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The Individual Activity Coefficients of a Solvent Primitive Model Electrolyte Calculated from the Inverse Grand-Canonical Monte Carlo Simulation and MSA Theory

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Abstract

The recently developed inverse grand-canonical Monte Carlo technique (IGCMC) [S. Lamperski. *Molecular Simulation*, **33**, 1193 (2007)] and the MSA theory are applied to calculate the individual activity coefficients of ions and solvent for a solvent primitive model (SPM) electrolyte. In the SPM electrolyte model the anions, cations and solvent molecules are represented by hard spheres immersed in a dielectric continuum whose permittivity is equal to that of the solvent. The ions have a point electric charge embedded at the centre. A simple 1:1 aqueous electrolyte is considered. The ions are hydrated while the water molecules form clusters modelled by hard spheres of the diameter d_s . The diameter d_s depends on the dissolved salt and is determined by fitting the mean activity coefficient $\ln \gamma_{\pm}$ calculated from IGCMC and from the MSA to the experimental data. A linear correlation is observed between d_s and the Marcus parameter ΔG_{HB} which describes the ion influence on the water association.

Keywords: Ionic activity coefficient; Solvent primitive model; Inverse grand-canonical Monte Carlo technique; Marcus parameter.

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Development of aqueous electrolyte theory since the solution of the linear Poisson-Boltzmann equation for the charged point model by Debye and Hückel [1] has been tremendous. Description of the thermodynamic properties, in particular the ionic activity coefficients, by the mean spherical approximation (MSA) [2,3], symmetric (SPB) [4] and modified (MPB) [5,6] Poisson-Boltzmann theories or by the hypernetted chain equations (HNC) [7] is in good agreement with the simulation results [8-12] for the 1:1 restricted primitive model. Now, the problem lies in the appropriate choice of the model of an electrolyte which will best reproduce the experimental data. Literature provides three basic models of electrolyte: primitive (PM), solvent primitive (SPM) and non-primitive (NP) model. In these models, ions are represented by hard or soft spheres with the point charge immersed in the centre while the solvent is approximated by: (i) a continuous dielectric medium of relative permittivity ϵ_r (PM), (ii) a dielectric medium with neutral spheres (SPM) or, (iii) spheres with a point electric dipole moment (NP). The question is how accurately can these models reproduce the experimental activity coefficients of an electrolyte? The PM electrolyte was investigated e.g. by Ebeling and Scherwinsky [13]. The authors calculated individual ionic activity coefficients for simple aqueous electrolytes using the MSA theory. The adjustable parameters were the effective ionic radii, which were obtained by fitting the MSA results to the experimental data. The anion radii results were in a good agreement with the Pauling crystallographic radii, while the cation radii decreased with increasing molecular mass of the alkali metal ions. Such a behaviour is characteristic of the hydrodynamic radii of these cations. Simonin et al. [14,15] treated ϵ_r as another adjustable parameter, while Fawcett and Ticanen [16] applied the experimental dependence of ϵ_r on the electrolyte concentration. Abbas et al. [17] made a detailed comparison of PM simulations with experimental activity and osmotic coefficients. Recently Vince et al. [18] used the Born theory to describe the ion-

solvent interaction and obtained very good agreement with the experimental data. Application of the Born theory is equivalent to the use of the Born radii. The Born radii of the alkali metal ions are greater than the Pauling radii, but also increase with increasing molar mass, although not as much as the Pauling radii.

The NP model is the most realistic, which explains considerable scientific interest in it. Blum and Wei [19,20] obtained an analytical solution within MSA of the NP model with equal and unequal ions and a dipolar solvent molecule sizes. The authors have shown only the influence of ionic concentration at different ion/solvent diameter ratio on the activity coefficient of the dipolar solvent. Li et al. [21] used the Blum-Wei theory [20] to calculate the ionic activity coefficients. The values they obtained were extremely low [$\ln \gamma_{\pm} \approx -100$ (the Coulombic contribution)] in comparison with the experimental data. Next, the authors discharged the ions by 50% which improved the results, but the coefficients were still too low. Boda et al. [22] met a similar problem when performing the Monte Carlo (MC) simulations of an electric double layer. They also had to use partially discharged ions to obtain reasonable results. It seems that the problem can be solved by application of the explicit water (solvent) model. Recently Gavryushov and Linse [23] used the Widom MC canonical simulation [24] to predict the mean activity coefficients of alkali and alkaline earth cations with chloride anions in a mixture with water molecules whose properties were described by the SPC/E model [25]. They obtained a qualitative agreement with the experiment.

