

Hofmeister series and specific interactions of charged headgroups with aqueous ions

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Abstract

Interactions of negatively charged headgroups with alkali cations in water are quantified by experiment and calculations. We present computational results of sodium and potassium interactions with methylsulfate and compare them to interactions with acetate. From these results, former simulations, and from a series of experimental observations we deduce a Hofmeister-like ordering of headgroups. We further combine this ordering with the law of matching water affinities in order to obtain general description and predictions of ion-headgroup interactions. Examples from colloidal chemistry and from biological systems are provided to illustrate the power of this approach.

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Introduction

Many phenomena in colloid, polymer, and interface science that involve electrolytes show pronounced ion specificity. More than a century ago, Franz Hofmeister noted a particular ordering of ions in the ability of salts of a common counterion to precipitate egg-white proteins.^{1,2} His main conclusion was that the effectiveness of the salts in precipitating proteins increases with “their water ordering capacity”. Today, one would call it hydration. Since the early work of Hofmeister and his group, the “Hofmeister series” or variations of it have been broadly observed in numerous phenomena.³⁻⁵

It has become common to speak about ion series rather than series of salts. By doing so, one usually neglects that the ions cannot be considered as isolated species in water. Either they interact with one another (except in very dilute solutions, where the Debye-Hückel expressions are strictly valid) or with surfaces. Consequently, the specificity not only depends on the type of the ion considered, but also on the counterion or on the chemical composition of the surface involved. As the simplest example, ions show varying propensities to the air-water interface. But even here, it was shown only recently that a satisfactory and fairly predictive explanation could be found for the Hofmeister series of measured surface tensions.⁶ For specific ion effects in solutions or at more complex surfaces, only empirical rules are known. Recently, a simple “law of matching water affinities” has been proposed by Collins.^{7,8} It relates the tendency of oppositely charged ions to spontaneously associate as inner sphere ion pairs in aqueous solution to matching absolute free energies of ion hydration. This is supposed to be due to the fact that the strength of interaction between the ions and the water molecules is correlated to the strength with which the ion interacts with other ions.⁸ With this model an impressive number of phenomena and properties can be described.

The above concept mainly concerns interactions between small ions. But what is the situation with interactions of ions and headgroups of phospholipids and surfactants, such as alkyl carboxylates, sulfates, phosphates, etc.? Such systems are widespread in biology and colloidal chemistry and, therefore, it is of major interest to define, further to ion series, a classification or Hofmeister series of headgroups together with a predictive theory of interactions between different types of ions and headgroups.

Recently, we reported on an extended computational study of pairing of sodium and potassium with a broad set of biologically relevant anions in water.^{9,10} Similarly as in the related case of ion hydration, accurate calculations of ion pairing in water are difficult and results are very sensitive to the interaction potential and other parameters of the simulations.^{11,12} In order to minimize the effect of such possible inaccuracies we focused at evaluating the difference between the strength of ion pairing involving Na⁺ vs. K⁺. This computed difference is much more reliable than the absolute values for the two ions thanks to a favorable cancellation of errors. Within the calculations we combined two different approaches: classical molecular dynamics (MD) simulations of aqueous salt solutions and *ab initio* calculations employing a polarizable continuum model for water. The former approach includes explicit solvent molecules, however, all interactions are based on a simple empirical potential, while the latter method very accurately describes the cation-anion interactions at the price of a continuum treatment of the solvent. Here, we employ this mixed approach to examine the monovalent sulfate and the carboxylate groups and their pairing with sodium vs. potassium.

Based on this solid computational background, we propose a way to classify headgroups in a Hofmeister-like series. These results together with Collins's concept are then used to explain how salt-induced micelle-to-vesicle transitions depend on both ion and headgroup specificities. To this end, new experimental results are compared to recently published ones. Finally, the proposed headgroup series in combination with the concept of matching water affinities are shown to be generally applicable for the explanation of a multitude of experimental results that were published over the last decades.

