups for DP^{2-} micelles will be about 1.7, which is more than double the ratio of 0.7 for DPH^- micelles. R_{obs} may also increase because of salt-induced increases in R_m, as it does in SDS micelles[29,30] (supplementary Figure S1). However, because the interfacial counterion concentration is probably on the order of 3–5 M[2,26,31,32] and the maximum ionic strength in the aqueous pseudophase is on the order of 0.5 M, the uncertainty in R_m is probably small and should not affect affinity orders at a particular set of surfactant and salt concentrations. The effectiveness of alkali metal cations in reducing R_{obs} again follows a Hofmeister series, showing that they displace micellar-bound Na^+. The shallow minimum in R_{obs} produced by added alkali metal cations is probably caused by the balance of two opposing effects, salt-induced micelle formation, which increases R_{obs}, and displacement of micellar-bound Na^+ into the aqueous phase, which reduces R_{obs}. Added TMA^+ and TEA^+ increase R_{obs} because they increase the concentration of micellar-bound Na^+ by increasing the ionic strength and lowering the cmc but cannot displace tightly bound Na^+ from the interface of DP^{2-} micelles.[67]

Discussion

The precipitation of DP and SDS by certain cations and the change in counterion affinity order of DP micelles with head group charge provide important information about the requirements for forming stable micelles and the interactions of monovalent cations with phosphate head groups of amphiphiles. On the basis of his work on the selectivity of glass electrons, Eisenman developed a theory to explain the difference in affinity orders for different glasses based on shifts in the energy balance between the hydration energies of the cations and surfaces and the electrical filed strengths of the surfaces; i.e., either the local field is sufficiently strong to overcome the hydration energy of an ion and form a tight ion pair or it is not.[20–22] Eisenman identified 11 out of 120 possible selectivity orders for the five alkali metal cations relative to glass electrodes of varying compositions. The two extreme and opposing orders correlate with the sizes of the hydrated (the Hofmeister

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series, low field strengths) and partially dehydrated cations (high field strengths). The nine intermediate orders occur for interfaces where the electrical field strength is sufficiently strong to overcome the hydration energy with one or more, but not all, of the ions in the series. These same 11 affinity orders also appear to be important biologically because they are related to a variety of membrane functions and the properties of proteins and nucleic acids.[21,22,68]

As noted in the Introduction, specific counterion effects on a wide variety of micellar properties and micellar effects on chemical reactivity follow a Hofmeister series. All available evidence indicates that micellar-bound counterions remain hydrated; i.e., they do not form tight ion pairs. Changes in selectivity order have probably not been observed because surfactants that form very strong complexes with their counterions are water insoluble. For example, divalent metal ions, Li^+, and the two guanidinium ions precipitate DP; K^+ and Rb^+, but not Li^+, Na^+, and Cs^+, form precipitates with dodecyl sulfate at room temperature; insoluble Mg^{2+} and Ca^{2+} salts of long-chain alkanecarboxylates aid in the formation of the infamous hard water bathtub ring; and ClO_4^- precipitates alkyltrimethylammonium surfactants. In moderately acidic solutions (pH $\leq$1), the proton, the premier site-binding ion, precipitates long-chain alkylanecarboxylates and alkyl phosphates[44] because protons bind covalently to their weakly acidic head groups. Thus, the fact that the affinity order for those alkali metal ions that form stable solutions with SDS, DP^-, and DP^{2-} follows a Hofmeister series indicates that these counterions remain hydrated, i.e., do not form tight ion pairs, at the micellar surface.

The simplest explanation for the change in affinity orders of the quaternary ammonium and alkali metal ions is that alkali metal ions bind more strongly at the interfaces of DP^{2-} micelles that those of DPH^- micelles. Quaternary ammonium ions are "wrapped in a plastic bag" and cannot interact specifically, but only Coulombically with anionic head groups and hydrophobically with exposed hydrocarbons at DPH^- or DP^{2-} micellar interfaces. Apparently, alkali metal cations interact relatively weakly with DPH^- surfaces because Na^+ is easily displaced by TMA^+ and TEA^+. Their interactions with DP^{2-} surfaces are stronger because TMA^+ and TEA^+ do not displace Na^+. One possible explanation is that DP^{2-} head groups and alkali metal cations interact specifically through an intervening water molecule with its oxygen adjacent to the cation and hydrogen-bonded to the phosphate. Na^+ complexed with di- and trivalent orthophosphates and organic phosphates is known to relax more rapidly than fully hydrated Na^+.[69,70]