To our best knowledge, the SPM electrolyte was not used to reproduce the experimental activity coefficients of electrolytes. In this paper, we want to fill this gap.

Recently we have analysed the behaviour of electrolyte within the primitive model of solvent [26]. In SPM solvent molecules are modelled by hard spheres. The mean activity coefficient of ions, γ_{\pm} , and the activity coefficient of solvent molecules, γ_s , were calculated from the inverse grand-canonical Monte Carlo (IGCMC) simulation [12], and from the MSA

[13] and SPB [4] theories. Comparison of our simulation results have also been made with the MPB and HNC equations [27]. We observed from both the simulation and theoretical results that, for a 1:1 electrolyte, the dependence of $\ln\gamma_{\pm}$ and $\ln\gamma_s$ on the electrolyte concentration is influenced by the diameters of ions and solvent molecules (the diameters of anions and cations being equal in this work). When the diameter of solvent molecules was smaller than that of the ions, then the ionic activity coefficient decreased monotonically with increasing electrolyte concentration, while for the diameter of solvent larger than that of the ions the initial decrease changed into a small increase at high concentrations. This behaviour is evidently different from that observed for a PM electrolyte for which a strong increase in $\ln\gamma_{\pm}$ at high electrolyte concentrations is observed [8,9], but is similar to that obtained from the experiment. This similarity allows a supposition that by a proper choice of a solvent diameter one will be able to describe the experimental results by simulation techniques or in terms of a theory. However, the diameter of a solvent molecule is well defined and cannot be treated as an adjustable parameter. But, as known, the molecules of water and some other solvents form clusters due to the association process involving hydrogen bonds. In accordance to the Marcus conception [28], the ions influence the size of such clusters. So, in this paper, we also assume that water molecules form clusters and their sizes depend on the kind of salt dissolved. We approximate the clusters as hard spheres of the diameter d_s . This diameter is treated as the adjustable parameter.

Our intention is to obtain the ionic activity coefficients for the SPM electrolyte from the simulation and within the theoretical approach. We have found earlier that the MSA and SPB results are very similar [26]. However, the advantage of MSA is that it yields an analytical solution for the activity coefficient. It means that in the MSA calculations one can use any value of ion and solvent molecule diameters. In SPB, the equations are solved numerically using the quasi-linearisation technique [29], so the diameter must be a multiple of

the distance between two closest mesh points. The IGCMC method does not impose any restrictions on the diameters. Thus in this paper results following from the MSA theory and IGCMC simulation are presented.

2. The model

We consider the SPM model of electrolyte. This is a simple, yet non-trivial model of an electrolyte that takes into account the molecular nature of the solvent. In the SPM electrolyte, the ions and solvent molecules are represented by hard spheres of diameter d_k , with $k = -, +, s$ denoting anions, cations and solvent molecules, respectively. The ions have a point electric charge $z_k e$ located at the centre (e is the elementary charge and z_k is the charge number of the ion of species k). The ions and solvent molecules are embedded in the dielectric continuum whose relative permittivity ϵ_r is equal to that of the solvent. The potential of the hard-sphere interaction is given by

$$V^{\text{HS}}(r_{ij}) = \begin{cases} 0, & r_{ij} > d_{ij} \\ \infty, & r_{ij} \leq d_{ij} \end{cases} \quad (1)$$

where r_{ij} is the distance between the centres of the hard spheres i and j , while d_{ij} is given by

$$d_{ij} = \frac{d_i + d_j}{2} \quad (2)$$

The potential of inter-ionic Coulombic interactions is described by

$$V^{\text{C}}(r_{ij}) = \frac{z_i z_j e^2}{4\pi\epsilon_0\epsilon_r r_{ij}} \quad (3)$$

where ϵ_0 is the vacuum permittivity.

We have slightly modified the original SPM model by assuming that the ions are hydrated and the solvent (water) molecules form clusters. The hydrated ions were considered as hard spheres with the diameter determined via experiment. According to *ab initio* methods

[30-32] water molecules form clusters composed of 3 to 80, even to 240 molecules, but 5, 6, and 8 molecular clusters dominate in the pure water bulk phase. To simplify the model of a cluster, we have assumed that: (i) each cluster is composed on average of n molecules, where n need not be an integer, (ii) the cluster is approximated by the hard sphere of diameter d_s , (iii) the volume of the hard sphere is the product of n and the volume of one water molecule. After these modifications we still have the SPM model, but the symbols have a new meaning: d_- and d_+ stand for the diameters of hydrated ions while d_s is the average diameter of a water cluster.