Computational methodology

The combined molecular dynamics and *ab initio* approach is analogous to that employed in our previous studies.^{9,10} Briefly, MD calculations using a non-polarizable forcefield were performed first.¹²⁻¹⁶ Each of the systems contained 800 water molecules in a cubic periodic box with up to six cation/anion pairs. After sufficient equilibration, several ns of production runs were performed at 300 K and 1 atm with a 2 fs time step, using the program package Gromacs version 3.3.1.¹³ Cation-anion radial distribution functions were then extracted from the production runs.

In the second step, *ab initio* calculations were performed employing a polarizable continuum solvent model. For each of the contact ion pairs the geometry was obtained from a gas phase *ab initio* optimization, however, in order to get the most relevant aqueous phase anion-cation distance we took this value from the above MD simulations (corresponding to the cation-anion oxygen peak of the radial distribution function). The structures of the four investigated contact ion pairs, together with the employed cation–anion oxygen distances are shown in Figure 1.

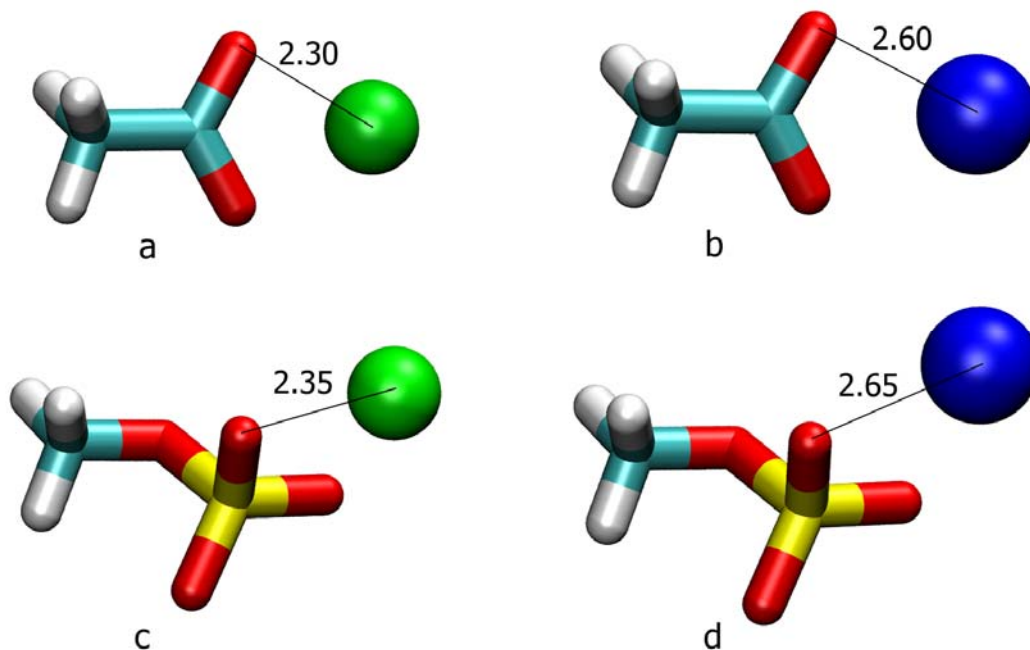


Figure 1: Geometries of the contact ion pairs of a) sodium-acetate, b) potassium-acetate, c) sodium-methylsulfate, and d) potassium-methylsulfate. The cations bind bidentally to two anionic oxygens.

