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Surface charge reversal and hydration forces explained by ionic dispersion forces and surface hydration

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ABSTRACT

The first direct measurements of forces between mica surfaces in electrolytes showed an apparent short range repulsion additional to the predictions of DLVO theory. The origins of such "secondary hydration forces" have remained a mystery. We show they can be explained as an repulsive entropic force appearing due to a hydration surface layer with longer range secondary hydration forces appearing as a consequence of ionic dispersion forces. Ionic dispersion forces are calculated from dynamic polarisabilities and finite ion sizes. Both are determined by *ab initio* quantum chemical methods. An hydration model is applied to describe the hydration layer of cosmotropic ions as well as hydration of the mica surface. Strongly hydrated cosmotropic ions are allowed to penetrate the surface hydration layer. Weakly hydrated chaotropic ions are excluded from the surface hydration layer. The combination of *ab initio* ionic polarisabilities and the hydration model allows the extended theory to account for secondary hydration forces.

Ionic dispersion forces are also shown to enhance surface adsorption of ions leading to charge reversal. Repulsive ionic dispersion forces for cations at a hydrocarbon surface reverse the entropic force, making it attractive rather than repulsive.

The DLVO theory of surface forces, developed by the Russian School of Derjaguin and Landau [1] and supported by the Dutch School of Verwey and Overbeek [2], is based on a point ion model in a continuum solvent and neglects a variety of effects. Surface induced solvent structure or hydration layers is usually taken into account by phenomenological models that use the notion of Stern layers, and with finite ion size, of inner and outer Helmholtz planes of unknown dielectric properties. Further extensions can include near surface ionic hard core repulsion and cooperative ion induced dipole interactions. Others allow oscillatory (depletion) forces due to ion sizes in bulk at high solute concentrations. Yet another extension relaxed the usual boundary conditions of constant surface charge or constant surface potential to include dissociable surface groups. None of these extensions explained the wide variations in "extra DLVO" forces, and their ion specificity satisfactorily. Agreement with theory could apparently be achieved, sometimes. In part this has been due to the restriction of experiments to a limited range of electrolytes like a few alkali halides. This means that ion specific Hofmeister effects are not revealed and necessarily masked.

Along with secondary hydration forces another phenomenon not accounted for is that of surface charge reversal. With increasing salt concentration, negatively charged interacting surfaces can switch from negative to positive surface potentials.

One component is missing from all standard decorations of DLVO theory, which admits only electrostatic forces between interacting ions and surfaces. Attractive quantum mechanical fluctuation forces between surfaces are included by adding a Hamaker (van der Waals, Lifshitz, dispersion) force contribution. Even so the theory as underlined by Derjaguin and Overbeek 60 years ago fails to explain the phenomenon of repeptisation and its ion specificity. The missing universal ion specific contribution resides in the neglect of ion–ion and ion–surface dispersion forces. The same is true for all theories involving electrolytes, be it Born free energies of transfer, activities, viscosities, interfacial tensions, zeta and membrane potentials, ion binding and electrochemistry. The ion specificity, or Hofmeister effect, is not included except by taking these forces into account. It can be shown that without their inclusion the theory is physically inconsistent, even at the level of the primitive model [3]. It can be shown further that at high concentrations especially, but sometimes even at very low concentrations the ion specific forces dominate electrostatics [4–6]. We have recently summarised the current level of understanding of Hofmeister effects [7] and the subject matter is also addressed by others [8].

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In this paper we illustrate the role of ionic dispersion forces in causing charge reversal and in secondary hydration effects (we use the term dispersion forces to encompass the totality of many body fluctuation forces, cooperative dipolar as well as induced dipolar forces included in extended Lifshitz theory). To account for our phenomena we find it necessary to introduce a surface model that allows a surface hydration layer, itself ultimately due to specific surface-induced solvent structure due to the same forces. We argue that such a surface hydration layer is responsible for the appearance of short-range repulsive forces. The mechanism is entropic: chaotropic counterions are excluded from the surface layer, so a diminishing volume is accessible to these ions which provide overall electroneutrality for the charged surface. Consequently, repulsive entropic forces increase in magnitude at small separations, giving rise to the observed short-range repulsion.

1. Background to the DLVO force framework

The background to the framework has been so well rehearsed that it hardy seems necessary to recapitulate it further. However we do need to do so schematically to illustrate its extension to include the dispersion forces. The surface forces in a system composed of surface–electrolyte–surface are treated via the total (Helmholtz) free energy (F) of the system. In the DLVO theory the total free energy is composed of three separate contributions: an electrostatic component $F_{\text{electrostatic}}$ due to the electric field generated by surface and electrolyte charges, an entropic component F_{entropic} due to the concentration distribution of the electrolyte, and a surface–surface dispersion energy (van der Waals interaction) F_{Hamaker}. To distinguish the direct van der Waals interaction from later contributions due to ionic dispersion forces, we call the surface–surface dispersion interaction a “Hamaker” interaction. Then

$$F_{\text{DLVO}} = F_{\text{electrostatic}} + F_{\text{entropic}} + F_{\text{Hamaker}} \tag{1}$$

where the electrostatic energy is

$$F_{\text{electrostatic}} = \frac{1}{2}\int d^3r D(r)E(r). \tag{2}$$

The electric field $E(r)$ can be taken as $E(r) = -\nabla\psi(r)$, with $\psi(r)$ the electrostatic potential. $D(r)$ is the electric displacement $D(r) = \varepsilon_0\varepsilon(r)E(r)$. Here $\varepsilon(r)$ is the dielectric function of the solvent (water), ε_0 is the permittivity of the vacuum.