3. The method

The ionic activity coefficients of an electrolyte were calculated from the IGCMC simulation method and from the MSA theory. The IGCMC method is based on the grand-canonical MC simulation (GCMC), but its advantage over GCMC is that it allows evaluation of the mean and individual activity coefficient for a specified concentration of an electrolyte. The details of IGCMC are described in our previous papers [12,26]. Malasics *et al.* [33,34] developed other algorithms to invert the GCMC simulation. The MSA equations were taken from the work of Ebeling and Scherwinski [13].

The computations were carried out for the constant packing fraction $\eta = 0.35$. For a three component mixture η is given by

$$\eta = \frac{\pi}{6} (\rho_- d_-^3 + \rho_+ d_+^3 + \rho_s d_s^3) \quad (4)$$

where ρ_k is the number density of species k

$$\rho_k = N_k / V, \quad k = -, +, s \quad (5)$$

N_k is the number of molecules of species k used in the simulation, and V is the volume of the simulation box. We considered a 1:1 electrolyte, so $N_- = N_+$. In the simulations, we used $N_- =$

120 to 200, while N_s was calculated from Eqs (4)-(5). The cell index method [35] was applied to facilitate the computations. The method concerns the hard-sphere interactions and, as we have found, it was very useful at low electrolyte concentrations where N_s exceeded 20,000.

The diameter of a water cluster, d_s , was obtained by fitting the theoretical value of $\ln\gamma_{\pm}$ to the experimental data at the molal concentration $m = 1$ mol/kg. We describe the procedure applied using the NaCl aqueous electrolyte as the example. The hydrated ion diameters were taken from literature [36] and they are listed in Table 1. The other physical parameters were $T = 298.15$ K and $\epsilon_r = 78.5$. All the ionic activity coefficient results were related to the values at $m \rightarrow 0$. (The details are described in the next section.) We calculated the mean activity coefficient $\ln\gamma_{\pm}$ of the electrolyte considered at $m = 1$ mol/kg for several d_s and keeping η constant. The simulated $\ln\gamma_{\pm}$ values calculated for the ion diameters of NaCl and different d_s are shown in Fig. 1 (circles). As seen, the points lie approximately on a line, so we fitted a straight line to these points. We calculated d_s by solving the line equation for the experimental mean activity coefficient [37,38]. A graphic solution is shown in Fig. 1 where the line parallel to the d_s axis represents the experimental value of $\ln\gamma_k$. The determined d_s was used in the calculations of $\ln\gamma_{\pm}$ for all the electrolyte concentrations considered.

A similar procedure was applied to determine d_s from the MSA equations. A dashed line in Fig. 1 shows the MSA dependence of $\ln\gamma_{\pm}$ on d_s . This dependence is linear. The diameter obtained by MSA is by about 5 pm smaller than that calculated by IGCMC (see Table 1).

4. Results and discussion

The aqueous electrolytes considered in this paper are listed in Table 1. At the beginning, we calculated the diameter d_s of the water cluster for each electrolyte using the procedure described in the previous section. The cluster diameters obtained by IGCMC and MSA are

given in Table 1. The IGCMC diameters are greater than those of the MSA, on average by 4.61 pm. Overall, both the simulation and MSA d_s are comparable with the diameters of the hydrated ions. The average number n of water molecules forming a cluster was estimated by dividing the volume of a cluster (according to our model this volume is $\pi d_s^3/6$) by the volume of a water molecule (the molar volume divided by the Avogadro constant). This number obtained by IGCMC changes from 4.66 for CsI to 5.97 for NaI. The corresponding MSA diameters are very similar and range from 4.57 to 5.78. These results are in a quite good agreement with the *ab initio* predictions [30-32], although the model for the water cluster applied here is actually primitive.

Next, we calculated the individual and mean activity coefficients of the electrolytes considered. The IGCMC simulations and the MSA calculations were carried out for $m / \text{mol kg}^{-1} = 0.2, 0.3, \dots, 1.0, 1.2, 1.4 \text{ and } 1.6$. The IGCMC and MSA individual activity coefficients $\ln \gamma_k$ for Na^+ , Cl^- and solvent clusters are shown in Fig. 2. In accordance with the conclusions presented in our previous work [26], the smaller chloride ions exhibit lower values of $\ln \gamma$ than the larger sodium ions. At low electrolyte concentrations the solvent $\ln \gamma_s$ curves take the intermediate position and they are flat. In the range of high concentrations, the curves exhibit small rising tendency, although the MSA curve still looks flat. In the limit $m \rightarrow 0$, the Coulombic interactions disappear and we will denote this hard-sphere activity coefficient at the trace amount of ions by $\ln \gamma_k^0$.