The free energy of ion pairing was evaluated as the difference between the energy of the solvated contact ion pair and the energies of the separately solvated cation and anion in water. *Ab initio* calculations were performed at the second-order Moller-Plesset perturbation theory level (MP2). We used the aug-cc-pVTZ basis sets for acetate with additional core-valence basis functions (cc-pCVTZ) added for C and O.¹⁷ For methylsulfate, because of the large size of the anion, we used the aug-cc-pVDZ basis sets for H, C, O, S atoms and cc-pVDZ for both sodium and potassium.^{17,18} In *ab initio* calculations water was described within a polarizable continuum solvent using the COSMO model.^{19,20} All COSMO parameters were taken as the default ones except for the ionic radius of sodium, which was reduced by 1.3% to match exactly the experimental difference between hydration free energies of Na⁺ and K⁺ amounting

to 17.5 kcal/mol.²¹ *Ab initio* calculations were performed using the Gaussian03 program package.²²

Experimental procedure

Materials. The surfactants, sodium dodecyl sulfate (SDS; Merck, Germany; assay > 99%) and sodium dodecanoate (SL; Sigma, Germany; grade: 99-100%) and dodecyltrimethylammonium bromide (DTAB; Merck, Germany; assay > 99%) were used as received. All sodium and chloride salts used in the experiments were supplied by Merck, Germany. Millipore water was used as solvent in all cases.

Sample preparation. The preparation of surfactant stock and mixed surfactant solutions was previously described.^{23,24} The anionic-rich region of the phase diagrams was used in both cases. A fixed anionic / cationic surfactant mass ratio of 70 / 30 (this corresponds to a molar ratio of about 2.5 / 1) and of 60 / 40 (molar ratio 2 / 1) was used for SDS / DTAB and SL / DTAB mixtures, respectively. The reason for these ratios is explained in our previous work.^{12,13} The total surfactant concentration was kept at 1 wt.% at all times.

Dynamic Light Scattering (DLS) measurements. Particle size analysis was performed using a Zetasizer 3000 PCS (Malvern Instruments Ltd., England), equipped with a 5 mW helium neon laser with a wavelength output of 633 nm. The scattering angle was 90° and the intensity autocorrelation functions were analyzed using the Contin software. All measurements were performed at 25 °C.

Freeze-Fracture Electron Microscopy. Samples used for Cryo-fracture were prepared as described previously.²³ Freeze-fracture was performed in a BAF 060 (Balzers, Switzerland) apparatus at -130°C under a vacuum of 10⁻⁷ Torr. Metallic replicas were obtained by Pt and

carbon shadowing of fracture surfaces. The replica were examined and photographed with a Philips CM 12 transmission electron microscope.

Results

Computational results

A combination of *ab initio* calculations with a polarizable continuum solvent model and molecular dynamics simulations were used to quantify the relative cation-anion association free energies, i.e., the values of $\Delta\Delta G$ connected with replacing potassium with sodium in a contact ion pair with acetate or methylsulfate anion. These two free energy differences are presented in Table 1. We see that CH_3COO^- and CH_3SO_4^- behave differently with respect to their relative preference for Na^+ vs K^+ . On one hand, acetate strongly prefers sodium over potassium (by about 2.5 kcal/mol), which is in accord with our previous calculations and experimental indications.^{9,10} On the other hand, methylsulfate weakly (by roughly 0.4 kcal/mol) prefers potassium over sodium. Our findings are consistent with the empirical law of matching water affinities⁸ stating qualitatively that small cations (sodium) prefer small anions or anionic groups (acetate), while larger cations (potassium) are preferentially attracted to larger anions or anionic groups (methylsulfate).

	$\Delta\Delta G (\text{Na}^+ \rightarrow \text{K}^+) [\text{kcal/mol}]$
acetate	- 2.50
methylsulfate	+ 0.37

Table 1. Free energy change upon replacing potassium with sodium in a contact ion pair CH_3COO^- and CH_3SO_4^-

Experimental results

In the present set of experiments, the effect of various cations on the salt-induced micelle-to-vesicle transition is presented (Figure 2). During this transition the mean curvature of the surfactant aggregates changes. As usual, the local aggregate curvature can be described by a surfactant packing parameter $P = v/(l_{\max} a)$, where v and l_{\max} are the volume and length of the hydrophobic part, respectively and a the apparent area per molecule at the interface (hydrated headgroup).^{25,26} A necessary condition for the formation of vesicles from either single or mixed surfactants is that the packing parameter increases up to values close to one. This is mainly due to a decrease in the value of a with increasing salt concentration, which does not significantly influence v and l_{\max} .

