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On the dissociation degree of ionic solutions considering solvation effects

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ABSTRACT

In this work the impact of solvation effects on the dissociation degree of strong electrolytes and salts is discussed. The investigation is based on a thermodynamic mixture theory which explicitly accounts for the solvation effect. Based on a remarkable relationship between differential capacity maxima and partial molar volume of ions in solution the solvation number of specific ions in solution is determined. A subsequent investigation of the electrolytic space charge layer shows that a saturated solution of 1 mol L^{-1} solvated ions forms near the electrode, and we point out some fundamental similarities of this state to a saturated bulk solution. This finding challenges the assumption of complete dissociation, even for moderate electrolyte concentrations, whereby we introduce an undissociated ion-pair in solution. We re-derive the equilibrium conditions for a two-step dissociation reaction, including solvation effects, which leads to a new relation to determine the dissociation degree. A comparison to Ostwald's dilution law clearly shows the shortcomings when solvation effects are neglected and we emphasize that complete dissociation is questionable beyond 0.5 mol L^{-1} for aqueous, mono-valent electrolytes.

1. Introduction

Strong electrolytes and salts are frequently assumed to completely dissociate into their respective ionic species, for all concentrations up to saturation [1-6]. After Arrhenius introduced the idea of dissociation (and also incomplete dissociation) at the end of the 19th century [7], Debye and Hückel concluded in 1923 [8] that strong electrolytes always completely dissociate in their respective ionic species [9]. From a thermodynamical point of view, this is a very strong *a priori* assumption and we show within this letter that solvation effects challenge this assumption, especially for concentrations beyond 0.5 mol L^{-1}. The concept of incomplete dissociation, ion association, or formation of ion-pairs in strong electrolytes was re-introduced several times [10-13] and is again of great scientific interest [14], especially investigated by MD simulations [15,16].

Our investigation presented here is based on a thermodynamic model [17] which is capable to predict qualitatively and quantitatively the double layer capacity of various electrolytes (see Fig. 1). It turns out that the capacity maxima are determined by the partial molar volume of the anion and the cation, respectively, whereby capacity measurements can be consulted to determine explicit values for different ions. For mono-valent ions in water we find that the partial molar volume of the ionic species is about 45 times larger than the solvent [17]. This suggests that the ionic species are strongly solvated, and based on a simple relation for the molar volume we can determine the solvation number from a single capacity measurement. An investigation of the double layer structure in the potential region beyond the capacity maximum shows the formation of an ionic saturation layer [19,20,21], which has some fundamental and remarkable similarities to a saturated bulk solution.

This is then the starting point for our reflections on the dissociation degree, and it is shown that even for simple salts at concentrations of (0.5–1) mol L^{-1} the assumption of complete dissociation is questionable.

2. Theory

Consider exemplarily a mono-valent salt AC of concentration c which completely dissociates in solvated anions A^- and cations C^+. Each ion A^- and C^+ is assumed to bind κ_A and κ_C solvent molecules S in its solvation shell, whereby the number density of free solvent molecules S in solution is

$$n_S = n_S^R - \kappa_A \cdot n_A - \kappa_C \cdot n_C. \tag{1}$$

The parameter n_S^R corresponds to the mole density of the liquid solvent, *i.e.* for water $n_S^R = 55.4$ mol L^{-1}. The number of mixing particles is then $n = n_S + n_A + n_C$, and **not** the total number of molecules in solution, which is $n^T = n_S^R + n_A + n_C$.

2.1. Entropy of mixing

For the entropy of mixing this is extremely important. In a solvation

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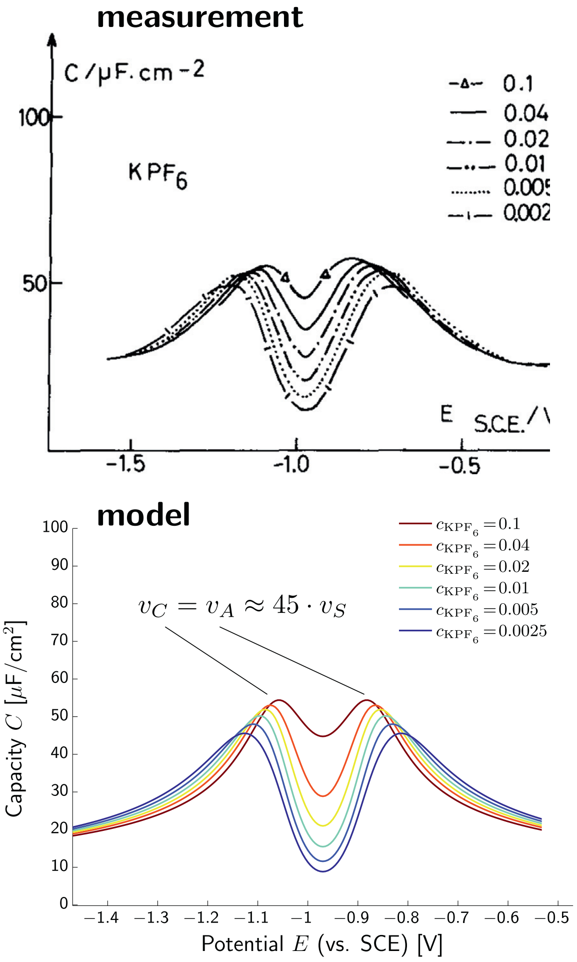

Fig. 1. Comparison between measured and computed double layer capacity for a non-adsorbing and completely dissociated salt KPF$_6$.
Source: Top: Fig. 2.a from [18], reprinted with permission of Elsevier.

