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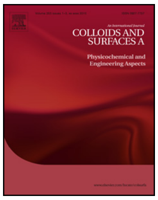


Specific ion adsorption on alkyl carboxylate surfactant layers

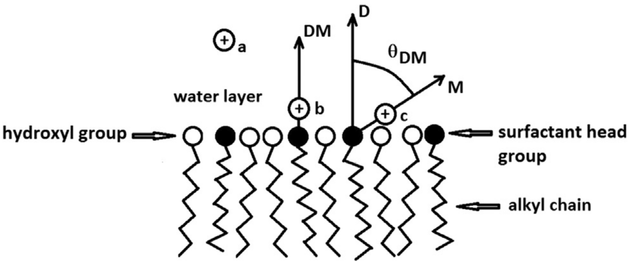
Susanne Dengler[a], Gordon J.T. Tiddy[b], Lydia Zahnweh[a], Werner Kunz[a,*]

[a] Institut für Physikalische und Theoretische Chemie, Universität Regensburg, Regensburg, Germany
[b] School of Chemical Engineering and Analytical Science, University of Manchester, Oxford Road, Manchester M13 9PL, UK

HIGHLIGHTS

- Rubidium and caesium cations prefer bb-binding site.
- Affinity of rubidium and caesium to carboxylate is very weak and there is no detectable ion specificity.
- A sufficient interaction between anion and cation is a precondition for the determination of ion specificities by NMR.

GRAPHICAL ABSTRACT



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ABSTRACT

Mixtures of dodecyl carboxylate, CsOH, RbOH and octanol in D_2O were investigated to determine the relative ion specificity of Cs^+ and Rb+ in their interactions with dodecyl carboxylate in a liquid crystalline phase. Octanol as cosurfactant was necessary to obtain the lamellar liquid crystalline phase. The technique used was the measurement of the NMR quadrupole splitting of ^{137}Cs and ^{87}Rb. The ratio of Rb to Cs was varied as well as the concentration of surfactant and octanol, whereas the ratio of surfactant to octanol was kept constant at 1:3. It turned out that there is no significant difference between both ions in their affinity towards carboxylate head groups.

1. Introduction

1.1. Ion specificity

The specific interaction of charged headgroups with different counter ions matters in many biological as well as industrial systems [1,2]. An example is the transition of micellar structures to vesicles [3]. To cite a more applied case, the Krafft temperature of surfactants used in washing processes increases with increasing ion binding. These behaviours can often be explained by Collins' concept of matching water affinities, together with a Hofmeister-like classification of both ions and charged headgroups (Fig. 1) [4–9]. In Hofmeister series anions and cations are listed in separate series, sorted from salting out to salting in of proteins.

In this concept, it is supposed that two ions with high charge densities ("hard" ions or headgroup) of opposite charge have a very strong electrostatic interaction which is greater than the interaction between the ion and the water shell around them resulting in the formation of a contact ion pair. Some of the hydration water between the ions is released. Regarding "soft" ions (low charge density), the interaction between water and these ions is weak and hydration water molecules between the ions can easily be released, which enables also the formation of a contact ion pair of two soft oppositely charged ions. By contrast, for the combination of hard and soft ions the formation of contact ion pair is not possible. The soft ion cannot penetrate the water shell of the hard ion. Hence, the general rule of this concept is "like seeks like" (Fig. 2) [10,11].

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* Corresponding author. Tel.: +49 941 9434296.
E-mail address: Werner.Kunz@ur.de (W. Kunz).

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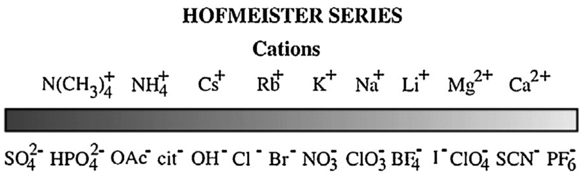

Fig. 1. A typical Hofmeister series.

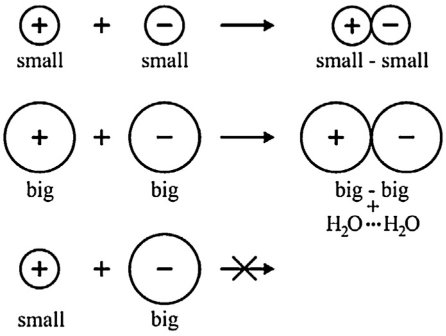

Fig. 2. Depending on the ion size direct ion pairs are formed.