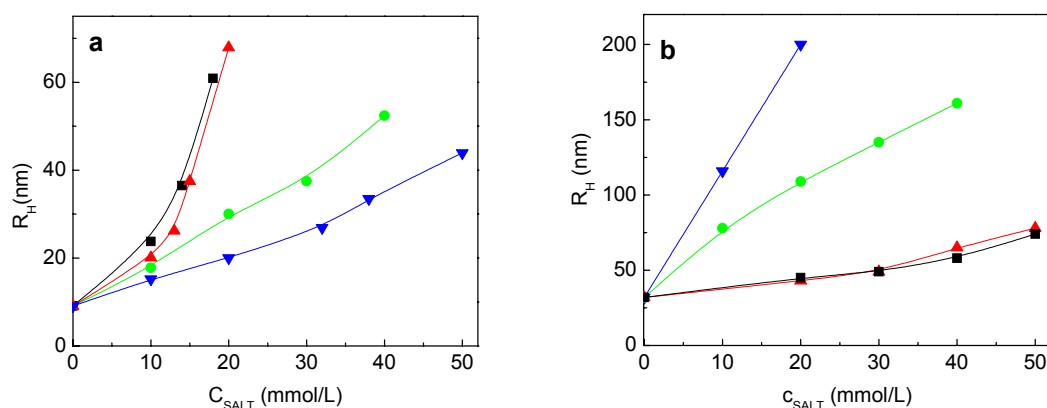


Figure 2: The effect of various cations on the growth of the hydrodynamic radii R_H of the cationic aggregates in (a) SDS / DTAB and (b) SL / DTAB systems with an excess of anionic surfactant in both systems: LiCl (\blacktriangledown), NaCl (\bullet), KCl (\blacktriangle), CsCl (\blacksquare); reprints from Langmuir and JCIS.

According to Fig. 2 a is increased by all added salts considered. A plausible explanation is the assumption that the additional ions compete with the headgroups for water

and that consequently the headgroups are less and less hydrated with increasing ionic strength. However, as can be expected, not all salts have the same effect on increasing the size of the surfactant aggregates. In the case of an excess of dodecyl sulfate, lithium is the less efficient cation whereas cesium is the most efficient one. By contrast, having an excess of dodecyl carbonate in the mixed aggregates, the cation series inverts. Note that the stronger preferential binding of ions can also be experimentally observed by the distortion of the vesicle membrane as it becomes dehydrated (FF-TEM images in Supporting Information, Figure S1).

The opposite behavior of the two surfactant headgroups in alkali chloride solutions can be easily explained now, taking into account the simulation results and the concept of matching water affinities. Alkyl sulfates exhibit a lower charge density on their headgroups than alkyl carbonates. (Note that this is different from the double-charged sulfate ion with a higher charge density than the single charged carboxylate ion.) This means that an alkyl sulfate headgroup can be classified as a chaotrope, whereas alkyl carboxylates can be considered as cosmotropes.

Following Collins's concept, chaotropes can form direct ion pairs with other chaotropes, much as cosmotropes with other cosmotropes (although for different reasons), but chaotropes do not come into close contact with cosmotropes. Applied to our example, this means that cesium will form the closest ion pairs with dodecyl sulfate and lithium with dodecyl carboxylate. Such ion pairs or dipoles will be much less hydrated than separate ions and headgroups. This smaller hydration is reflected in smaller effective headgroup areas a leading to higher packing parameters and bigger objects and this is precisely what is found experimentally.

Assuming that the computed free energy differences $\Delta\Delta G$ value semi-quantitatively represents the relative binding strength to a given anion (strong binding represented by the close contact of two ions), then $\Delta\Delta G$ can be related to the effective headgroup size a . This

would explain why different salt concentrations are needed in order to get the same hydrodynamic radius when the cations of the salts are varied. By inserting a parameter connected to the free energy of ion pairing into the packing equation, we are also able to predict the reversed series of the carboxylates as opposed to the sulfates.