In Fig. 3, we present the $\ln \gamma_k$ results lowered by $\ln \gamma_k^0$. Now, all the curves start from $\ln \gamma_k = 0$. At low electrolyte concentrations the activity coefficients of Na^+ and Cl^- are similar. Some divergence appears at high electrolyte concentrations. The small divergence is due to the similar diameters of hydrated Na^+ and Cl^- ions, but now the larger cations give the lower activity coefficient than the smaller anions.

The mean activity results, $\ln \gamma_{\pm}$, for NaCl calculated from the data presented in Fig. 3 are shown in Fig. 4 by filled circles (IGCMC) and a dashed line (MSA). They are compared with the experimental results shown in Fig. 4 by squares. The agreement is good especially at low electrolyte concentrations for which also the slope of the theoretical and experimental curves is similar. Some deviations are observed in the middle part of the plot. They may be due to smaller influence of ions on the structure of water clusters at lower electrolyte concentration. Again, the full agreement is observed at $m = 1$ mol/kg where the d_s parameter is evaluated. For other electrolytes considered we obtained very similar results to those of NaCl, and that is why we do not present them here.

A separate problem is connected with the physical interpretation of the cluster diameters determined in this work. Here the Marcus [39] theory can be helpful. According to this theory, the ions influence water association. The presence of some ions can enhance the size of water clusters while the presence of other can diminish them. Marcus called them the “structure making” and “structure breaking” ions, respectively. Large ions are mainly the “structure making” ones, while small highly charged ions are usually the “structure breaking” ones. Marcus quantitatively expressed the ion influence on the water cluster structure as the change in the average number of hydrogen bonds per a water molecule ΔG_{HB} . Noting similarity in the structure, bond length and the electric dipole moment between the ordinary (light) H_2O and heavy D_2O water, he assumed that the change in the number of hydrogen bonds ΔG_{HB} due to the presence of ions is proportional to the standard molar Gibbs free energy of ion transfer from heavy to light water $\Delta_{tr}G^\circ$

$$\Delta G_{HB} = \Delta_{tr}G^\circ (\text{ion}, D_2O \rightarrow H_2O) / 929 \quad (6)$$

where the value 929 J/mol is the difference between the energy of the hydrogen bond in D_2O and H_2O . The values of ΔG_{HB} for all the electrolytes investigated are listed in Table 1. Fig. 5 shows that there is a linear correlation between the cluster diameter and the Marcus

parameter. This correlation confirms independently the correctness of the Marcus theory. Also, it shows the role which the water clusters play in modelling the aqueous electrolytes.

5. Conclusions

In this paper we have considered the model of an electrolyte composed of hydrated ions and clusters of water molecules immersed in a homogeneous dielectric medium. The water clusters were treated as neutral hard spheres. Although the diameter of the cluster was an adjustable parameter, we found it has a linear dependence on the Marcus parameter which describes the influence of ions on the size of water associates. We have shown that the mean activity coefficients of the electrolyte calculated for this model by the IGCMC simulation and MSA theory are in a good agreement with the experimental data with the reasonable values of the ion and cluster diameters. Our results show also that the individual activity coefficients of smaller ions can be greater than those of larger ions.

Acknowledgments

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Table 1. Hydrated ions diameters [36], water clusters diameters, and Marcus parameters for electrolytes considered.

Electrolyte	d_+ / pm [36]	d_- / pm [36]	d_s / pm (IGCMC)	d_s / pm (MSA)	ΔG_{HB}
NaCl	716	664	696.73	691.80	0.91
NaBr	716	660	699.22	694.42	0.72
NaI	716	662	707.08	701.86	0.43
KCl	662	664	659.36	654.98	0.42
KBr	662	660	659.64	654.89	0.23
KI	662	662	665.01	660.18	-0.06
CsCl	658	664	646.69	642.64	0.25
CsBr	658	660	644.08	639.86	0.06
CsI	658	662	643.81	639.50	-0.23

Figure Captions

Fig. 1. Graphical determination of the water cluster diameter d_s for a NaCl aqueous electrolyte at molal concentration $m = 1$ mol/kg. Circles represent the IGCMC results of $\ln\gamma_{\pm}$, a straight line is fitted to the IGCMC results, a broken line represents the MSA results, the experimental $\ln\gamma_{\pm}$ is given by the line parallel to the d_s axis.

