# Are Antagonistic Salts Surfactants?

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ABSTRACT: It is well known that surfactants decrease both water/air and water/oil interfacial tensions whereas in contrast inorganic salts increase both. We study a new, third class of surface-active ionic solutes, which have been called antagonistic salts, consisting of an organic group with a small inorganic counterion. These show decreased interfacial tension at the oil/water interface due to a redistribution of the organic group in the oil but do not show any surface activity at the air/water interface and are consequently different from surfactants that lower both tensions. We use a simple modeling using Poisson–Boltzmann theory that accounts for the surface activity of the antagonistic salt at the water/oil interface.
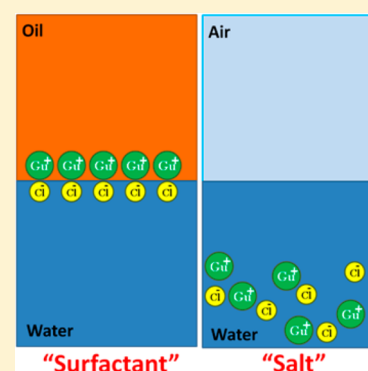
Knowledge of the surface activity of ionic solutes is of key importance for manifold applications and industries, such as coating and dispersion processes,[1−3] oil recovery,[4,5] digital microfluidics,[6,7] and biochemical research.[8] Surfactants are the most prominent example of surface-active ions and are commonly viewed as having both a hydrophobic (organic) and a hydrophilic (inorganic) part within the same molecule. For this reason, surfactant molecules will spontaneously adsorb onto an interface between water and any apolar medium, usually either air or oil. Whenever molecules adsorb onto a surface or interface, the surface tension γ will be lowered according to the Gibbs adsorption equation (eq 1)

$$\Gamma = \frac{d\gamma}{d\mu} \cong -\frac{1}{k_B T}\frac{d\gamma}{d\ln C} \tag{1}$$

where Γ is the adsorption and μ is the chemical potential of the adsorbing solute and where the approximation on the right-hand side holds for dilute solutions with a bulk concentration C of the solute (surfactant). If $\Gamma > 0$, then the surface tension should decrease with increasing bulk concentration of surfactant. Upon the addition of a typical surfactant, the surface tension of water can decrease from ∼70 mN/m to roughly 25 mN/m; however, the interfacial tension with oil can decrease by many orders of magnitude to go from ∼50 mN/m to ultralow tensions of roughly a few μN/m.[9,10] The difference between the air/water and the oil/water interfaces is that for the latter the surfactant may also be soluble in the oil phase and may be capable of dissolving part of the water into the oil phase or vice versa. Ultralow surface tensions are then reached when, because of the presence of the surfactants, the mutual solubility becomes so high that the difference in composition becomes very small; consequently, the interfacial tension also becomes very small. Such an ultralow tension often leads to the formation of a third phase (in addition to the oil and water phases) that contains most of the surfactant and similar amounts of oil and water; well-known examples of this are swollen lamellar or sponge phases.[9−13]

Conversely, many inorganic salts such as NaCl are known to increase both the surface tension of water with air and the interfacial tension.[14−17] According to the Gibbs equation (eq 1), this means that the salt molecules are negatively adsorbed, i.e., depleted from the interface. This happens for both water/air and water/oil interfaces and is usually understood in terms of the repulsion between an ion and its image charge that becomes important when an ion comes close to the surface.[15−17]

In view of what precedes, it becomes clear that ionic solutes, regarding their surface activity, are commonly classified either as surfactants or inorganic salts. In light of this, recent reports of certain ionic solutes that are not surfactants but produce a lamellar phase, implying an ultralow water/oil interfacial tension,[18,19] are surprising. The authors of refs 18 and 19 dubbed the solute sodium tetraphenyl borate an antagonistic salt; this salt, when added to a D_2O/3MP (3-methylpyridine) system, gave the lamellar phases. Somewhat similarly to ionic surfactants, this antagonistic salt consists of a small inorganic ion, Na^+, and a large organic counterion. The question is then what distinguishes it from a charged surfactant: perhaps the most commonly used surfactant, SDS, also dissociates into Na^+ and a large organic counterion.

