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Historical perspective

Ion-specific effects in foams

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ABSTRACT

We present a critical review on ion-specific effects in foams in the presence of added salts. We show the theoretical basis developed for understanding experimental data in systems with ionic surfactants, as well as the nascent approaches to modeling the much more difficult systems with non-ionic surfactants, starting with the most recent models of the air–water interface. Even in the case of ionic surfactant systems, we show methods for improving the theoretical understanding and apply them for interpretation of surprising experimental results we have obtained on ion-specific effects in these systems. We report unexpectedly strong ion-specific effects of counterions on the stability and the rate of drainage of planar foam films from solutions of 0.5 mM sodium dodecyl sulfate (SDS) as a function of concentration of a series of inorganic salts (MCl, M = Li, Na, K). We found that the counterions can either stabilize the foam films (up to a critical concentration) or destabilize them beyond it. The ordering for destabilization is in the same order as the Hofmeister series, while for stabilization it is the reverse Therefore, the strongest foam stabilizer (K^+), becomes the strongest foam destabilizer at and beyond its critical concentration, and *vice versa*. Though the critical concentration is different for different salts, calculating the critical surfactant adsorption level one could simplify the analysis, with all the critical concentrations occurring at the same surfactant adsorption level. Beyond this level, the foam lifetime decreases and films suddenly start draining faster, which may indicate salt-induced surfactant precipitation. Alternatively, formation of pre-micellar structures may result in slower equilibration and fewer surfactant molecules at the surface, thus leading to unstable foams and films.

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1. Introduction

The specific effect of the salts on the physicochemical properties of solvents, solutes, dispersed systems and biological cells was reported in series of works since the middle of XIX-th century. Arrhenius and Kreichgauer [1] reported that the different inorganic salts affect the inner friction of their aqueous solution almost identically. On the contrary, Poiseuille [2] reported that some salts increase the inner friction of their aqueous solutions, while other ones decrease the latter, although these effects appeared to be difficult to distinguish. Ostwald [3] reported at first that the lowering of the vapor pressure of water, caused by the different salts with the same concentrations is almost the same. However after careful analysis he established that the vapor pressure depends weakly on type of the added salt. Similarly, Raoult [4] reported about approximate identical lowering of the freezing point of the water caused by different salts and found out certain small differences depending on the type of the salt. Moreover, Long [5] reported that the molecular diffusion of the inorganic salts against water depends on both the inner friction of their aqueous solutions and their water absorbance. He established some differences in the molecular diffusion of the salt molecules in water under identical conditions, but the results remained doubtful due to the complexity of the experiment conducted at the end of XIX-th century. Hugo de Vries [6] determined the behavior of live plant cells in different salt solutions. He reported that at certain specific concentration for each salt, the protoplasm of the cell peels away from the cell wall, leaving gaps between the cell wall and the membrane (plasmolysis). Sometime later Hamburger [7] confirmed the same salt effects on red blood cells. The above-mentioned authors reported the first cases of salt-specific effects. However, only the salt-specific effects on living cells were found to be evident.

Furthermore, the most significant and meaningful contribution in this area belongs to Hofmeister [1]. He and his team [8–14] published a whole series of seven papers entitled “About the science of the effect of salts”. They established that the blood proteins precipitate at specific concentrations of added salts. Thus, some salts are stronger precipitators than other ones. They found out that both cations and anions of the salt contribute to this precipitation, but the effect of the anions is stronger. These findings were confirmed recently by means of small angle X-ray scattering (SAXS) on interacting protein molecules [15]. Moreover, it was found that the salt ions affect the very properties of the protein molecules in a specific way [16]. Furthermore, the findings of Hofmeister and his team were used for building of a series of anions and cations ordered according to their precipitation ability:

$$\begin{aligned}&\text{Cations}:\ \mathrm{Li^+}<\mathrm{Na^+}<\mathrm{K^+}<\mathrm{Rb^+}<\mathrm{Cs^+}<\mathrm{NH_4^+}<\mathrm{NMe_4^+}\\&\text{Anions}:\ \mathrm{ClO_4^-}<\mathrm{BF_4^-}<\mathrm{NO_3^-}<\mathrm{Br^-}<\mathrm{Cl^-}<\mathrm{OH^-}<\mathrm{F^-}<\mathrm{CH_3COO^-}.\end{aligned}$$