Fig. 2. Dependence of the individual activity coefficient $\ln\gamma_k$ on $m^{1/2}$ for Na^+ , Cl^- ions, and solvent clusters. The ion and cluster diameters are given in Table 1, $T = 298.15$ K and $\epsilon_r = 78.5$. Diamonds represent the IGCMC results of Na^+ , triangles – the IGCMC results of Cl^- , circles – the IGCMC results of solvent clusters, broken line – the corresponding MSA results. The lines through the IGCMC points are given as a visual aid.

Fig. 3. Dependence of the individual activity coefficient $\ln\gamma_k$ lowered by $\ln\gamma_k^0$ on $m^{1/2}$ for NaCl electrolyte. The physical parameters and symbols as in Fig. 2.

Fig. 4. Dependence of the mean activity coefficient $\ln\gamma_{\pm}$ on $m^{1/2}$ for NaCl. The physical parameters as in Fig. 2. Circles represent the IGCMC results, a broken line – the MSA results, squares – the experimental data. The lines through the IGCMC and experimental points are given as a visual aid.

Fig. 5. Correlation between the cluster diameter d_s and the Marcus parameter ΔG_{HB} for the salts considered (circles – the IGCMC results, hexagons – the MSA results). Solid and broken lines are the straight lines fitted to the IGCMC and MSA results, respectively.

Figures

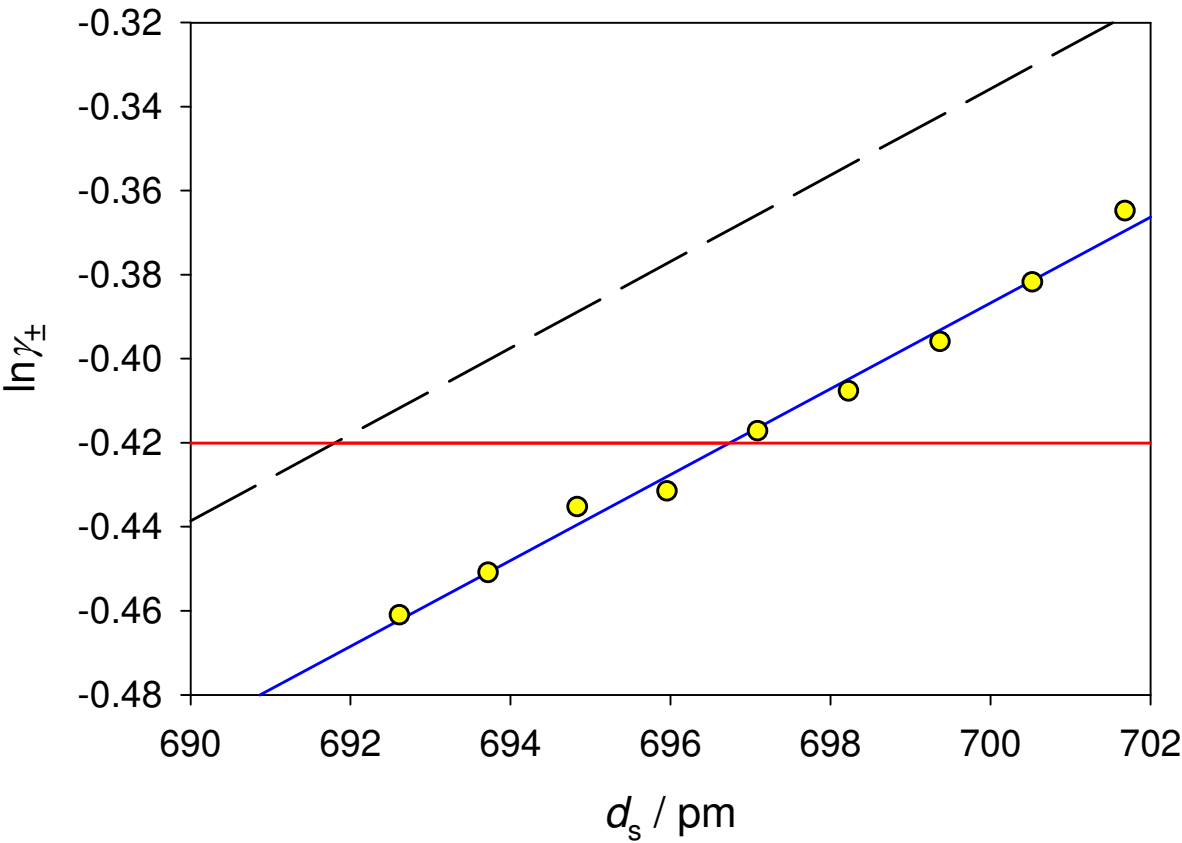


Fig. 1.