Alkali metal affinity orders determined by a variety of methods for phospholipid vesicle surfaces with different head groups are all opposite of the Hofmeister series; i.e., selectivity decreases with the increasing size of the naked cation.[12,39] Indeed, NMR studies of counterion binding of phospholipid vesicles are consistent with site binding by alkali metal[71] and alkaline earth metal counterions[72] and indicate that TMA^+ and TEA^+ do not effectively displace Na^+ ions specifically bound to phosphatidylserine vesicles.[73] One major difference between simple alkyl phosphate head groups and phospholipid head groups is that most phospholipid head groups have other polar or ionic functionalities attached such as a quaternary ammonium (phosphatidylcholine), carboxylate and ammonium groups (phosphatidylserine), or a dihydroxy group (phosphatidylglycerol). These groups can remain hydrated even if a cation is site-bound to the phosphate group. Even phosphatidic acid, which has the same head group as DP, has polar ester linkages attached to the glycerol backbone which can hydrogen-bond to water. Finally, because vesicles, unlike micelles, are a separate phase dispersed in water, complete hydration of their head groups and counterions may not be required for vesicle stability. However, this interpretation may not be general. Mortara et al. found that the selectivity order for flocculation rates at 50 °C for sonicated vesicles of dihexadecyl phosphate is $Cs^+ > Na^+ > K^+ > Li^+$.[74]

The affinity order of alkali metal and quaternary ammonium ions binding to DP^{2-} is somewhat related to that of DNA: $NH_4^+ > Cs^+ > Rb^+ > K^+ > Li^+ > Na^+ > TEA^+ >$ tetra-*n*-butylammonium.[34] NH_4^+ cannot be used in basic solutions of DP because it will be deprotonated. However, both guanidinium ions, which have much higher pK_a's than NH_4^+, precipitate DP, indicating a strong affinity for the phosphate head groups, perhaps by hydrogen bonds. The affinity order of alkali metal ions binding to DNA almost follows a Hofmeister series, but Li^+ is out of place. Site binding has been proposed to explain the volume changes for interactions of alkali metal ions with polyphosphates in aqueous solution, $Li^+ > Na^+ > K^+$,[40] but a different order was obtained using an ultrasonic technique.[75] Changes in affinity orders have also been observed with ion-exchange resins. For example, alkali metal ion binding to loosely cross-linked polystyrene sulfonate resins follows a Hofmeister series, but increasing the cross-linking changes the affinity order.[14]

Conclusions

Mono- and divalent decyl phosphate micelles show marked differences in their affinity for monovalent cations. TMA^+ and TEA^+ bind more strongly to micellized monovalent decyl phosphate head groups than alkali metal cations, but the reverse is true for micellized divalent decyl phosphate, suggesting that alkali metal cations undergo stronger interactions with divalent than with monovalent phosphate head groups. However, the affinity order of the alkali metal cations remains the same for both head groups, $Cs^+ > Rb^+ > K^+ > Na^+$, indicating that the alkali metal cations remain at least partially hydrated. Decyl phosphate salts of alkaline earth metal cations, Li^+, and two different guanidinium ions are completely insoluble in water, showing that strong specific interactions prevent the partial or full hydration of decyl phosphate head groups and counterions required for micelle stability. Although we have explained our results using Eisenman's approach for interpreting affinity orders, little is actually known about the extent of hydration of ions at aqueous interfaces and counterion-induced precipitation also depends upon the crystal lattice energies of the insoluble surfactant salts. Future work will focus on quantitative estimates of counterion selectivity, e.g., determination of ion-exchange constants, and on counterion binding to micelles having multifunctional head groups that more closely mimic those of membrane phospholipids.

Acknowledgment. We are grateful to Dr. Pat O'Connor for running several control experiments and to a number of colleagues for helpful discussions: C. A. Bunton, C. Bravo, G. Cerichelli, P. O'Connor, U. P. Strauss, and J. Yao. We appreciate the financial support of the following funding agencies: the NSF U.S.-Latin American Cooperative Program-Brazil, the National Science Foundation (Grant CHE-9113331), NATO (Grant CRG 920260), the Busch and Biological Sciences Research Fund of Rutgers University, the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corp., and the National Institutes of Health (Grant GM32972).

Supplementary Material Available: Figure S1, showing a plot of R_{obs} for ^{23}Na versus 1/[SDS] (M^{-1}), and Tables S1–S4, containing numerical values of R_{obs} and δ (5 pages). Ordering information is given on any current masthead page.

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