Discussion

Generalization of the concept

In the previous section a first example was given for the comparison of two headgroups. However, other headgroups are also of interest in colloidal chemistry and biology, particularly sulfonates and phosphates. We propose that the ordering from cosmotropic to chaotropic headgroups is –carboxylate, –sulfate \approx –sulfonate (presented in Figure 3). Concerning the monovalent phosphate group, both the charge density argument and several experimental results²⁷⁻²⁹ suggests that it can be classified between the carboxylate and the sulfate/sulfonate headgroups. The calculated $\Delta\Delta G$ ($\text{Na}^+ \rightarrow \text{K}^+$) for H_2PO_4^- amounts to approximately -0.5 kcal/mol,¹⁰ which fits with the series shown in Fig. 3. For CH_3SO_3^- simulations predict $\Delta\Delta G$ ($\text{Na}^+ \rightarrow \text{K}^+$) around 4-5 kcal/mol. This is higher than for methylsulfate and would classify alkylsulfonates as stronger chaotropes than alkylsulfates, while the experiments rates them as roughly similar. Note that an ordering of interactions, similar to that presented in Fig. 3, can be done also for anions in contact with alkylammonium cations (c. f. Figure S2, Supporting Information).

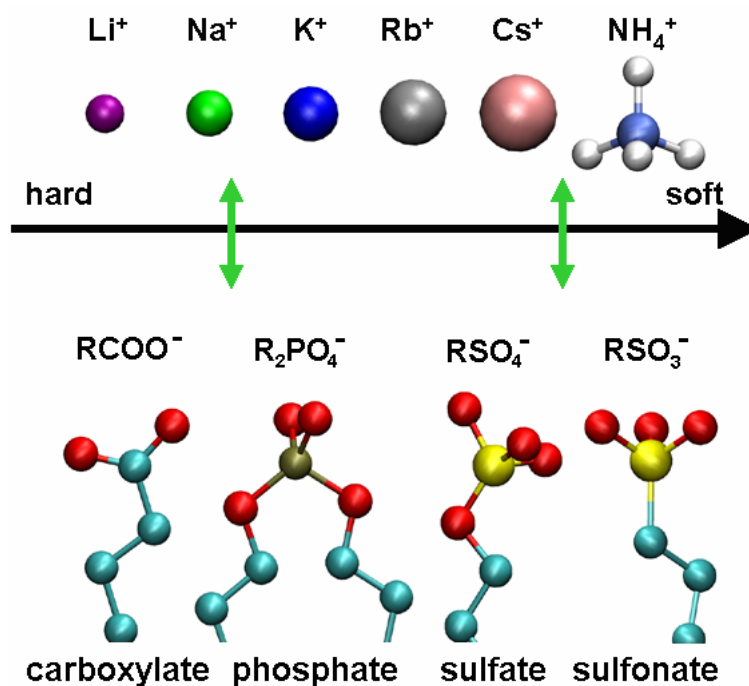


Figure 3. Ordering of anionic surfactant headgroups and the respective counterions regarding their capabilities to form close pairs. The green arrows mean strong interactions (close ion pairs).

As already mentioned, many examples of ion specificities in colloidal and biological systems have been published over the last decades. As far as specific headgroups are involved, they all can be explained now by combining the Hofmeister series for both ions and headgroups with the concept of matching water affinities. In the next subsections we discuss in detail several important examples.

Polyelectrolyte Solutions

Similar counterion specificity as reported in the cationic systems is observed in the case of polyelectrolytes. Nevertheless it should be kept in mind that ion effects do not depend only on the individual properties of the participating ionic group and its counterion (i.e., charge, size, charge distribution and polarizability), but also on the overall charge of the polyion, as well as on the possible cooperating binding sites. Furthermore, even at high dilution a substantial

number of counterions is forced into close proximity to the polyion by the long-range electrostatic forces,^{30,31} so that there always exists a large number of ion pairs, for which solvation effects should be observable.