The entropic energy is [9]:

$$F_{\text{entropic}} = kT\int d^3r \sum_i \left\{ c_i(r)\ln\frac{c_i(r)}{c_{i0}} - c_i(r) + c_{i0} \right\} \tag{3}$$

where $c_i(r)$ is the concentration of ion i at a distance r from the left surface, c_{i0} is its bulk concentration. Note the appearance of the term “$+c_{i0}$” at the rightmost side; this term has sometimes been incorrectly omitted in the literature [10,11]. Without it, the entropic energy will diverge linearly with $-kTc_{i0}L$ as separation between surfaces is increased.

The surface–surface dispersion energy (Hamaker energy) is, neglecting retardation:

$$F_{\text{Hamaker}} = -\frac{A}{12\pi L^2} \tag{4}$$

where A is the Hamaker constant for the surface–solvent–surface system, L is the separation between the two surfaces.

In the crossed-cylinder geometry for surface force measurements using the the surface forces apparatus (SFA) or the sphere-plane geometry used in atomic force microscopes (AFM), the measured force (f), scaled to the radius (R) of the curved surface, is conveniently proportion to the interaction free energy, $f/R = 2\pi F_0(L)$, after subtracting out the asymptotic surface energy at infinite separation, $F_0(L) = F(L) - F(L=\infty)$.

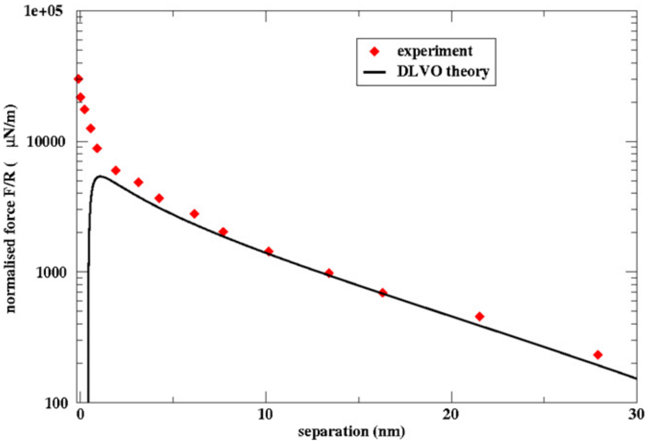

Fig. 1. DLVO force curve (constant charge) compared against experimental SFA measurements of mica in 10^{-3} M KCl [12].

In normal materials such as water, the electrostatic contribution to the surface energy increases monotonically to a maximum asymptotic value at infinite separations. The corresponding surface force is therefore negative at all separations, that is the electrostatic contribution is always attractive. Likewise the Hamaker surface force is usually attractive. The entropic contribution on the other hand tends to increases as separation decreases, due mainly to an increase in counterion concentration near the surface. That is, repulsion in DLVO theory arises due to the entropic contribution rather than the electrostatic contribution. By way of counter-example, the general theory of surface interactions applies to nonelectrolytic solutions (e.g. a sugar solution) at an uncharged surface. With the sugar molecule being uncharged, electrostatic interactions are not present, but adsorption of sugar molecules still occurs due to molecular dispersion forces. The entropic contribution therefore still appears (and is still repulsive), even though the electrostatic contribution is zero. It is a matter of semantics, with the phrase “electrostatic repulsion” frequently used in the literature referring to the entropic repulsion that arises in the case of an electrolyte solution. It would be more accurate to use the phrase “entropic repulsion”, if not “electrolytic repulsion”.

However, the entropic repulsion in conventional DLVO theory is not strong enough to overcome attraction due to the Hamaker force, resulting in the appearance of a primary minimum at small surface separations. This contrasts with experimental force measurements which commonly show short-range repulsion [12–14]. The situation is illustrated in Fig. 1. The short-range repulsion could not be explained by DLVO theory.

Similarly, experimental force measurements of mica in $Ca(NO_3)_2$ suggest that charge reversal takes place at high salt concentrations, changing the sign of the surface potential from positive to negative. DLVO theory, however, only predicts neutralisation, not reversal, of the surface charge, as illustrated in Fig. 5 (red dotted curve indicates the DLVO curve, black diamonds indicate experimental estimates of surface potential).

We explain these discrepancies between experiment and DLVO theory through a combination of ion specific properties and surface hydration.

2. Ion specific properties

We now take up the question of how, for instance, a sodium ion differs from a potassium ion. We identify at least four sources of ion specificity: