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APPLICATION OF THE MEAN SPHERICAL APPROXIMATION TO DESCRIBE THE GIBBS SOLVATION ENERGIES OF MONOVALENT MONOATOMIC IONS IN NON-AQUEOUS SOLVENTS

by

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Application of the Mean Spherical Approximation to Describe the Gibbs Solvation Energies of Monovalent Monoatomic Ions in Non-Aqueous Solvents

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Abstract

The mean spherical approximation for the ion-dipole mixture is used to study the solvation energies of monovalent monoatomic ions in polar solvents. From the structure of the analytical solution it is inferred that there are two parameters that should be used to describe the solvation: the dielectric constant and a polarization parameter which plays the role of a mean field parameter to account for non-sphericity, chemical interactions, and other effects related to failure of the hard sphere model for the system. The model was successfully fitted to data for the Gibbs solvation energy of five alkali metal cations and their halide ions in 17 different solvents including water. On the basis of this analysis, it was shown that a single value of the polarization parameter describes the data for the cations in each solvent, a quite different value being appropriate for the anions. The polarization parameters were found to be linearly correlated with empirical parameters characterizing the solvents basicity (DN) in the case of cations, and its acidity (E_T) in the case of anions.

Introduction

Considerable advances have been made over the last thirty years in the statistical mechanical description of electrolyte solutions in molecular solvents. This work has been carried out using different approaches: computer simulations,[1,2] accurate integral equations, such as the hypernetted chain equation[3-5] and simple analytical theories, based on the mean spherical approximation (MSA).[3] The last approach is attractive for the chemists examining the thermodynamic properties of electrolyte solutions not only because the model gives rather simple analytical results but also because it shares with the Debye Hückel theory, the remarkable simple description in terms of a single screening parameter for any arbitrary mixture of electrolytes, and has the added bonus of satisfying the large charge, large density limits of Onsager.[6,7]

In the present work we consider a mixture of a salt of equal size hard sphere ions, and a solvent which is represented by a hard sphere of different size with a permanent point dipole. Early work at the non-primitive level[8,9] was restricted, for technical reasons, to the case of ions and solvent of equal diameter. The extension of the analytical result to mixtures of arbitrarily sized ions and solvents is considerably more complex[10,12-14] but the remarkable fact that the excess ionic properties depend on a single scaling, Debye-like parameter is still retained by this approximation. The equations for the most general case appear to be rather complex, but the semirestricted case of equal size ions of diameter σ_i and a different size dipole of diameter σ_n is both interesting and tractable.

In recent years[15], it has become apparent that the underlying structure of the MSA consists of a number of scaling parameters which is equal to the number of independent interaction parameters of the problem. For example, for the ion-dipole mixture, there are only two interaction parameters, the charge and the dipole moment, and correspondingly, there are only two scaling parameters, Γ for the charges, and λ for the dipoles.

For the primitive model of ionic solutions in the semirestricted case[16], the parameter Γ is determined from the equation

$$\frac{4\pi e^2}{\varepsilon_n k_B T} \sum_i \frac{\rho_i z_i{}^2}{1 + \Gamma\sigma_i} = 4\Gamma^2 \tag{1}$$

where the ionic charge is $z_i e$ and number density $\rho_i = N_i/V$, where N_i is the number of ions and V is the volume of the system. The dielectric constant of the pure solvent is ε_n, the temperature is T, and Boltzmann's constant is k_B. For the case of only one ion with diameter σ_i the screening parameter Γ is related to the Debye screening parameter

$$\kappa^2 = \frac{4\pi e^2}{\varepsilon_n k_b T} \sum_i \rho_i z_i^2 \tag{2}$$

by

$$(1 + 2\Gamma\sigma)^2 = (1 + 2\kappa\sigma) \tag{3}$$

For a system of spheres of diameter σ_s and a permanent dipole moment μ_n, the MSA result can be expressed in terms of a single parameter λ. Following Wertheim,[17] we have

$$d_2^2 = \frac{\lambda^2(\lambda + 2)^2}{9} \left(1 - \frac{1}{\varepsilon_n}\right) \tag{4}$$

where

$$d_2^2 = \frac{4\pi \rho_n \mu_n{}^2}{3k_B T} \tag{5}$$

and ρ_n is the solvent number density. Furthermore, the MSA dielectric constant ε_n of the solvent is given by

$$\varepsilon_n = \frac{\lambda^2(\lambda + 1)^4}{16} \tag{6}$$

As has been often done in the literature, the parameter λ can be computed directly from the dielectric constant ε_n using the above equation, which is a cubic. This parametrization defines an effective polarization parameter which mitigates the harsh aproximations that go into the hard dipole model of the solvent, and is designed to take into account polarizabilities, softness and the non-sphericity of the core.

In this paper we show that for the semirestricted case of the ion-dipole model of ionic solutions, an ion-dipole interaction parameter b_1 is obtained from a cubic equation[18,12] which depends on Γ, the dielectric constant ε_n and the combination

$$\xi_i = \frac{\sigma_n}{\sigma_i \lambda} \tag{7}$$

Although both ε_n and ξ_i are functions of λ, they play different roles. When $\sigma_n \to 0$ we recover the primitive model MSA equations, and the solvation thermodynamics is that of the continuum model as described by the Born equation. The single parameter ξ_i appears in a modified form when sticky interactions are added to the ion-solvent potential. These sticky potentials could be used to represent specific short range bonding between the ion and the solvent. In a way, ξ_i can be considered as a mean field parameter, similar to the interaction parameter in the van der Waals theory of imperfect gases. When the size of the solvent is finite, then we get different expressions for the solvation thermodynamics.[20,12,13] These will be the subject of this paper.

Single ion Gibbs solvation energies have been tabulated by Abraham and Liszi[21,22], Conway[23] and Marcus[24,25] for a large number of systems. These authors have considered carefully the extra-thermodynamic assumptions necessary to estimate single ion quantities from experimentally measured properties of the salts. Standard Gibbs energies of hydration are available for over sixty, chiefly monovalent, ions and Gibbs energies of transfer from aqueous to non-aqueous solutions reported for over twenty different solvents. As a result, one has a rich source of experimental data with which one can test predictions of the MSA in estimating the Gibbs energy of solvation $\Delta G_s^o(i)$.