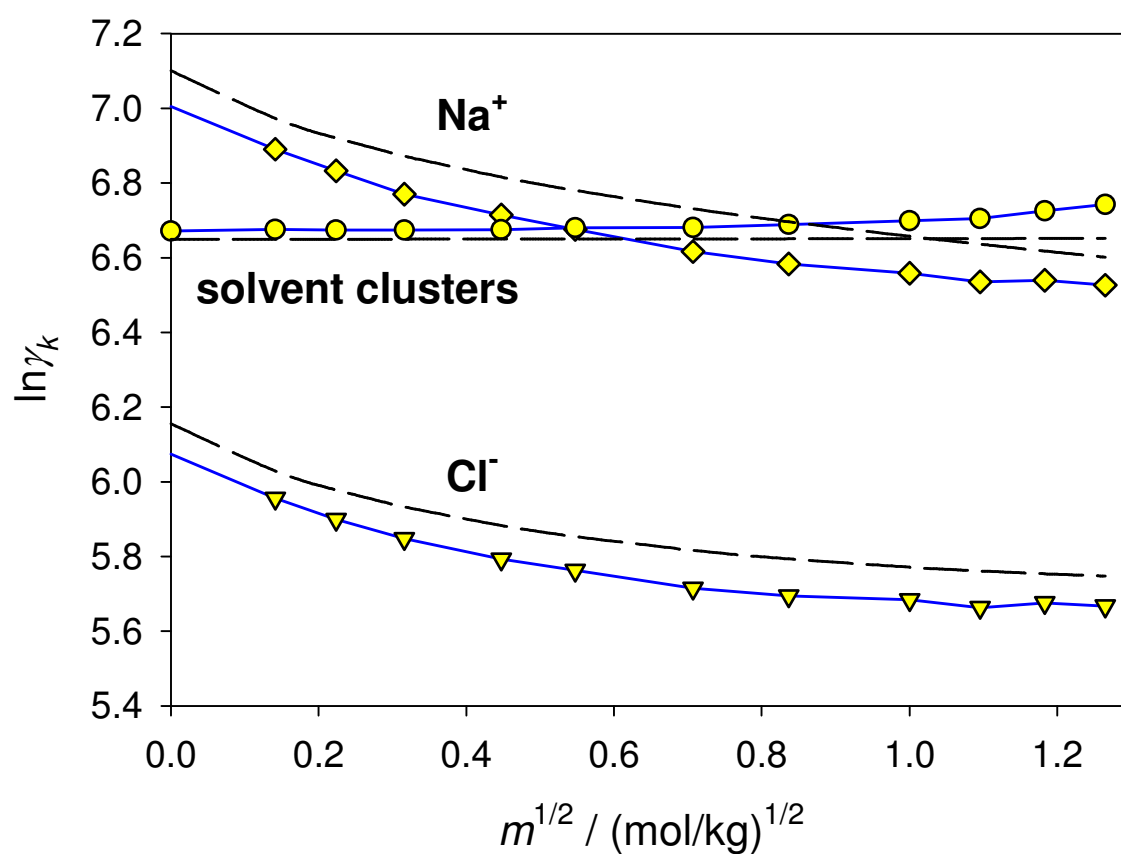


Fig. 2.