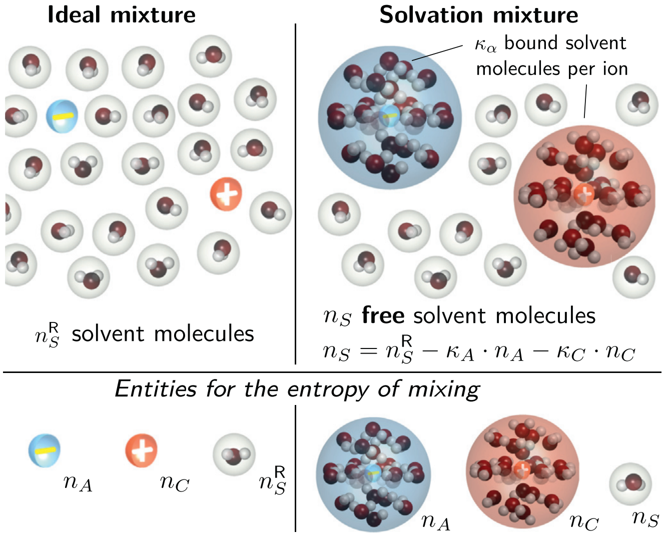
Ideal mixture
Solvation mixture
κ_α bound solvent molecules per ion
n_S^{R} solvent molecules
n_S free solvent molecules
$n_S = n_S^{\mathrm{R}} - \kappa_A \cdot n_A - \kappa_C \cdot n_C$
Entities for the entropy of mixing
n_A
n_C
n_S^{R}
n_A
n_C
n_S

Fig. 2. Sketch of solvation effect in a liquid mixture and the consequence on the entities for the entropy of mixing.

mixture the mixing entities are now the **free** solvent molecules, the **solvated** anions and the **solvated** cations (see Fig. 2), leading to an entropy of mixing

$$s = -k_{\mathrm{B}} \left(n_S \ln\left(\frac{n_S}{n}\right) + n_A \ln\left(\frac{n_A}{n}\right) + n_C \ln\left(\frac{n_C}{n}\right) \right). \tag{2}$$

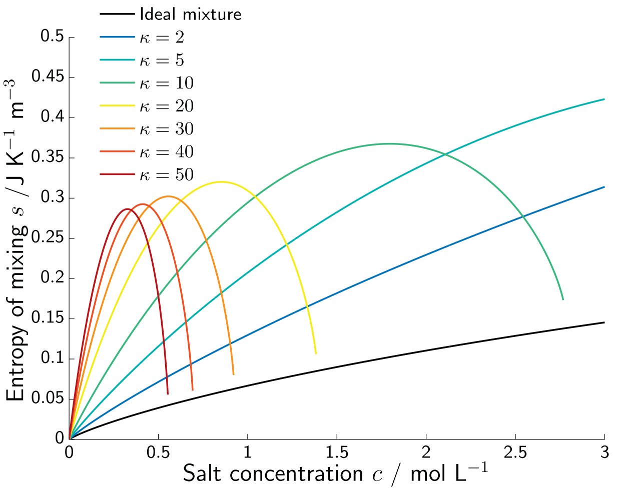

Fig. 3. Entropy of mixing various solvation numbers $\kappa = \kappa_A = \kappa_C$ and an ideal mixture.

For an ideal solution, however, the mixing entities are **all** solvent molecules in addition to the dissolved ions, which gives for the entropy of mixing

$$s^{\mathrm{ideal}} = -k_{\mathrm{B}} \left(n_S^{\mathrm{R}} \ln\left(\frac{n_S^{\mathrm{R}}}{n^{\mathrm{T}}}\right) + n_A \ln\left(\frac{n_A}{n^{\mathrm{T}}}\right) + n_C \ln\left(\frac{n_C}{n^{\mathrm{T}}}\right) \right). \tag{3}$$

Fig. 3 displays the difference between the models and shows that the impact of the solvation effect is enormous, even for small solvation numbers.

2.2. Chemical potential

Based on the entropy of mixing (2) it is possible to derive the chemical potential of the constituents in the liquid, incompressible electrolyte [17]. The chemical potential of the free solvent, the solvated anion and the solvated cation is

$$\mu_\alpha = g_\alpha + k_{\mathrm{B}} T \, \ln(y_\alpha) + v_\alpha \cdot (p - p^{\mathrm{E}}) \qquad \alpha \in \{S, A, C\}, \tag{4}$$

where $y_\alpha = \frac{n_\alpha}{n}$ denotes the mole fraction with respect to the number density $n = n_S + n_A + n_C$ of mixing particles, g_α the constant molar Gibbs energy, v_α the partial molar volume, and p^{E} the bulk pressure.

2.3. Partial molar volume of solvated ions

While the solvation effect decreases the number of free solvent molecules in the mixture, it actually increases the molar mass and the partial molar volume of the solvated ions. The molar mass of a solvated ion is clearly $m_{A,C} = \widetilde{m}_{A,C} + \kappa_{A,C} \cdot m_S$, where $\widetilde{m}_{A,C}$ be the mass of the central ion and m_S the molar mass of the solvent. A quite similar relation holds for the partial molar volume $v_{A,C}$ of a solvated ion. However, while the molecular mass is conserved during the solvation process, the volume is not necessarily.

However, for the sake of this work it is sufficient to assume that the partial molar volume of a solvated ion is

$$v_{A,C} = \widetilde{v}_{A,C} + \kappa_{A,C} \cdot v_S \quad \text{with} \quad v_S = (n_S^{\mathrm{R}})^{-1}, \tag{5}$$

where $\widetilde{v}_{A,C}$ is the molar volume of the central ion, v_S the molar volume of the solvent and $\kappa_{A,C}$ the solvation number. This relation allows us then to deduce the solvation number from a measured value of the partial molar volume.

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