The most common explanation[18−25] of the difference is that antagonistic salts go to the oil/water interface because of the opposite preference of solvation of both ions. This leads to
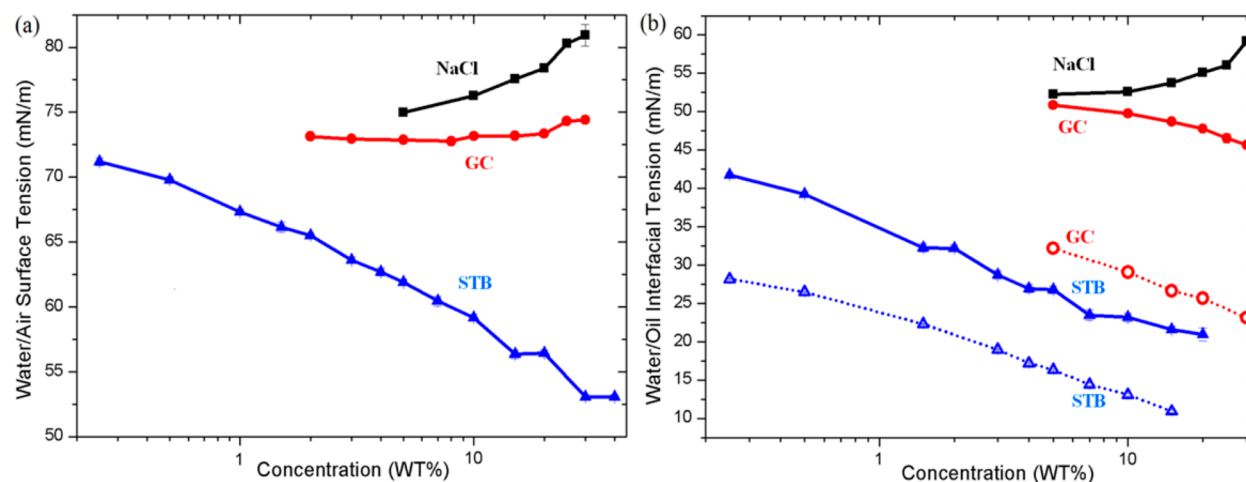
Figure 1. (a) Surface tension at the water/air surface of aqueous solutions of sodium chloride (NaCl, black squares), guanidinium chloride (GC, red circles), and sodium tetraphenyl borate (STB, blue triangles) as a function of the ionic solute concentration in weight percent. (b) Interfacial tension at the water/heptane interface (full symbols, straight line) and water/toluene interface (hollow markers, dashed line) of the same solutions as in (a). The interfacial tension at the pure water/toluene interface is roughly 35 mN/m whereas that at the water/heptane interface is 52 mN/m, which explains the shift between the heptane and toluene data.

microphase separation, with the organic ions becoming dissolved by the oil phase and the inorganic ions being left in the water.[20] The electrostatic attraction between both ions then leads to the formation of a double layer at the interface. Light-scattering measurements confirm that for antagonistic salts at the oil/water interface the small inorganic ions are on the aqueous side and the large organic ions are on the oil side.[18] It is thus believed that it is this antagonistic redistribution that is required for antagonistic salts to adsorb at an interface and, according to eq 1, lower the interfacial tension. In contrast to the oil/water surface, the redistribution process is not expected at the water/air surface, so there should be no surface activity. The fundamental difference between surfactants and antagonistic salts should then be that surfactants lower both the water/air and the water/oil tension, whereas antagonistic salts should decrease only the water/oil tension. This is the definition of antagonistic salts that we will use in what follows.

The goal of this article is to demonstrate that this fundamental difference between antagonistic salts and surfactants really exists and that therefore antagonistic salts (besides inorganic salts and surfactants) are indeed a new, third class of surface-active solutes.