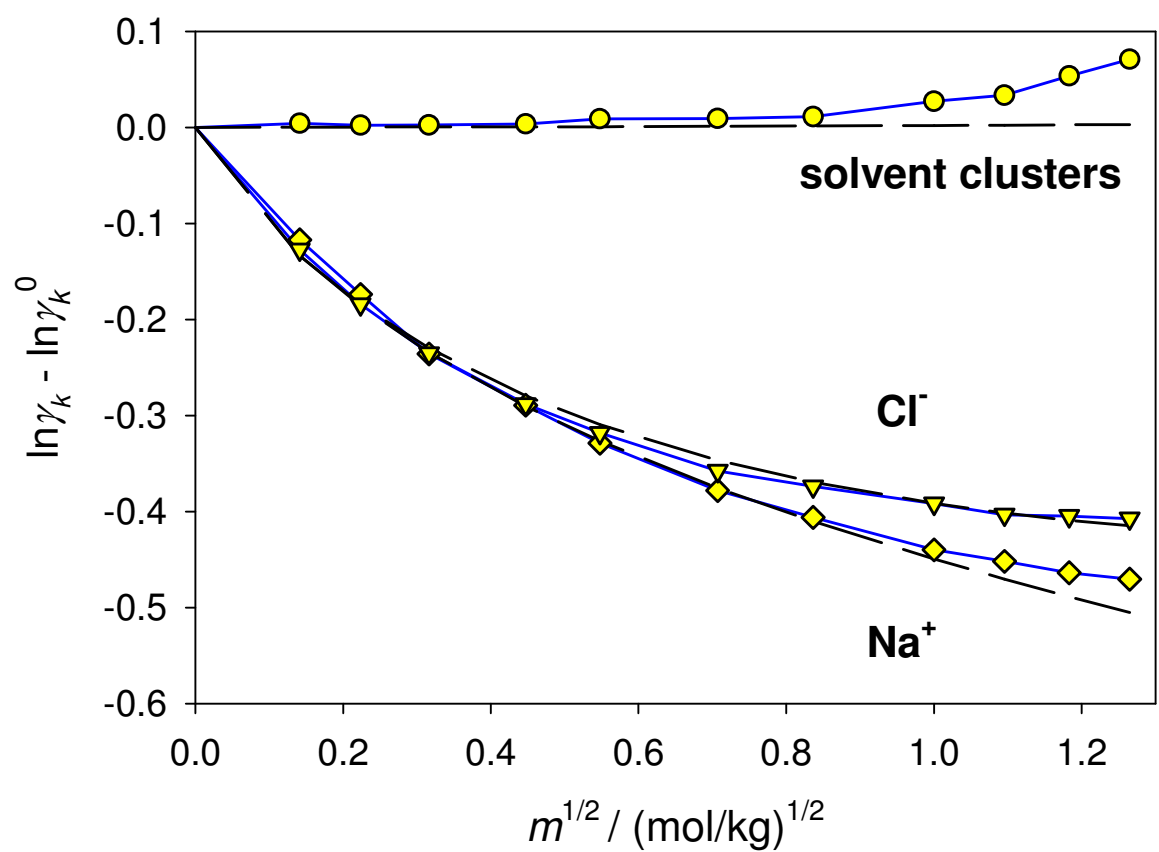


Fig. 3.