Strauss^{32,33} used the dilatometric method to measure the volume changes that occur when polyelectrolyte solutions are mixed with solutions containing different specifically interacting counterions. Polyelectrolytes containing sulfate and carboxylate headgroups exhibit opposite series of counterion binding, similar to the series observed in our experiments on surfactant micelles. That is, in the case of polysulfonates the volume increase becomes smaller with increasing ionic radius, whereas in the case of carboxylates this series is reversed. Dilatometric results clearly show specificities depending on both the polyion and on the metal ion which would not be expected on the basis of long-range electrostatic density of the polyion. The effects of the latter are governed predominantly by the linear charge density of the polyion and the linear charge densities of the studied sulfonates and acrylates are the same. It follows that the interactions giving rise to the observed volume changes involve specific sites on the polyions. Similar results for interactions of alkali cations with polyacrylates and polysulfonates have been discussed also by other authors.³⁴⁻³⁸ The reversal of the cation series in the presence of polyacrylates was attributed to a competition between hydrating water molecules and the anion for a given cation, which qualitatively related to the charge distributions, polarizabilities, and the effective field strengths of the ions.^{39,40}

MD simulations show similar results. Chialvo and Simonson⁴¹ modeled a short-chain polystyrenesulfonate and found the interaction with Li^+ too weak to cause desolvation. Consistently, Lipar et al.³⁶ reported binding to polyanetholesulfonic acid to be strongest for Cs^+ . MD calculations for cationic polyelectrolytes⁴² with linked tetramethylammonium groups predict the same ordering of counter-cations ($\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$) as that observed for a cationic trimethylammonium headgroup (compare to Figure S2).

Micellar and Lamellar Systems

The reversion of the ion series was observed also when measuring the cation affinity to ion-exchange resins,⁴³⁻⁴⁵ in studies of membrane potentials,⁴³ of electrophoretic mobility of colloids,⁴⁰ ion-transport phenomena,⁴⁰ swelling of hydrogels⁴⁶ and counter-ion binding to long-chain fatty acids.^{34,47-51} For instance, the competition of cations for charged fatty-acid monolayer interfaces was studied by Rosano et al.⁵² Again, it was observed that Li^+ is less easily displaced at the interface as the other alkali ions. The degree of binding is in line with their degrees of hydration in the bulk.

Counter-ion binding to micelles has been studied extensively.^{27,51-56} Schulz et al.⁵⁷ reported the selective binding of alkali counterions to anionic SDS surfactant films by ion floating technique. The selectivity order of the metal ions was found to match the present observations. The selectivity of SDS micelles derived from the ion flotation agrees well with interfacial probe studies of alkali metal ion binding performed by He et. al.⁵⁸ and Hafiane et al.⁵⁹ Similarly to previous cases, a reversed series of cation binding is observed when sodium dodecyl micelles are replaced by sodium dodecanoate micelles. As measured by Haverd and Warr,²⁷ the binding strength of alkali cations to the carboxylate micelles decreases in the order $\text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$. The same order was observed also by electromotive force measurements.⁵³

Similar trends are observed when the effects of ion species and concentration on the swelling behavior of hydrogels are investigated. Xu et al.⁴⁶ studied the swelling and de-swelling of PSSA (Poly(styrene sulfonic acid)) hydrogels in aqueous solution of selected alkali cations. The de-swelling extent of PSSA hydrogel was found to follow the sequence $\text{Li}^+ < \text{Na}^+ < \text{K}^+$. This series was reversed in hydrogels fibers composed of PAA (polyacrylic acid).⁶⁰

Already 20 years ago Ninham et al.^{56,61,62} and Khan et al.⁶³⁻⁶⁵ reported on the unusual behaviour of acetate, hydroxide and formate double-chain surfactants.

Didodecyldimethylammonium sulfate (DDAS) is practically insoluble in water. However, it swells in water, producing a lamellar liquid crystalline phase. On the other hand, didodecyldimethylammonium acetate and hydroxide are highly water soluble and form an extended micellar phase. Similar counterion effects have been observed for the swelling of lamellar phases.⁶⁶⁻⁶⁸ Many possible explanations for the observed phenomenon are given. Ninham et al.^{56,61,62} attributed these peculiarities to the high hydration of the headgroups. Morgan et al.⁶⁹ proposed that partial dehydration of the competing counterions dominates their exchange at the interface, while Robinson and Harned⁷⁰ suggested the formation of a solvent-shared ion pair (effect of the so-called “localized hydrolysis”). However, before the present study no convincing explanation has appeared which could fully rationalize this phenomenon.

Phospholipids

The counterion selectivity can be extended to phosphate containing systems. Previous results have shown that the counterion selectivity for the phosphate headgroups depends strongly on the charge of the headgroup (single or double). For comparison reasons, only the single chain hydrogen alkyl phosphate is considered. The selectivity order of alkyl phosphate micelle surfaces as determined from flotation experiments²⁷ resembles that of alkyl sulfate micelles; the alkali metal ion selectivity coefficients follow the order $\text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$. This order is found also for phosphoric acid resins. At medium pH (6-8.5), where hydrogen phosphate is present, the order of selectivity coefficients is $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$.²⁸ However, while in the case of alkylsulfates and alkylcarboxylates the trend always follows the described series, different results are observed in the case of phospholipids. Experiments performed on the negatively charged phospholipid dioleoylphosphatidylglycerol (DOPG) show that the maximum in binding is found for K^+ .²⁹ As was presented in Figure 3, it is as if the negatively charged phosphate group behaves like an intermediate case somewhere

between a cosmotropic and a chaotropic object. Perhaps this behavior is due to the combined effects of hydration and specific (site) binding to the DOPG group.

Recently, we reported on specific ion binding to lipid membranes.⁷¹ For diphytanoyl phosphatidylcholine it was found that chaotropic anions and kosmotropic cations were attracted to the lipid surface. This is in agreement with our concept, keeping in mind that the choline group can be regarded as chaotrope and the phosphate group more as a cosmotropic group. Qualitatively the same result was obtained for the overall charged headgroups in dioleoyl trimethylammonium propane (DOTAP) and in dioleoyl phosphatidylglycerol (DOPG).

Conclusion

In the present paper a comprehensive attempt is made to establish a Hofmeister-like series for surfactant and lipid headgroups. Further to computer modelling, the proposed series is based on numerous experimental observations. Together with the concept of matching water affinities, the present headgroup ordering allows us to describe and predict at least qualitatively specific ion interactions for a wide range of systems and applications.

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Supporting Information:

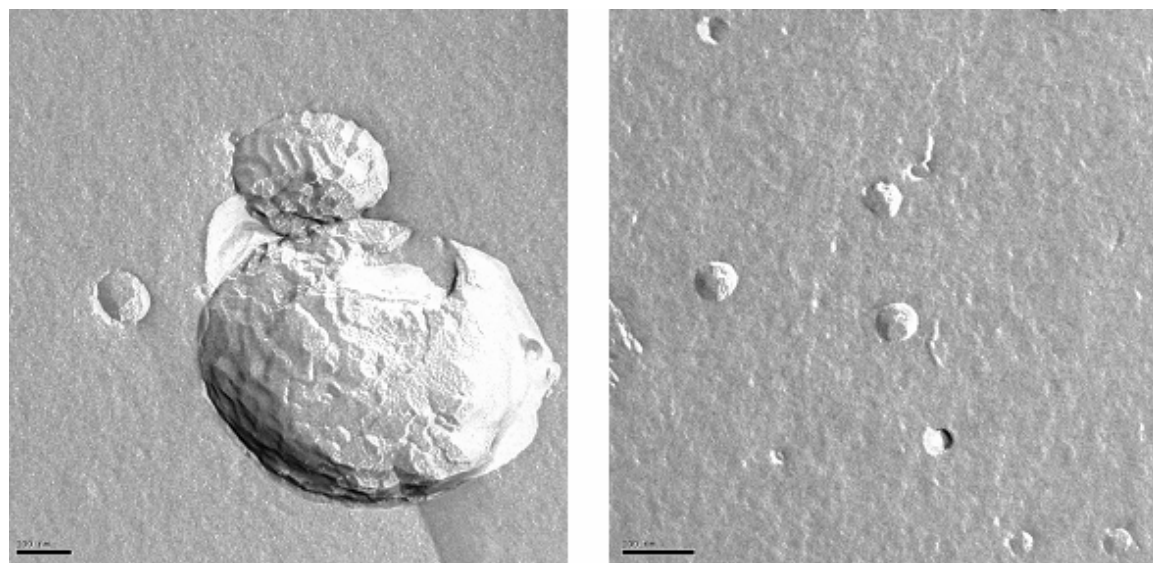


Figure S1: FF-TEM images the effect of 45 mM (a) CsCl and (b) LiCl on the reference SDS/DTAB micellar solution. The bars represent 100 nm in both cases.

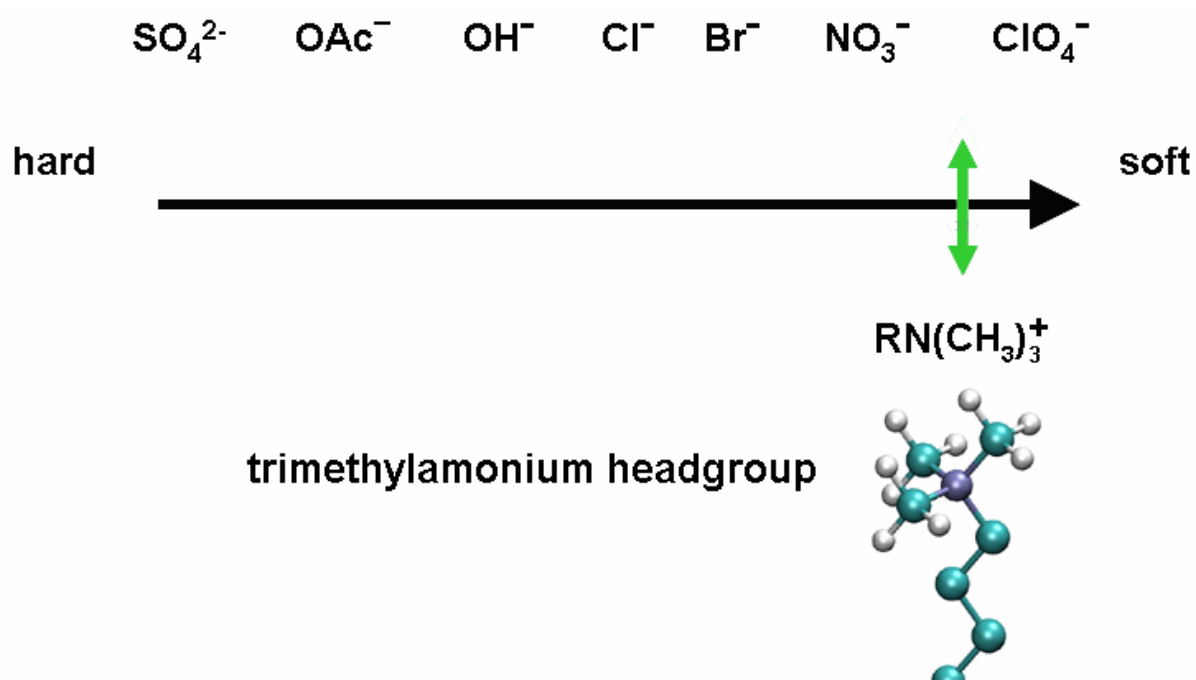


Figure S2. Ordering of anionic counterions with respect to their affinity for the trimethylammonium headgroup.