We study the surface activities at the water/air and water/oil interfaces of two organic salts and use NaCl as a reference salt. Our experiments suggest that the salt used in refs 18 and 19 is perhaps better characterized as a surfactant because it lowers both the water/oil and the water/air interfacial tension. In addition, no ultralow interfacial tension is found in this system. We do, however, uncover another truly antagonistic salt. This salt lowers the water/oil tension but does not influence the water/air tension. We find the lowering of the oil/water tension to be on the order of a few mN/m, in agreement with a model calculation of the electrostatic problem using Poisson–Boltzmann theory for the adsorption of antagonistic salts at the water/oil interface.

We consider solutions of a simple inorganic salt, sodium chloride (NaCl), and two other ionic solutes, guanidinium chloride (CH_6N_3 Cl) and sodium tetraphenyl borate ((C_6H_5)$_4$BNa, all purchased from Sigma-Aldrich) in ultrapure Millipore water. It is worth mentioning that the solubility in

water of sodium chloride and guanidinium chloride is very high ($\sim$6 M[26,27]) whereas the solubility of the relative bulky sodium tetraphenyl borate lies at $\sim$1.37 M;[28] the lower the solubility of a charged molecule in water, the more likely the solute adsorbs at an interface, as we will see later. The solutes were added to water and stirred for 1 day and left at rest for another day. The concentration of the solutes was measured in weight percent (wt %), whereby this refers to the weight of the amount of pure water used for the preparation. In our experiments, we used different oil phases (decane, heptane, hexane, cyclohexane, and toluene, all purchased from Sigma-Aldrich)). However, we detected roughly the same effect on the interfacial tension of the ionic solutes, regardless of the nature of the oil phase. This we illustrate in Figure 1b where we compare the interfacial tension at a water/heptane and a water/toluene interface. For simplicity we therefore discuss the results only for heptane throughout the text. Because the addition of electrolytes influences the surface activity of many charged surfactants,[29,30] we also prepared solutions of guanidinium chloride and sodium tetraphenyl borate in the presence of 10 wt % (where the wt % also refers to the weight of the pure water) sodium chloride.

We probe the surface activity of the ionic solutions at the water/air and water/oil (alkane) interfaces as a function of the solute concentration using the pendant drop method. With the tensiometer (Easy Drop DSA 100 from Kruess), a droplet of the aqueous solution was created that then hangs from a syringe needle (1.82 mm in diameter). The shape of the droplet is vertically distorted by the effect of gravity; the deviation from the droplet shape from a sphere (droplet shape in the absence of gravity) is thus a measure of the surface tension. The droplet is captured by a digital camera, and the contours of its surface are evaluated and software then measures this deviation in the droplet shape. As the droplet is formed, a fresh interface between the aqueous solutions and the embedding phase (air or oil) is created. We observed that the tension measured is transient when sodium tetraphenyl borate is dissolved in the aqueous phase but constant for sodium chloride and guanidinium chloride. The tension decreases in the first 100 s by roughly 2 mN/m and then remains roughly constant. The tension data in Figures 1 and 2 are the average value of the
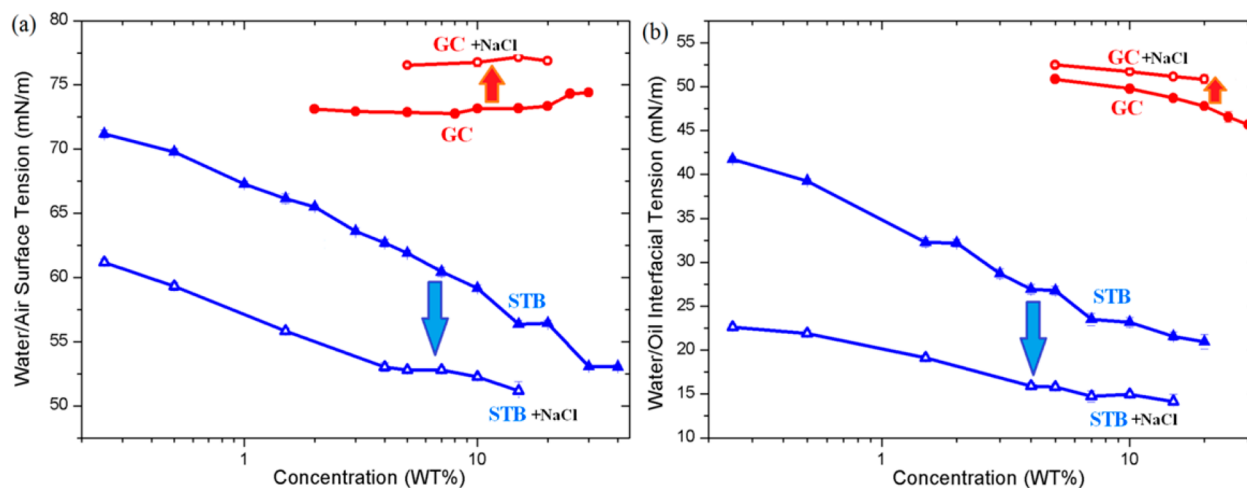
Figure 2. (a) Surface tension at the water/air surface and (b) interfacial tension at the water/heptane interface of aqueous solutions of guanidinium chloride (GC, red circles) and sodium tetraphenyl borate (STB, blue triangles) in the absence (filled markers) and the presence (hollow markers) of 10 wt % sodium chloride (NaCl).

tension in these 100 s for all thee solutes. The error bars are smaller than the plot markers, which is why they can hardly be seen.

Figure 1a,b shows the surface tension and interfacial tension, respectively, of aqueous solutions containing the three ionic solutes NaCl, guanidinium chloride, and sodium tetraphenyl borate as a function of solute concentration. We find that NaCl slightly increases both the surface tension and the interfacial tension. This behavior of NaCl is well known, is general for inorganic salts, and is due to the depletion of ions near the interface. More striking is the surface activity of the two other ionic solutes in our experiment. As mentioned at the beginning of this article, sodium tetraphenyl borate was considered to be an antagonistic salt in earlier experiments.[18,19] Figure 1, however, shows that the surface tension and the interfacial tension both decrease as a function of sodium tetraphenyl borate concentration by several tens of mN/m. The redistribution of ions into the apolar phase, a requirement for antagonistic salts to lower the interfacial tension, is not possible at the water/air interface. Thus, if the surface activity of sodium tetraphenyl borate originates predominantly from an antagonistic redistribution, then the surface tension of water with air should not decrease in the same way as the water/oil tension, which it does. Therefore, Figure 1 suggests that sodium tetraphenyl borate is perhaps better classified as a surfactant.

The situation is qualitatively different for the aqueous solutions of guanidinium chloride: the surface tension (Figure 1a) is unchanged, and the interfacial tension at the water/heptane interface decreases (Figure 1b). The surface activity of guanidinium chloride is consequently dependent on whether a water/air or water/oil interface is considered. As mentioned at the beginning, this can be explained by the antagonistic redistribution of ions that takes place at a water/oil interface but is impeded at the water/air interface.

To understand the data of Figure 1 it is worth noting that there is a correlation between the surface activity of the solutes and their solubility in water. Guanidinium chloride (GC) has a very high solubility (~6 M) in contrast to sodium tetraphenyl borate (~1.3 M); guanidinium chloride is consequently less hydrophobic than sodium tetraphenyl borate, which is a hint as to why guanidinium chloride does not lower the water/air tension but sodium tetraphenyl borate does. An additional

finding that clearly distinguishes between the surfactant-like and antagonistic behavior of the two organic solutes is what happens to the surface tension and interfacial tension upon the addition of sodium chloride. Figure 2a,b shows that the addition of NaCl causes both the surface tension and the interfacial tension of the sodium tetraphenyl borate solutions to decrease further. This is a common observation made for ionic surfactants[29,30] and thus supports our earlier conclusion: sodium tetraphenyl borate behaves like a surfactant. However, guanidinium chloride shows the opposite behavior; the surface tension (Figure 2a) and the interfacial tension (Figure 2b) slightly increase upon the addition of 10 wt % NaCl. This probably happens because the two ionic solutes compete with each other near the surface and the effects appear to be roughly additive.