The above mentioned series are known as Hofmeister series in the literature [17–21]. Hofmeister established the same effects of the added salts on the stability of aqueous suspension of isinglass, colloidal ferric oxide, and sodium oleate [9] as well. These discoveries unveiled a whole interdisciplinary field in the science. For example, it was recently found out that the ions affect specifically the catalytic activities of some enzymes [18], thus being important in medicine, pharmacy and biophysics. Almost at the same time Setschenow established independently [22] that the organic solutes in water precipitate (salt out) at sufficient amount of added sodium chloride. He arrived at an empirical equation predicting the solubility of many non-electrolyte organic substances at different concentrations of sodium chloride. He introduced the “Setschenow's empirical constants”, which are specific for every organic substance. It was established much later [23] that both the anions and the cations of the salt have specific contributions to the values of “Setschenow's constants”.

A few years after Hofmeister, Heydweiller [24] found that the salt increases the surface tension of the air/water interface in surfactant free solutions (Fig. 1). Moreover, he established that the relative effect of the ions on the surface tension follows closely the Hofmeister series, thus drawing the conclusion that the two phenomena are related. His discovery was followed by significant contributions by Langmuir [25], Wagner [26], Onsager and Samaras [27], Jones and Ray [28–32] and many other renowned scientists since the 1930s to the present [33–49]. Their studies revealed complicated interactions between the ions of the salt and the air/water (oil/water) interface resulting in the formation of spatially separated cation-depleted and anion-depleted layers at the very inter-phase boundary, thus increasing its surface tension. The parameters of these layers and the corresponding increase of the surface tension depend on the types of ions in the salt. Thus, for example, considerable efforts have been put into developing the statistical mechanical models for describing the behavior of strong electrolytes in close proximity to the interface boundary.

The Poisson–Boltzmann (PB) theory treats the ions in close proximity of charge interfaces in the classical way. It is good for predicting the behavior of univalent ions not too close to the interface for low electrolyte concentrations. Unfortunately, this theory breaks down at the very surface at higher surface charge densities. Consequently, further development with fewer approximations of the PB equation is needed to describe a more realistic picture. More importantly, this theory does not account for any differences between the different counter-ions, while experiments reveal clear differences in interactions at either biological or non-biological surfaces. The “counterion effect” is related to the Hofmeister series for cations or anions [50]

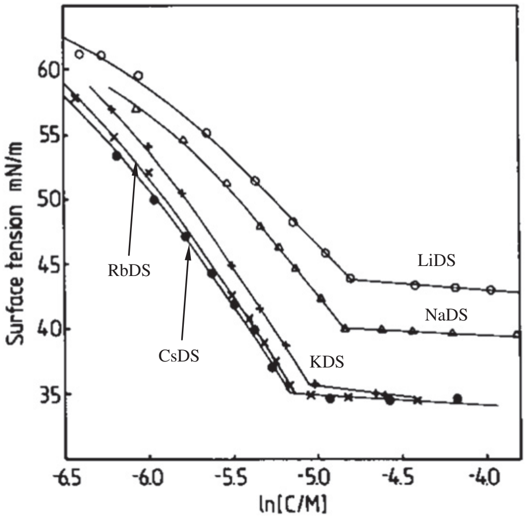

Fig. 1. Surface tension *versus* ln (concentration) for LiDS, NaDS, KDS, RbDS and CsDS. Reprinted with the permission from Elsevier, Lu, J.R., Marrocco, A., Su, T.J., Thomas R.K., and Penfold J., “Adsoprtion of Dodecylsulfate Surfactants, with Monovalent Metal Counter-Ions at the Air–Water Interface Studied by Neutron Reflection and Surface Tension”, J. Colloid Interface Sci., 1993, 158, 303–316 [80].