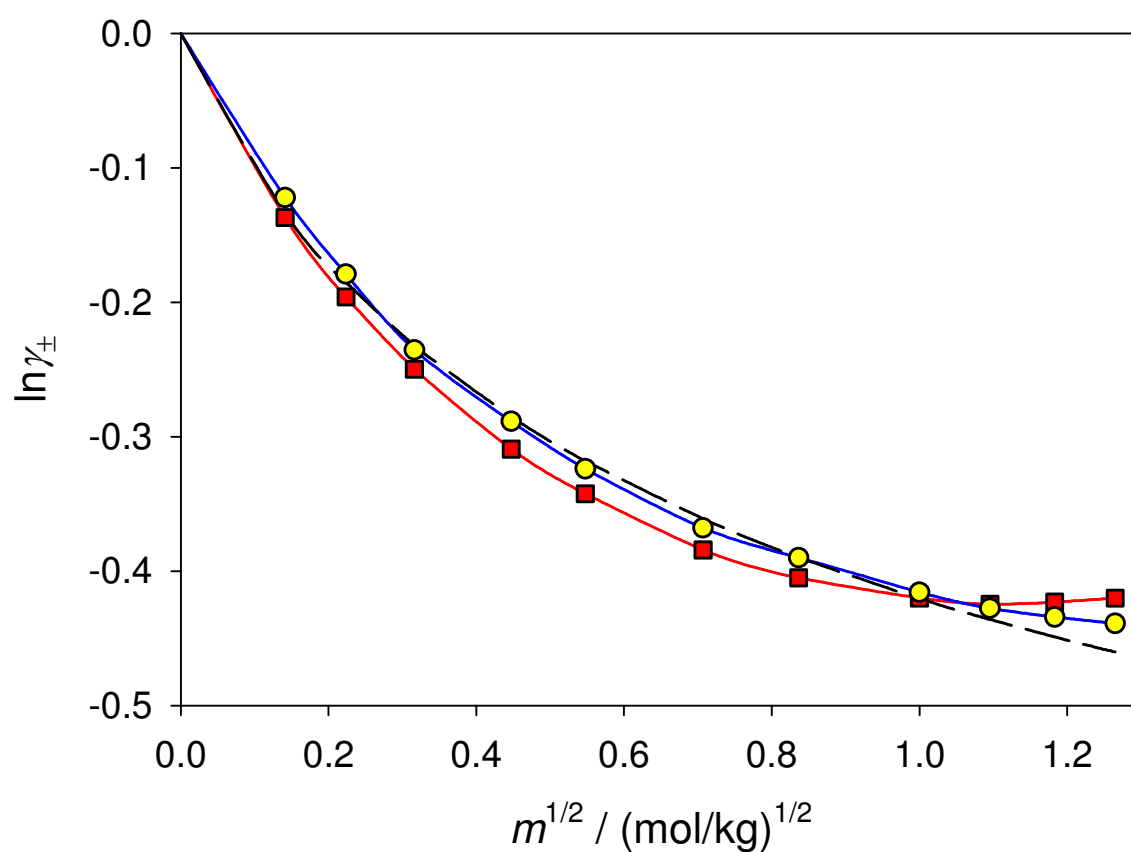


Fig. 4.

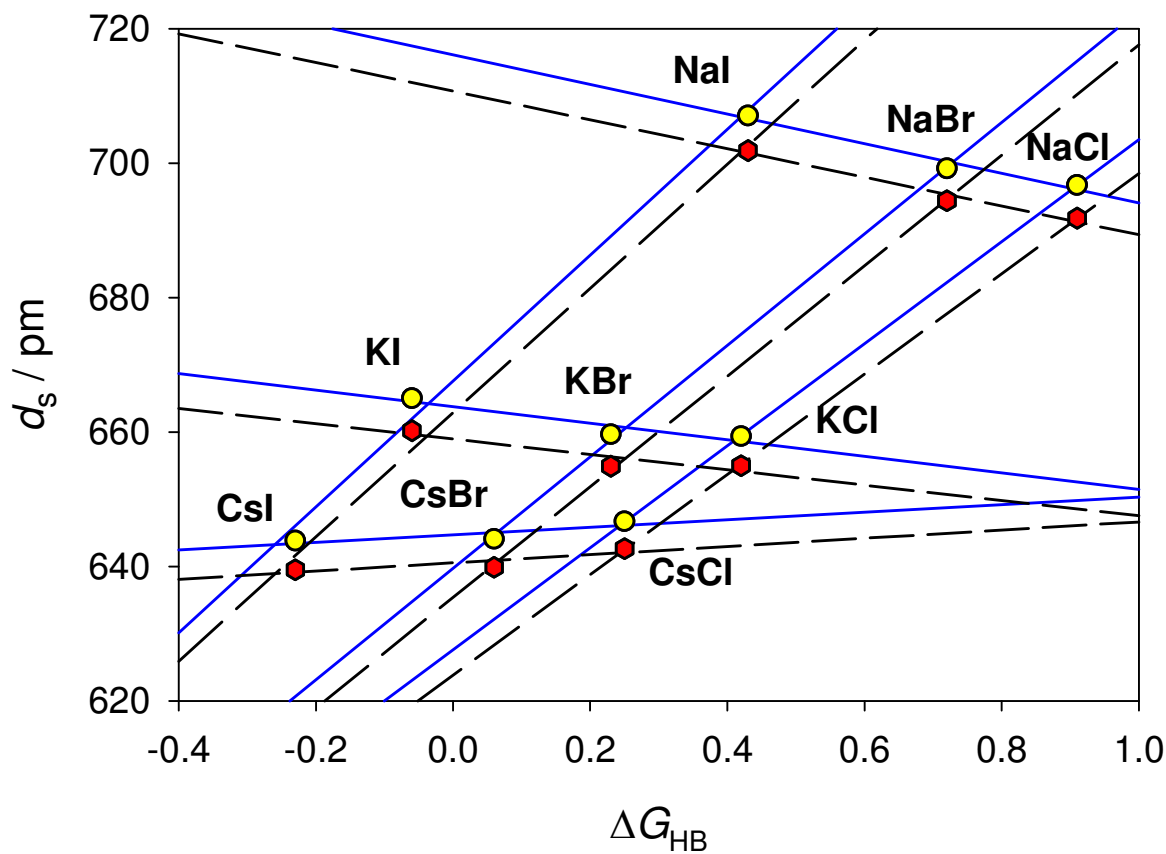


Fig. 5.