

Reply to Comment on the “Osmotic Coefficients and Surface Tensions of Aqueous Electrolyte Solutions: Role of Dispersion Forces”

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In their Comment¹ on our recent paper² Manciu and Ruckenstein raised several important points. In particular, they argued that we only considered the high-frequency ion–ion dispersion forces that will probably become negligible even in the bulk solution, if we do not neglect the (low-frequency) ion–water interactions that give rise to ordered hydration layers and a low local dielectric constant. To solve the problem, they propose *ab initio* calculations as were done, e.g., by Jungwirth et al.

We agree that this is a crucial issue. For that reason, in our paper we emphasized that the dispersion energy “includes all electromagnetic frequency distributions, microwave (permanent dipole), infrared (permanent dipole–induced dipole correlation), and optical and UV frequency (induced dipole–dipole correlation)”, but that in the present paper we only consider the high-frequency fluctuation correlation and further that “if such a model fails then we have to consider hydration profiles in more detail”. So, in a sense, we anticipated Manciu’s and Ruckenstein’s comment except insofar that we probably did not emphasize enough that a good fit to the osmotic coefficients does not necessarily mean that hydration forces can be neglected. For the surface we wrote explicitly “Hydration forces, incomplete hydration at the interface, and the resulting dipole must be taken into account. This can be tackled now with more confidence”.

The last quotation seems to be also valid for the bulk and, insofar as it is, we agree. But the point is that the hydration cannot be tackled correctly if the high-frequency interactions are neglected. To solve this problem, we did what the authors proposed and we made a computer simulation (for simple alkali

halides) in the framework of the nonprimitive model with polarizabilities both of the water molecules and of the ions.³ The result is that the attractive Lennard-Jones part between the ions partly includes the dispersion effects, but not completely, and that in the bulk both high-frequency and low-frequency correlations contribute to the “true” structure.

In terms of perhaps more familiar language, within the primitive model one of us tried several years ago to include the ion–water dipole interactions in a HNC calculation with the help of the old Booth-Graham model in order to simulate the influence of a distance dependent dielectric function.⁴ It turned out that dielectric values go rapidly up from 2 to 80 already at very small ion–water distances. If this model is right, the cation–cation and anion–cation interaction functions would not be much influenced by the distance dependence of the dielectric function, because we chose “dressed” cations including already the tightly bound first hydration shell.

But indeed for nitrate–nitrate interactions the situation might change. However, anions are much less hydrated than cations and this is in particular true for “soft” ions such as nitrate. In this case the dipole orientation of the water molecules would be much less pronounced and so would be the distance dependence of the dielectric functions. It can be that low frequency dispersion forces prevent a very strong ordering of the hydration layer around a soft anion, whereas it strengthens the hydration shell around a “hard” or “cosmotropic” ion, in addition to the electrostatic interactions between the ions. Therefore, it is not straightforward to argue that the dielectric distance dependence would completely dominate the high-frequency ion–ion interactions.

In any case the problem is still unresolved and we thank Manciu and Ruckenstein for their helpful comments.

References and Notes

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