In summary, Figures 1 and 2 suggest that guanidinium chloride behaves like an antagonistic salt according to the definition given at the beginning. The decrease in the interfacial tension of aqueous guanidinium chloride solutions with heptane (Figure 1b) should therefore be due to the redistribution of guanidine ions in the heptane phase. To see whether such a mechanism can indeed describe the decrease in interfacial tension with heptane (Figure 1b), in the following text we will present a model of the antagonistic effect using a Poisson−Boltzmann model that accounts not only for the redistribution of ions but also, albeit in a very simplified way, for the image charge effect.[31−35] Specific ion effects such as hydration and polarizability,[36,37] specific adsorption,[38,39] and the role of fluctuations[40] have been left out for now in order to isolate the antagonistic effect of interest here, leaving their interplay for future research.

We consider a planar surface of area A separating two half spaces $z < 0$ and $z > 0$ filled with water (dielectric constant $\epsilon_w = 80$) and oil ($\epsilon_O = 1.9$, representing heptane), respectively, at temperature T. The system also contains two monovalent ionic species, labeled by $\alpha = +1$ for the cations and $\alpha = -1$ for the anions, and we seek the change $\Delta\gamma$ of the water/oil surface tension due to the ions by minimizing the mean-field grand potential functional

$$\frac{\Omega[\{\rho_\alpha\}]}{k_B T} = A \sum_{\alpha=\pm} \int_{-\infty}^{\infty} dz \, \rho_\alpha(z) \left[\log\left(\frac{\rho_\alpha(z)}{\rho_w}\right) - 1 + \frac{V_\alpha(z)}{k_B T} \right.$$

$$\left. + \frac{\alpha}{2}\phi(z) \right] \qquad (2)$$

with respect to the two ionic concentration profiles $\rho_\alpha(z)$.[41] The first term in the square brackets in eq 2, where ρ_w denotes the ion concentration in bulk water at $z \to -\infty$, represents the ideal gas entropy of the two ionic species (favoring a homogeneous distribution of ions over the two liquids). The second term in square brackets includes the interaction of the ions with the solvent through the shifted Verwey−Niessen potential $V_\pm(z) = 0$ for $z < S$ and $V_\pm(z) = f_\pm$ for $z > s$, were $f_\pm$ denotes the ionic self-energy difference (or the Gibbs transfer energy) of the ions in oil compared to that in water. The location of the potential discontinuity at $z = s \neq 0$ is a simplified way to describe image charge interactions,[41] where shift parameter s is negative here because $\epsilon_W > \epsilon_O$. Note that f_+ and f_- take opposite signs for an antagonistic salt. The last term in the square brackets of eq 2 accounts for the Coulombic ion−ion interactions described in terms of electrostatic potential $k_B T\phi(z)/e$ that satisfies the Poisson equation.[41] The minimization of Ω leads to $\rho_\pm(z) = \rho_w \exp[\mp\phi(z) - V_\pm/k_B T]$, which with the neutrality of bulk oil leads to $\phi(z \to \infty) = (1/2)(f_- - f_+) \equiv \phi_D$, the Donnan potential, from which we find that $\rho_\alpha(z \to \infty) = \rho_w \exp[(f_+ + f_-)/2] \equiv \rho_O$, the bulk ion concentration in oil.

Following ref 41, one derives the full z-dependent equilibrium density profiles by minimization of the grand potential functional.[2] The electrostatic contribution to the tension is given by $\Delta\gamma = (\Omega - \Omega_{bulk})/A$, which yields within linear screening theory[41]

$$\frac{\Delta\gamma}{k_B T} = 2(1 - p^2)s\rho_o - \frac{p\phi_D^2}{2D\sqrt{2\pi\lambda_B^O}}(n\cosh(\kappa_i s)$$

$$+ \sinh(\kappa_i s))\sqrt{\rho_o} \qquad (3)$$

where $p = \exp[(f_+ + f_-)/4]$, $\lambda_B^O = ((e^2)/(\epsilon_O k_B T))$ is the Bjerrum length in oil, $\kappa_i = (8\pi\lambda_B^O\rho_w)^{1/2}$ is the interfacial Debye screening parameter for $s < z < 0$, $n = (\epsilon_w/\epsilon_O)^{1/2}$, and $D = (1 + np)\cosh(\kappa_i s) + (n + p)\sinh(\kappa_i s)$.

In Figure 3 we compare our experimental result of the reduction of the tension of the water/heptane interface with the guanidinium chloride concentration with our linearized Poisson−Boltzmann equation, where we use fit parameters $f_- = -3.3k_B T$, $f_+ = 3.1k_B T$, and $s = -0.1$ nm. Except at extremely low concentrations, this set of fit parameters renders the first term of our expression for $\Delta\gamma$ dominant, with $p < 1$. This term is bilinear in ion concentration and s and stems from the net desorption due to the image charge (and possibly other specific) forces.[41] Although the reasonable agreement between the experimental observations and the linearized theory comes with a very reasonable value for s on the order of a molecular size, the numerical values for the self-energies are rather low. It is interesting to speculate that a full nonlinear treatment of the problem and perhaps a better account of the image-charge interactions and ion polarization should give rise to more realistic (higher) values of the best fit of the self-energies, but this is left for future research. For now we conclude that linearized Poisson−Boltzmann theory qualitatively supports the
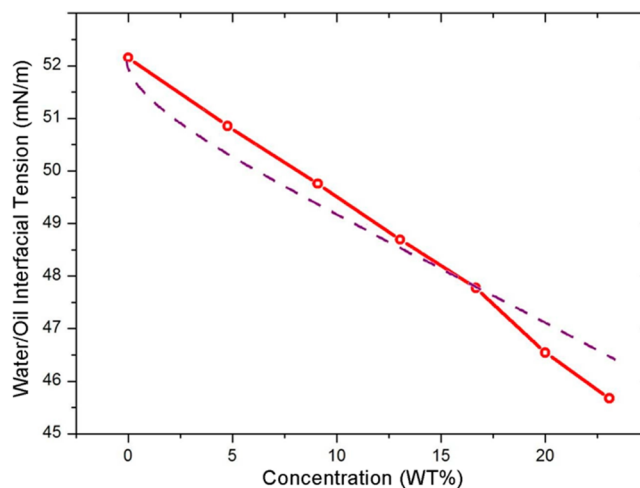

Figure 3. Interfacial tension at the water/heptane interface as a function of the bulk concentration in water, ρ_w, in weight percent. The red graph denotes the experimental data for the interfacial tension measurements in the presence of guanidinium chloride (the same as in Figure 1b). The dashed line is the result of linearized PB theory for an antagonistic salt with self-energy differences of $(f_-, f_+) = (-3.3, 3.1)$ $k_B T$ and $S = 0.1$ nm.

experimental finding that guanidinium chloride is of an antagonistic nature.

In summary, we tested two ionic solutes, sodium tetraphenyl borate and guanidinium chloride, by comparing their influence on the surface and interfacial tensions. Because sodium tetraphenyl borate lowers both the surface and interfacial tension, this suggests that sodium tetraphenyl borate behaves similarly to a surfactant. The enhancement of its surface activity in the presence of an NaCl supports this suggestion. Because sodium tetraphenyl borate behaves as a surfactant, the observation of a lamellar phase in refs 18 and 19 is less surprising because, as mentioned before, surfactants are known to produce lamellar phases. This of course does not exclude the fact that surfactants may also exhibit an antagonistic redistribution processes; as mentioned before, the antagonistic redistribution process at the D$_2$O/3MP (3-methylpyridine) interface was detected by light-scattering measurements.[18] Our results (Figure 1), however, suggest that the redistribution process contributes very little to lower the water/oil interfacial tension because the water/air surface tension is lowered by the same amount. In this framework it is also interesting to determine the molecular distribution of sodium tetraphenyl borate at the water/air surface by light-scattering experiments. This, however, clearly goes beyond the scope of the work we present here.

Thus, sodium tetraphenyl borate is a good example of a solute where one may discuss whether to classify it as a surfactant or an antagonistic salt. It would be interesting to consider whether one can predict whether a given ionic solute adsorbs on its own (as surfactants do) and/or with the help of the antagonistic redistribution. One measure for this could be the hydrophilic−lipophilic balance (HLB) of a specific solute. The HLB is a common measure of the solubility of surfactants in aqueous and oil phases and allows the classification of different types of surfactants. There are two methods to determine the HLB.[42,43] Both methods allow the determination of c of HLB from the molecular structure of a surfactant; however, only the Griffins method[42] can be applied to our

system because the other requires a knowledge of the HLB values of the individual groups that make up the molecule. The HLBs found for our solutes are HLB ~2 (sodium tetraphenyl borate) and HLB ~8 (guanidinium chloride). According to these values, sodium tetraphenyl borate is more hydrophobic than guanidinium chloride, which supports our conclusion that we drew from the solubility in water and the tension measurements. However, the values also suggest that both of the solutes are more soluble in the oil phase than in water. This contradicts our own solubility measurements of both solutes in heptane. We found that neither sodium tetraphenyl borate nor guanidinium chloride dissolves in heptane even at concentrations as low as a few mM whereas in water their solubility limit is on the order of a few M. This is probably a drawback of the method that was originally devised for nonionic surfactants.

The question then remains as to why we could not detect an ultralow interfacial tension in any of our systems, regardless of the oil phase or salinity that we used. A possible interpretation of the observation in refs 18 and 19 is that their $D_2O/3MP$ system was near a critical temperature T_c below which D_2O and 3MP become miscible and consequently the interfacial tension between D_2O and 3MP vanishes. The interfacial tension of a pure (surfactant-free) $D_2O/3MP$ system is given by the relation[44]

$$\gamma = 0.128 \frac{k_B T_c}{\xi^2} \tag{4}$$

Here the solvent length ξ is a function of the temperature and describes the correlation length scale of the composition fluctuations.[44] The closer the temperature T of a system is to the critical temperature T_c (for the $D_2O/3MP$ system considered, $T_c = 318$ K) at which the two phases mix, the longer the length scale of these fluctuations becomes. The correlation length for the $D_2O/3MP$ system was measured in ref 19 at exactly the same temperature ($T = 313$ K) at which the lamellar phase in refs 18 and 19 was observed and was found to be $\xi \approx 20$ nm, for which eq 4 yields $\gamma \approx 2 \times 10^{-3}$ mN/m for the interfacial tension of the $D_2O/3MP$ system. This shows that the interfacial tension in their system is already 4 orders of magnitude lower even in the absence of sodium tetraphenyl borate than in our system.

Guanidinium chloride shows no surface activity at the water/air interface but does show a slight decrease in the interfacial tension at the water/heptane interface, indicating that the tendency for the migration of the bulky organic counterions into the oil phase is the key mechanism for antagonistic salts to lower the interfacial tension. This is in agreement with a linearized Poison−Boltzmann model that correctly predicts the interfacial tension lowering that supports our conclusion that guanidinium chloride is of an antagonistic nature.

Our experiments and theoretical considerations show that the world of surface-active compounds is not distinctly divided into inorganic salts and surfactants.[1−17] A third class has to be considered that lowers the interfacial tension at a water/oil interface by a peculiar redistribution mechanism. At the same time this mechanism prevents a truly antagonistic salt from lowering the surface tension at the water/air interface. Our attempt to determine the HLB of the two solutes considered here failed, which illustrates that predicting the surface activity of a specific solute is still not trivial. However, antagonistic salts have been barely considered in surface science, even though their selective surface activity might play a crucial role and open

new perspectives for all applications and industries that are based on surface-active compounds.[1−8] A specific example for a technology that might be significantly affected by the unique antagonistic redistribution of ions may be electrophoresis, a microfluidic separation and driving mechanism for droplets.[45]

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