Ion–water interactions are reflected in many properties of electrolyte solutions, for example in the viscosity of aqueous solutions. Especially, the Jones–Dole viscosity *B* coefficient is believed to be a good parameter to estimate ion hydration. It can be calculated from salt solution viscosity η in Eq. (1) with η_0 the viscosity of pure water, *A*, an electrostatic term, being 1 for moderate salt concentrations and *c* the salt concentration. *B* is a direct measure of the strength of ion–water interactions normalised to the strength of water–water interactions.

$$\frac{\eta}{\eta_0} = 1 + Ac^{1/2} + Bc \qquad (1)$$

The coefficient can be positive or negative. Strongly hydrated ions have positive *B* coefficients and weakly hydrated ions have negative *B* coefficients. The point of change in Jones–Dole coefficient sign represents the ideal behaviour at which the interaction water–ion is the same as water–water interaction. In Table 1 the *B* coefficients of some ions are given [12,13]. Consequently, Rb$^+$ as well as Cs$^+$ are weakly hydrated whereas the carboxylate head group of fatty acid is strongly hydrated. So, according to Collins' concept the interactions between the head group and the counterions should be very small and of comparable weakness. Admittedly, this is a very indirect conclusion, because it is not evident that viscosities of simple electrolyte solutions reflect partition coefficients as they are measured here in liquid crystalline systems. Nevertheless, we could show in a former work that the different ion bindings of lithium and sodium ions to carboxylate and sulphate headgroups in such lamellar systems reflect surprisingly well the expected trend as predicted by Collins. As in the present study, the used technique was NMR quadrupole splitting [14]. Here we check now if the expected (non-)binding of caesium and rubidium to carboxylate headgroups can also be detected by this technique and we further show how nicely the results fit with viscosity B coefficients.

Table 1
Jones–Dole viscosity *B* coefficients.

Cations	*B*	Anions	*B*
Ca^{2+}	0.285	CH$_3$COO$^-$	0.250
Li$^+$	0.150	SO$_4{}^{2-}$	0.208
Na$^+$	0.086	Cl$^-$	−0.007
Rb$^+$	−0.030	NO$_3{}^-$	−0.046
Cs$^+$	−0.045	I$^-$	−0.068

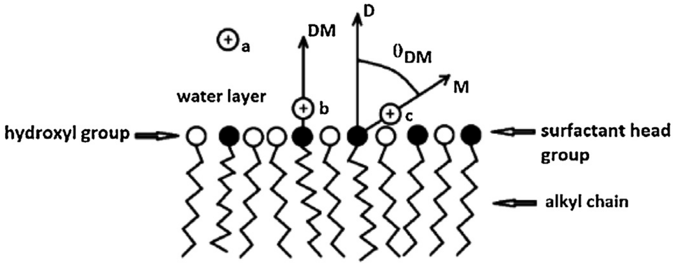

Fig. 3. Schematic drawing of counter ion binding at the lamellar surface. Three possible binding situations are shown: (a) Ion moves freely in the bulk phase. (b) The ion is located perpendicular to the surfactant head group in the lamellar layer. (c) The ion is bound between amphiphile head groups.

1.2. NMR quadrupole splitting

The core requirements for detecting quadrupole splittings of counter ions are the existence of an electric quadrupole moment and an anisotropic environment of the ion. Hence, only ions with a spin quantum number $I > 1/2$ can be detected. The anisotropy causes an electric field gradient with some orientations favoured over others. The splitting of the NMR resonance is the result of the interaction between the electric field gradient and the electric quadrupole moment at the nucleus. In an isotropic solution the orientation dependent quadrupole splitting averages to zero. For an anisotropic solution the resonance splits up into 2*I* peaks [4,5,15]. The frequency between the central peak and the first neighbouring peak is defined as the quadrupole splitting Δ. The magnitude of Δ is given in Eq. (2) for a powder sample (one with no macroscopic alignment of the liquid crystal phase) with S_i, the order parameter describing the orientation of the fraction of molecules at site *i* (p_i), given by $S_i = <3\cos^2\theta_{DMi} - 1>/2$. θ_{DMi} is the angle between the liquid crystal axis (the director) and the electric field gradient. $4\nu_{Qi}$ is equal to the quadrupole coupling constant. Δ is a weighted average of the different values for the *i* sites. The quadrupole coupling constant is not known. Hence, absolute values of Δ cannot be determined. But the relative change of Δ can be observed and delivers an insight in the binding situation of the ions [4,6,14,16].

$$\Delta = \left|\sum p_i \nu_{Qi} S_i\right| \qquad (2)$$

1.3. Ion interaction within lamellar phase

Within the investigated concentration range and in all compositions considered here, lamellar phases exist (Fig. 3) [14]. The ionic strength of the samples in water without considering the ion-binding is given in Table 2.

The counter ions can be free in the bulk phase, bound between the surfactant head groups (bb-site) or on the surface of the head groups (bs-site). Depending on the binding situation of the cation, the corresponding quadrupole splitting Δ changes. For free ions the contribution to Δ is zero. Bound ions have an anisotropic environment, giving a certain Δ value. The Δ value can be positive or negative depending on the angle between the liquid crystal axis and the electric field gradient. Ions bound in the bs-site give a positive value, whereas ions bound at the bb-site give a negative quadrupole splitting value.