The purpose of this paper is to examine the usefulness of the MSA in accounting for the variation in $\Delta G_s^o(i)$ with solvent and ion. It will be shown that using only two parameters ε_n and ξ_i excellent fitting of the experimental data for monoatomic, monovalent ions is obtained. The parameter ξ_i can be related in a more fundamental way to short ranged, highly directional interactions such as chemical bonding. The consequences of the present work are discussed with respect to the development of more detailed models for the electrolyte solution and applications in non-equilibrium situations.

On the basis of the MSA, expressions have been developed for the ion-dipole and dipole-dipole contributions to the Gibbs free energy of solvation.[10,12,19,20] An excellent fit between the tabulated data and the estimates of the model is obtained using one adjustable parameter, the polarization parameter λ. It is shown that the values of λ which bring about agreement between theory and experiment are roughly correlated with the solvent's basicity in the case of cations or with the solvent's acidity in the case of anions. These results can be interpreted within the MSA as indicating that specific short range interactions (chemical association effects) are important. The present paper describes a method of including these "sticky" interactions within the context of the MSA theory on the basis of an analysis of data for the Gibbs solvation energies of monovalent monoatomic ions in 17 solvents, both protic and aprotic.

Theory

We summarize the results of previous work.[10-12] We use the invariant expansion formalism.[2-6] in which the total pair correlation $h(12)$ is expanded in terms of rotational invariants

$$h(12) = \hat{h}^{000}(r_{12}) + \hat{h}^{011}(r_{12})\hat{\Phi}^{011} + \hat{h}^{101}(r_{12})\hat{\Phi}^{101} + \hat{h}^{110}(r_{12})\hat{\Phi}^{110} + \hat{h}^{112}(r_{12})\hat{\Phi}^{112} \tag{8}$$

where $\hat{h}^{mn\ell}(r_{12})$ is the coefficient of the invariant expansion. which depend only on the distance r_{12} between spheres 1 and 2. The rotational invariants $\hat{\Phi}^{mn\ell}$ depend only on the mutual orientations of the molecules. For the present case the relevant correlation functions are

- ion-ion:

$$h_{ii}(r) = (1/2)\left[\hat{h}^{000}_{++}(r) - \hat{h}^{000}_{+-}(r)\right] \tag{9}$$

- ion-dipole:

$$h_{in}(r) = (1/2)\left[\hat{h}^{011}_{+n}(r) - \hat{h}^{011}_{-n}(r)\right](\hat{\mathbf{r}} \cdot \hat{\mu}) \tag{10}$$

- dipole-dipole:

$$\begin{aligned} h_{nn}(r) &= -\sqrt{3}\hat{h}^{110}_{nn}(r)\hat{\mu}_1 \cdot \hat{\mu}_2 \\ &+ \sqrt{\frac{15}{2}}\hat{h}^{112}_{nn}(r)\left[3(\hat{\mathbf{r}} \cdot \hat{\mu}_1)(\hat{\mathbf{r}} \cdot \hat{\mu}_2) - \hat{\mu}_1 \cdot \hat{\mu}_2\right] \end{aligned} \tag{11}$$

where $\hat{\mu}$ is the unit vector in the direction of μ. The solution of the MSA is given in terms of the 'energy' parameters

- ion-ion:

$$b_0 = 2\pi\rho_i \int_0^\infty dr h_{ii}(r) r \tag{12}$$

- ion-dipole:

$$b_1 = 2\pi\sqrt{\frac{\rho_i\rho_n}{3}} \int_0^\infty dr h_{in}(r) \tag{13}$$

- dipole-dipole:

$$b_2 = 3\pi\rho_n\sqrt{\frac{2}{15}} \int_0^\infty dr \frac{\hat{h}^{112}(r)}{r} \tag{14}$$

which, as will be shown below are proportional to the ion-ion, ion-dipole and dipole-dipole excess internal energy.[11] In the MSA they are functions of the ion charge and the solvent dipole moment, through the parameters

$$d_0^2 = \frac{4\pi e^2}{k_B T} \sum_i \rho_i z_i^2 \sigma_i^2 \tag{15}$$

and

$$d_2^2 = \frac{4\pi \rho_n \mu_n^2}{3k_B T} \tag{16}$$

These parameters are required to satisfy the following equations[12]

$$a_1^2 + a_2^2 = d_0^2 \tag{17}$$

$$\frac{a_1 b_1 \sigma_n}{2\sigma} + a_2 \beta_3 = d_0 \Delta \mathcal{A} \tag{18}$$

$$\left[\frac{b_1}{2}\right. + \beta_3^2 = y_1^2 + \Delta^2 \mathcal{A}^2 \tag{19}$$

where we have used the definitions

$$a_1 = \frac{1}{2D_F^2}[\Delta - 2\beta_6 D_F]$$ (

$$a_2 = \frac{b_1}{\beta_6 2D_F^2}[\Delta/2 + \frac{\beta_3 \sigma_i}{\sigma_n}] \tag{21}$$

$$D_F = \frac{1}{2}\left[\beta_6(1 + b_0) + \frac{b_1^2 \sigma_n}{12\sigma_i}\right] \tag{22}$$

$$\Delta = \frac{b_1^2}{4} + \beta_6^2 \tag{23}$$

and

$$\mathcal{A} = d_2 - \frac{b_1 d_0 \sigma_n}{2\Delta \sigma_i}\left[\frac{1 + b_0}{2} + \frac{\beta_6 \sigma_n}{6\sigma_i}\right] \tag{24}$$

Also

$$\beta_6 = 1 - b_2/6 \tag{25}$$

$$\beta_3 = 1 + b_2/3 \tag{26}$$

$$y_1 = \frac{\beta_6}{(1 + b_2/12)^2} \tag{27}$$

As has been previously shown[18,12-14] Eq.(18) can be replaced by

$$-\frac{a_2 b_1 \sigma_n}{2\sigma_i} + a_1 \beta_3 = d_0 \Delta y_1 \tag{28}$$

which together with Eqs.(17) and (19) form a system of three equations for the three unknowns b_0, b_1, b_2. However these equations are still complex. A much simpler set of equations is obtained when we use the proper scaling lengths[16,17] We define Γ through the relation

$$b_0 = \frac{-\Gamma\sigma_i}{1+\Gamma\sigma_i} + \frac{b_1^2}{4\beta_6^2}\left[\frac{1}{1+\Gamma\sigma_i} + \frac{\beta_6\sigma_n}{3\sigma_i}\right] \tag{29}$$

or

$$\Gamma\sigma_i = -\frac{b_0 - \frac{b_1^2\left(1+\frac{\beta_6\sigma_n}{3\sigma_i}\right)}{4\beta_6{}^2}}{\left(1+b_0-\frac{b_1^2\sigma_n}{12\beta_6\sigma_i}\right)} \tag{30}$$

and λ from

$$\lambda = \frac{\beta_3}{\beta_6} \tag{31}$$

After some long but straightforward algebra we get

$$a_1 = \frac{2}{\mathcal{D}}\Gamma\sigma_i(1+\Gamma\sigma_i) \tag{32}$$

$$a_2 = a_1\frac{b_1}{2\beta_6\zeta_i} \tag{33}$$

where we have defined the convenient parameter ζ_i

$$\begin{aligned}\zeta_i &= \frac{\Gamma\sigma_i}{1+\Gamma\sigma_i+\frac{\lambda\sigma_i}{\sigma_n}}\\ &= \frac{\Gamma\sigma_i}{1+\Gamma\sigma_i+\frac{1}{\xi_i}}\end{aligned} \tag{34}$$

and

$$\begin{aligned}\mathcal{D} &= 1+\frac{b_1^2}{4\beta_6^2}\\ &= 1+\frac{b_1^2(\lambda+2)^2}{36}\end{aligned} \tag{35}$$

Furthermore we get for Eq.(24)

$$\mathcal{A} = d_2 - d_0\left(\frac{\sigma_n}{\sigma_i}\right)\left(\frac{b_1}{12\beta_6}\right)\left(\frac{2+\sigma_n/\zeta_i}{1+\Gamma\sigma_i}\right) \tag{36}$$

and the MSA equation 28 reduces to

$$2\Gamma\sigma_i(1+\Gamma\sigma_i)[1-(\mathcal{D}-1)(\xi_i/\zeta_i)] = \frac{d_0\mathcal{D}^2}{\sqrt{\epsilon_n}} \tag{37}$$

together with the subsidiary cubic equation for the ion-dipole parameter b_1

$$\mathcal{D}^2[\zeta_i^2+\mathcal{D}-1] = \epsilon_n\,[\zeta_i-(\mathcal{D}-1)\xi_i] \tag{38}$$

which can be written in a more convenient form using

$$\mathcal{B}_1 = \frac{b_1^2}{4\beta_6^2} = \frac{b_1^2(\lambda + 2)^2}{36} \tag{39}$$

Then, Eq.(37) reads

$$2\Gamma\sigma_i(1 + \Gamma\sigma_i)\left[1 - \mathcal{B}_1(\xi_i/\zeta_i)\right] = \frac{d_0(1 - \mathcal{B}_1)^2}{\sqrt{\epsilon_n}} \tag{40}$$

and Eq.(38) is a cubic equation in $\mathcal{B}_1$

$$(1 + \mathcal{B}_1)^2\left[\zeta_i^2 + \mathcal{B}_1\right] = \epsilon_n\left[\zeta_i - \mathcal{B}_1\xi_i\right]^2 \tag{41}$$

which is our most interesting new result for the ion-dipole MSA. This equation is considerably simpler than the ones derived previously, since the ion-dipole coupling parameter b_1, or $\mathcal{B}_1$, which is the responsible for the deviations of the molecular solvent model from the primitive, continuum dielectric model appears to be a function of ξ_i, the dielectric constant and the ionic screening parameter Γ. If we let the diameter of the solvent shrink to zero, then from Eq.(7) $\xi_i \rightarrow 0$, and Eq.(41) becomes

$$(1 + \mathcal{B}_1)^2\mathcal{B}_1 = 0 \tag{42}$$

which has only one real solution $b_1 = 0$. There is no coupling between the ions and the dipoles, and Eq.(40) reduces to

$$2\Gamma\sigma_i(1 + \Gamma\sigma_i) = \frac{d_0}{\sqrt{\epsilon_n}} \tag{43}$$

which should be compared to the primitive model MSA equation Eq.3 in the form

$$2\Gamma\sigma(1 + \Gamma\sigma) = \kappa\sigma \tag{44}$$

From the results of the sticky model[14] we know that when short ranged interactions are present, they change ξ_i and the dielectric constant ϵ in a different way. This means that if we are thinking of our model as a simple representation of a real solvent, the two parameters should be treated independently. The connecting equation (6) between the parameters λ and the dielectric constant ϵ_n is strictly a consequence of the oversimplified spherical dipole representation of the solvent. A more general mean field (in the van der Waals equation sense) model should treat both of these parameters independently, and consequently, assign their frequency behaviour accordingly. This is what is being done in the next section to study the solvation thermodynamics for a number of solvents.

A second limit of interest is the infinite dilution limit. This was first done by Blum[10] who derived the limiting expression for the excess internal energy parameter b_1. It was later discussed in much more detail by Chan and colaborators,[19] and in a more comprehensive way by Garisto et al.[20] From Eq.(41)

$$(1 - \mathcal{B}_1)^2 = \epsilon_n \mathcal{B}_1 \xi_i^2 \tag{45}$$

For very small values of the ion concentration ρ_i we get

$$\mathcal{B}_1 = \frac{1}{\epsilon_n \xi_i^2 - 2} \tag{46}$$

Using the new parameters we get for Eq.(28)

$$\frac{a_1}{\mathcal{D}}(1 - \mathcal{B}_1(\xi_i/\zeta_i)) = d_0/\sqrt{\epsilon_n} \tag{47}$$

or

$$\Gamma\sigma_i(1 + \Gamma\sigma_i) = d_0/\sqrt{\epsilon_n}\left(\frac{(1 + \mathcal{B}_1)^2}{1 - \mathcal{B}_1(\xi_i/\zeta_i)}\right) \tag{48}$$

The excess internal energy is found to be[11]

$$E/(Vk_BT) = \frac{1}{4\pi}(d_0^2 b_0 - 2d_0 d_2 b_1 - 2d_2^2 b_2) \tag{49}$$

for the pure solvent

$$E^{(0)}/(Vk_BT) = -1/2\pi d_2^2 b_2^{(0)} \tag{50}$$

and the difference

$$(E - E^{(0)})/(Vk_BT) = \frac{1}{4\pi}[d_0^2 b_0 - 2d_0 d_2 b_1 - 2d_2^2(b_2 - b_2^{(0)})] \tag{51}$$

is the MSA solvation energy. The internal energy can be re-expressed in terms of the scaling lengths of the problem, and the Gibbs and Helmholtz energies can be computed from them. This will be done in future work.

The excess Gibbs energy is estimated bo be one half of the excess internal energy which is an approximation within the MSA approximation, which is exact for the primitive (continuum dielectric solvent) model. Following Garisto et al.[20], we obtain for the ion-dipole term

$$G_{id} = \frac{E_{id}}{2} = -\frac{(z_i e_0)^2}{\sigma_i \varepsilon_n}(\varepsilon_n - 1)\left[\frac{1}{1+\xi_i}\right] \tag{52}$$

and for the dipole term

$$G_{dd} = \frac{E_{dd}}{2} = -\frac{(e_0 z_i)^2}{8\sigma_i \epsilon_W}\frac{(\epsilon_W - 1)^2}{(1 + \xi_i)^2}\left[\frac{4 + \xi_i\left(\frac{3\lambda+2}{\lambda+1}\right)}{\left(\epsilon_W + \frac{\lambda(\lambda+3)}{2(\lambda+1)^2}\right)}\right] \tag{53}$$

Results and Discussion

In order to test the application of the MSA expression for the Gibbs energy of ion solvation, one must choose experimental data which reflect the properties of single ions under standard conditions. Extensive lists of thermodynamic properties in water, and for transfer from water to various non-aqueous solvents have been compiled by Abraham[21,22], Conway[23], and Marcus.[24,25] Separation of the thermodynamic properties of electrolytes into components for the cation and anion is a well known problem in solution electrochemistry. It has been discussed in detail by Conway[23,27], who has assessed the relative merits of the commonly used extrathermodynamic assumptions especially for aqueous solutions. We avoid consideration here of the best source of Gibbs energies of solvation for single ions, and choose the values given by Conway[23] simply because these values give the best fit with the present theory.

The standard Gibbs energy of solvation of ion, i, in solvent n, ΔG^o_n (i), was estimated from the same quantity measured in water, ΔG^o_w (i), using tabulated values of the Gibbs energy of transfer, ΔG^o_{tr} (i) from water to the second solvent. Thus, the relationship between these quantities is

$$\Delta G^o_n (i) = \Delta G^o_w (i) + \Delta G^o_{tr} (i) \tag{54}$$

An extrathermodynamic assumption is also involved in obtaining single ion Gibbs energies of transfer. The commonly accepted assumption[21-25] is that the Gibbs energy of transfer for the salt tetraphenylarsonium tetraphenylborate may be divided into equal contributions for cation and anion (TATB assumption).

Separate fits of theory to thermodynamic data were performed for cations and anions. The cations considered were the five alkali metal ions for which extensive data are available, namely, Li^+, Na^+, K^+, Rb^+ and Cs^+. The monoatomic anions for which equally numerous data can be found are Cl^-, Br^-, and I^-. The fluoride ion was not considered because its salts are not very soluble in non-aqueous solvents and very few thermodynamic data have been tabulated for this ion.[25] The ionic radii needed to estimate the Gibbs energies were assumed to be the Pauling values. The values of ΔG^o_w (i) used together with these radii are given in Table 1.

As described above, the thermodynamic properties of a single ion, i, may be estimated in a given solvent using the MSA with knowledge of two parameters ε_n and ξ_i. In the following analyses, ε_n has been always set equal to the solvent's static dielectric constant. The parameter ξ_i may be resolved into two components, σ_i, the diameter of the ion, and λ/σ_n, which we will show depends only on the solvent and the sign of the charge on the ion. An initial estimate of λ/σ_n may be obtained by calculating λ on the basis of eq. (6) and using values of σ_n estimated on the basis of gas solubilities.[28] This estimate gives values of ΔG_n (i) which are close to those estimated from experimental data for the monoatomic monovalent ions considered here. In order to obtain a better fit between experimental data and theory, λ/σ_n was varied in each solvent, cations being considered separately from anions. The estimate of ΔG_n (i) was based on the ion-dipole contribution only (eq. 52), the dipole-dipole contribution being ignored; that is, we assume that G_{dd} is seriously overestimated[13] by eq. 53. Thus, our estimates of $\Delta G_{n,th}$ (i) are based on the equation

$$\Delta G_{n,th}(i) = -\frac{N_o (z_i e_o)^2}{\sigma_i}\left(1 - \frac{1}{\varepsilon_n}\right)\left(\frac{1}{1+\xi_i}\right) \qquad (55)$$

where N_o is Avogadro's number and ξ_i is given by eq.(7). The criterion used to determine the best fit was a minimum in the standard deviation defined as

$$\text{s.d.} = \left\{\sum_i [\Delta G^o_{n,ex}(i) - \Delta G^o_{n,th}(i)]^2 / (n-1)\right\}^{1/2} \qquad (56)$$

Values of λ/σ_n were determined in 17 different solvents including water on the basis of reported data for the five alkali metal cations. The fit of theory to experiment was excellent with an average standard deviation of 7.6 kJ mol^{-1}. The solvents considered were restricted to those which are reasonably polar, that is, with dielectric constants greater than 20. The resulting values of λ/σ_n are summarized in Table 2. This parameter is close to six for most solvents and usually greater than the estimate based on values of λ calculated using eq. (6), which are between 2 and 2.5 and values of σ_n obtained from gas solubilities[28], which are close to 0.5 nm. Thus, values of λ/σ_n on the basis of the simple model are typically between 4 and 5. The present result that the values obtained on the basis of a fit to experimental data are higher is attributed to the fact that the simple model does not account for the specific chemical interactions between the cation and the solvent dipole which contribute to its solvation.

In order to illustrate the quality of the fit of the present model to experiment, values of the estimated free energy of transfer are plotted against the experimental quantity for three of the cations considered in Figs. 1-3. It should be noted that this method of presenting our results is the most demanding since ΔG^o_{tr} constitutes only a fraction of the total free energy of solvation. In this regard, the estimated value of the Gibbs energy of transfer is defined by the equation

$$\Delta G^o_{tr,th} = \Delta G^o_{n,th} - \Delta G^o_{w,ex} \tag{57}$$

where $\Delta G^o_{n,th}$ is the estimated value of the Gibbs energy of solvation in solvent n. In the case of Na^+ (Fig. 1) the fit is excellent, the difference between the estimated and experimental values of ΔG^o_{tr} being only a few kJ mol^{-1}. Similar results are obtained for the K^+ ion, but in this case the estimated values tend to be lower than the experimental ones by a few kJ mol^{-1}. Results for the Li^+ system shown in Fig. 2 show greater deviations from experiment, the deviations in this case being usually positive. The poorest fit was obtained for Cs^+ (Fig. 3) where negative deviations approaching 20 kJ mol^{-1} are seen for some solvents. Some of the discrepancy between theory and experiment may be due to errors in the extrathermodynamic assumptions used to extract single ion solvation energies. However, the main reason for the variation in the quality of fit with the nature of the cation is the fact that the present analysis ignores the contribution to the Gibbs energy from dipole-dipole interactions. These will increase in importance with decrease in ion size because the strength of the ion-solvent bonds for small ions like Li^+. The other parameter which could be varied to improve the fit is the ionic radius, which has been arbitrarily set equal to the Pauling value. This assumption is considered further below. When one keeps in mind that the relative error for the total solvation energy is much smaller than that for the Gibbs transfer energy, it is clear that the MSA model gives a very good description of the experimental solvation energies for the alkali metal cations using one adjustable parameter for each solvent, namely, λ/σ_n.

A similar procedure was used to fit the Gibbs solvation energy data for the halide ions, Cl^-, Br^-, and I^-. In this case, the average standard deviation of the fit between theory and experiment was 8.3 kJ mol^{-1}. For anionic solvation, the estimated values of the parameter λ/σ_n are very different from those obtained for the cations (see Table 2). For the aprotic solvents, this quantity is usually in the range from 10 to 12 nm^{-1} whereas for protic solvents it is between 17 and 24 nm^{-1}. It follows that the MSA estimates of solvation free energies for anions are much closer to the Born estimate than those for cations. As λ/σ_n becomes larger, the quantity ξ_i is smaller, and the MSA factor, $(1 + \xi_i)^{-1}$ in eq. (55) becomes less important. This result is not unexpected because it is well known that typical polar solvents can effectively solvate cations through the lone electron pairs on the electro-negative group in the solvent molecule, whereas anion solvation is much weaker unless the solvent is protic and can stabilize the anion through hydrogen bonding.

A plot of $\Delta G^o_{tr,th}$ against $\Delta G^o_{tr,ex}$ is shown for the Cl^- ion data in Figure 4. Agreement between the theoretical estimate and experiment is quite good except for higher values of ΔG^o_{tr} where positive deviations are found. In the case of Br^- ion, the variation in $\Delta G^o_{tr,th}$ follows that in $\Delta G^o_{tr,ex}$ almost perfectly except that the theoretical estimates are high by about 8 kJ mol^{-1} (Fig. 5). These results suggest that the value of ΔG^o_w (Br^-) may be in error by 8 kJ mol^{-1}. Finally, the poorest fit between theory and experiment is found for the I^- data where negative deviations in $\Delta G^o_{tr,th}$ are seen for lower values of $\Delta G^o_{tr,ex}$. However, when one considers that the fitting was achieved with one adjustable parameter and that the relative error in ΔG^o_n (i) is much smaller, the results obtained are remarkably good.

As pointed out above, the values of the parameter λ/σ_n obtained in fitting the data for the Gibbs energy of transfer differ significantly from those predicted on the basis of the simple model (eq. 6), and differ between cations and anions. Since one expects that this parameter contains some measure of the chemical ability of the solvent to solvate ions, it is interesting to see whether there is any connection between the parameters obtained here and empirical parameters used to measure the solvent's ability to solvate cations and anions. In the case of cations, a well known parameter measuring the solvents basicity or cation solvating ability is the donor number (DN) introduced by Gutmann.[29] On the other hand, the solvent's anion solvating ability or acidity is empirically measured by the Dimroth-Reichardt parameter E_T.[30] It was shown earlier[31,32] that Gibbs' solvation energies and other thermodynamic parameters for ions in electrolyte solutions are linearly related to these parameters by the equation

$$Q = Q_0 + \alpha E_T + \beta DN \tag{58}$$

where Q is the thermodynamic quantity in question, Q_0, the solvent independent value, α, a quantity measuring response to solvent acidity, and β, that to solvent basicity. Since effects for cations and anions have been separated in the present analysis, it is reasonable to expect that only one of these parameters is important in explaining the variation in λ/σ_n with solvent nature.

A plot of λ/σ_n for cations against the solvent's donor number is shown in Fig. 7. A very good correlation is obtained using data for the 11 aprotic solvents involved in the present study with a correlation coefficient of 0.928. It should be noted that data are available for solvents with a wide range of donor properties from very poor Lewis bases like nitromethane and nitrobenzene to strong Lewis bases such as hexamethylphosphoramide. The present results provide str confirmation that the values of λ/σ_n obtained here by fitting data for the alkali metal cations n account for the specific chemical interaction between the electro-negative group on the solvent molecule and the cation. As is well known[24,29], the donor number is not well defined for protic solvents so that these data could not be included in the present correlation. However, in the case of water, the donor number is often assumed to be 18. The present result for water fits well with those for other solvents using this value.

A plot of the values of λ/σ_n obtained by fitting the data for the halide ions against the solvent's acidity parameter, E_T is shown in Fig. 8. In this case results for 16 solvents are available, and a very good correlation is obtained ($r = 0.944$). It is apparent that the properties of the correlation are determined to a great extent by the protic solvents which have both high values of E_T and λ/σ_n. The values of E_T for the aprotic solvents are close together, the corresponding values of λ/σ_n falling in the range from 9 to 13 nm^{-1}. A much larger variation in λ/σ_n is found for anionic solvation and it clearly is related to the solvent's acidity as estimated by the parameter E_T.

Having shown that reasonable fits between theory and experiment are possible using one adjustable parameter, and that this parameter is related to well known empirical parameters describing solvent basicity and acidity, it is interesting to test the ability of the present model to predict Gibbs solvation energies for other ions. We have carried out this test in two ways, namely, by examining data for monoatomic divalent ions, and for non-spherical monovalent ions.

A plot of the Gibbs energy of solvation for the alkaline earth metal ions together with data for Zn^{2+}, Cd^{2+} and Pb^{2+} ions is shown in Fig. 9. These estimates were also made assuming the Pauling radii for the ions. It is clear that the present theory gives an excellent estimate of $\Delta G_n^o(i)$ in aqueous solutions for Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} but that it underestimates this quantity for the other ions by approximately 200 kJ mol^{-1}. The failure for ions such as Cd^{2+} is attributed to the fact that the bonds between the water molecules and ions involve d electrons. Thus, the value of λ/σ_n derived here is not appropriate for transition metal cations. Gibbs energies of transfer from water to non-aqueous systems are available for Ba^{2+} in some solvents.[25] Values of ΔG_n^o estimated for this ion using the present model agree quite well with those obtained from the experimental data.[24,25]

An attempt was also made to apply the present model to data for non-spherical ions. In the case of ClO_4^-, a tetrahedral ion, the estimate of ΔG_n^o in water is -262 kJ mol^{-1} assuming an ionic radius of 0.241 nm .[33] The estimated value from experimental data is -214 kJ mol^{-1}. [24] Thus, the present model significantly overestimates the Gibbs solvation energy for small tetrahedral ions. This suggests that the mechanism of ionic solvation is significantly different from that for monoatomic anions, the resulting value of λ/σ_n being smaller. In the case of tetrahedral cations, the situation is somewhat better. The present model gives an estimate of ΔG_s^o equal to -297 kJ mol^{-1} for NH_4^+ assuming a radius of 0.148 nm, whereas the corresponding experimental estimate is -292 kJ mol^{-1}.[24] In the case of $(CH_3)_4N^+$ and $(C_2H_5)_4N^+$ the corresponding results are

-189 and -163 kJ mol^{-1} from theory, and -200 and -172 kJ mol^{-1} from experiment.[21] Comparison of theoretical and experimental results suffers for these systems since the experimental quantities have been estimated by several authors using different extrathermodynamic assumptions. However, it would seem that the estimates from the present model are reasonably close to experimental values for aqueous solutions.

It is interesting to speculate on the significance of the TATB assumption with respect to the present results. On the basis of the results for monoatomic cations and anions, the values of λ/σ_n are so different that one would not be able to choose large spherical ions for which ΔG^o_{tr} would be equal for a cation and anion of the same size. However, the brief examination of data for tetrahedral ions made here suggests that λ/σ_n appropriate for tetrahedral cations and anions may be much closer to one another than for monoatomic ions. In this case, the MSA model would predict that values of ΔG^o_n for these ions are equal, and the TATB assumption valid.

Some comment should be made here about the values chosen for the radii of the ions. It is clear from previous discussion in the literature[23,33], and also from our work, that the choice of ionic radius is very important in determining the magnitude of the estimate of ΔG^o_n (i), and, in the present case, the value of the MSA parameter λ/σ_n. In the present study, Pauling radii were used for monoatomic ions. Otherwise, the radii tabulated by Marcus[24] were chosen. In more recent work, Marcus[33] has recommended using revised radii obtained from crystallographic data, mainly for ions with a coordination number of six, as estimated by Shannon and Prewitt.[34] The same author has also tabulated[33] ionic radii estimated from X-ray data for aqueous solutions. However, the best fit to the present data was obtained for the alkali metal cations using the original Pauling radii. Variation in the thermodynamic properties of single ions with ionic size has been used as a method of assessing the extrathermodynamic assumptions made to separate cationic and anionic contributions so that the arguments used to select either the ionic radii or the extrathermodynamic assumptions are not independent of one another. However, on the basis of the single ion data currently used in the literature[24,25] the original Pauling radii are preferrable.

In summary, the approach used here in which the parameter λ/σ_n is estimated from the large body of experimental data available for monoatomic ions has proven to be remarkably successful. It shows clearly that the chemical interaction between the ion and solvent dipole needs to be considered in developing a reasonable statistical mechanical model for electrolyte solutions. In future papers, we will consider other thermodynamic properties of these systems.

Acknowledgement

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Table 1. Pauling radii and standard Gibbs energy of solvation of monovalent ions in water at 298° K[23]

Ion	Pauling Radius r_i, nm	Standard Gibbs energy of hydration ΔG^{o}_{w} (i), kJ mol^{-1}
Li^+	0.060	-487.5
Na^+	0.095	-387.6
K^+	0.133	-314.0
Rb^+	0.148	-292.7
Cs^+	0.169	-260.5
Cl^-	0.181	-339.7
Br^-	0.195	-325.9
I^-	0.216	-279.5

Table 2. Values of the MSA parameter λ/σ_n for monovalent monoatomic cations and anions obtained by fitting experimental data to eq. 55 in 17 different solvents

Solvent	λ/σ_n, nm^{-1}	
	Cations	Anions
1. Water (w)	6.06	24.00
2. Methanol (MeOH)	6.04	20.48
3. Ethanol (EtOH)	5.96	18.58
4. 1-Propanol (PrOH)	6.02	17.36
5. Formamide (F)	6.26	17.06
6. N-methylformamide (NMF)	6.35	-
7. Acetone (AC)	6.27	11.01
8. Acetonitrile (AN)	5.74	12.20
9. Dimethylacetamide (DMA)	6.75	10.04
10. Dimethylformamide (DMF)	6.60	11.10
11. Dimethylsulphoxide (DMSO)	6.64	12.77
12. Hexamethylphosphoramide (HMPA)	6.89	9.61
13. Nitrobenzene (NB)	5.31	13.18
14. Nitromethane (NM)	5.33	12.76
15. N-methylpyrrolidinone (NMP)	7.01	11.04
16. Propylene carbonate (PC)	5.71	11.93
17. Tetramethylene sulphone (TMS)	6.24	11.01

Figure Legends

Figure 1. Plot of the theoretical estimate of the Gibbs energy of transfer of Na^+ ion from water to a non-aqueous solvent against the corresponding value from experiment. The integers indicate the solvent according to the list given in Table 2. The straight line is drawn with unit slope.

Figure 2. As in Fig. 1 but for the Li^+ ion.

Figure 3. As in Fig. 1 but for the Cs^+ ion.

Figure 4. As in Fig. 1 but for the Cl^- ion.

Figure 5. As in Fig. 1 but for the Br^- ion.

Figure 6. As in Fig.1 but for the I^- ion.

Figure 7. Plot of the MSA parameter λ/σ_S estimated for monovalent cations in various non-aqueous solvents as indicated against the solvent's donor number DN.

Figure 8. Plot of the MSA parameter λ/σ_S estimated for monovalent anions in various non-aqueous solvents as indicated against the solvent's acidity parameter, E_T.

Figure 9. Plot of the Gibbs' solvation energy for various divalent cations in water against the ionic radius. The curve shows the estimate of the same quantity according to the MSA model using λ/σ_S equal to 6.06 nm^{-1}.

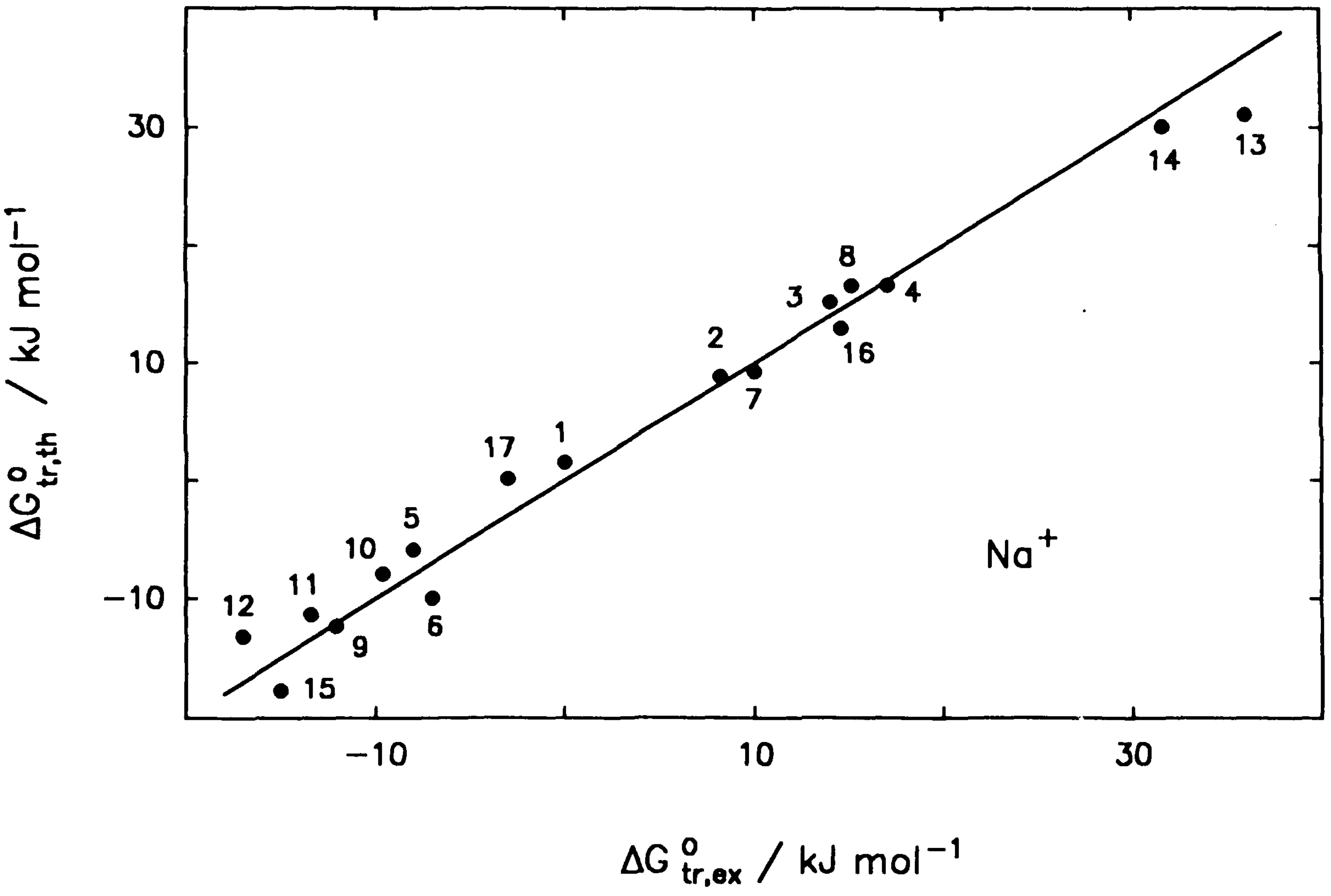
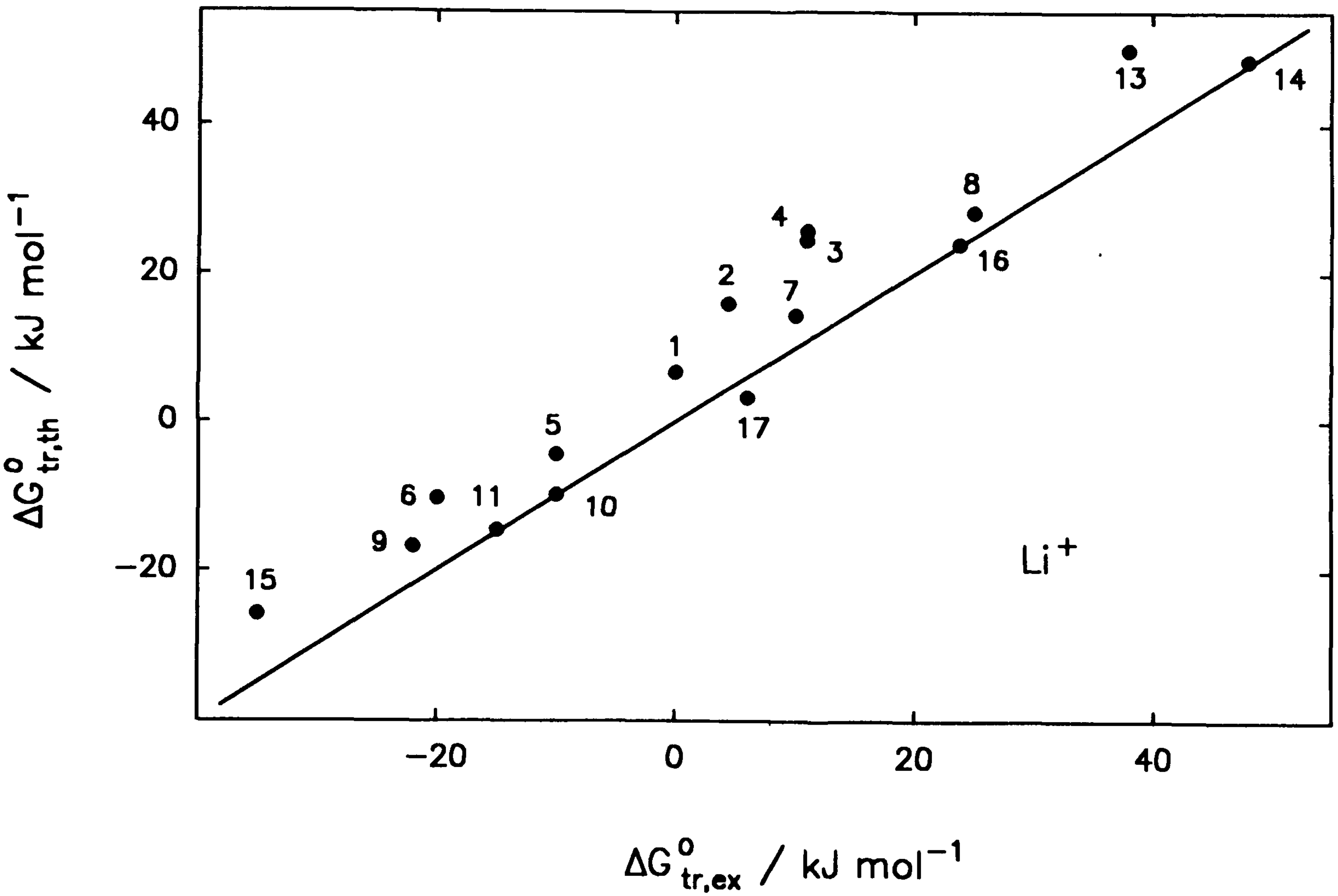
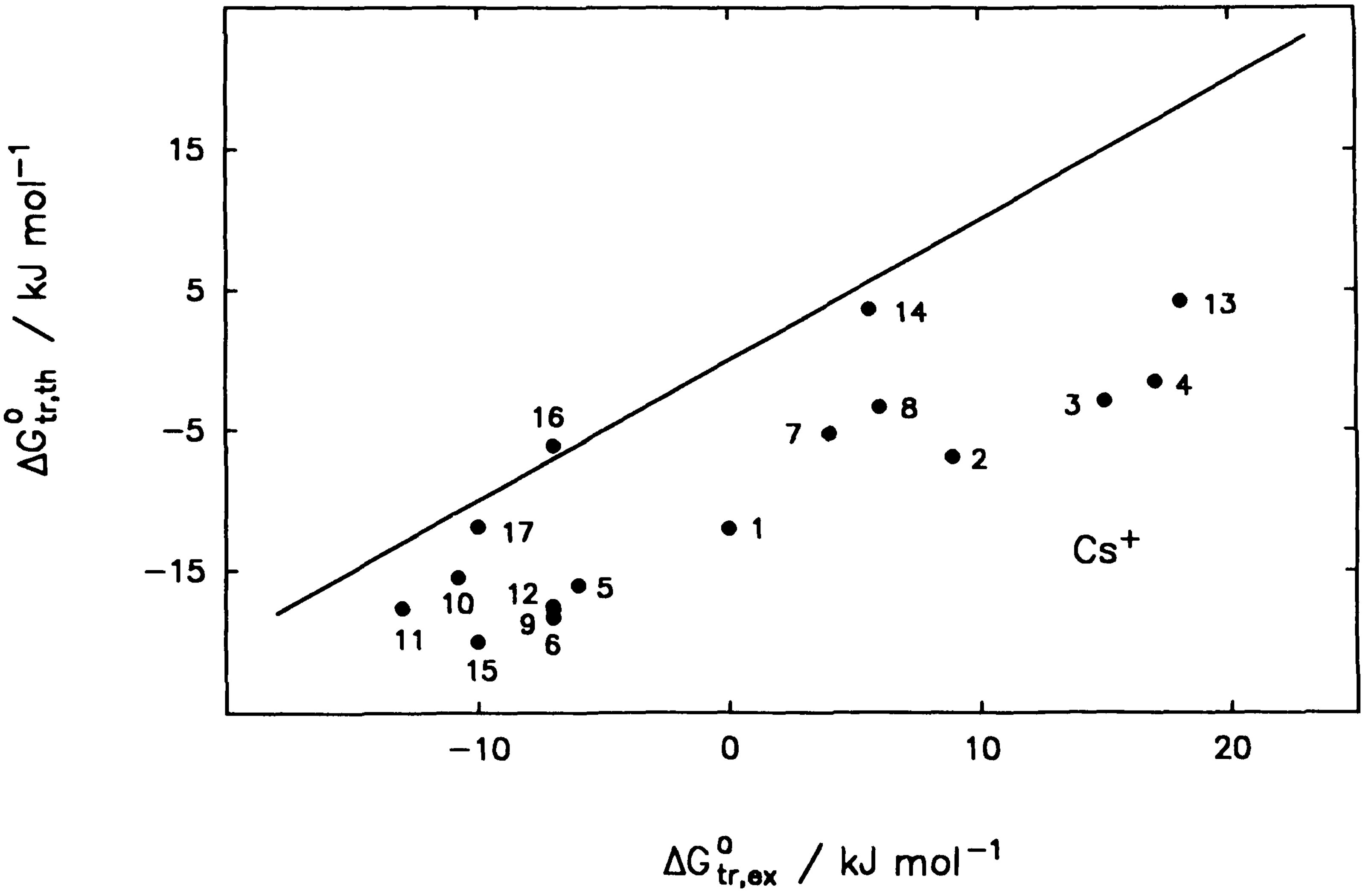

30
10
−10
−10
10
30
$\Delta G^{o}_{tr,th}$ / kJ mol^{-1}
$\Delta G^{o}_{tr,ex}$ / kJ mol^{-1}
Na^{+}
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

Fig. 1



$\Delta G^{o}_{tr,th}$ / kJ mol^{-1}
40
20
0
−20
$\Delta G^{o}_{tr,ex}$ / kJ mol^{-1}
−20
0
20
40
Li^{+}
1
2
3
4
5
6
7
8
9
10
11
13
14
15
16
17

Fig 2



15
5
−5
−15
−10
0
10
20
$\Delta G^{o}_{tr,th}$ / kJ mol^{-1}
$\Delta G^{o}_{tr,ex}$ / kJ mol^{-1}
Cs^{+}
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

Fig 3

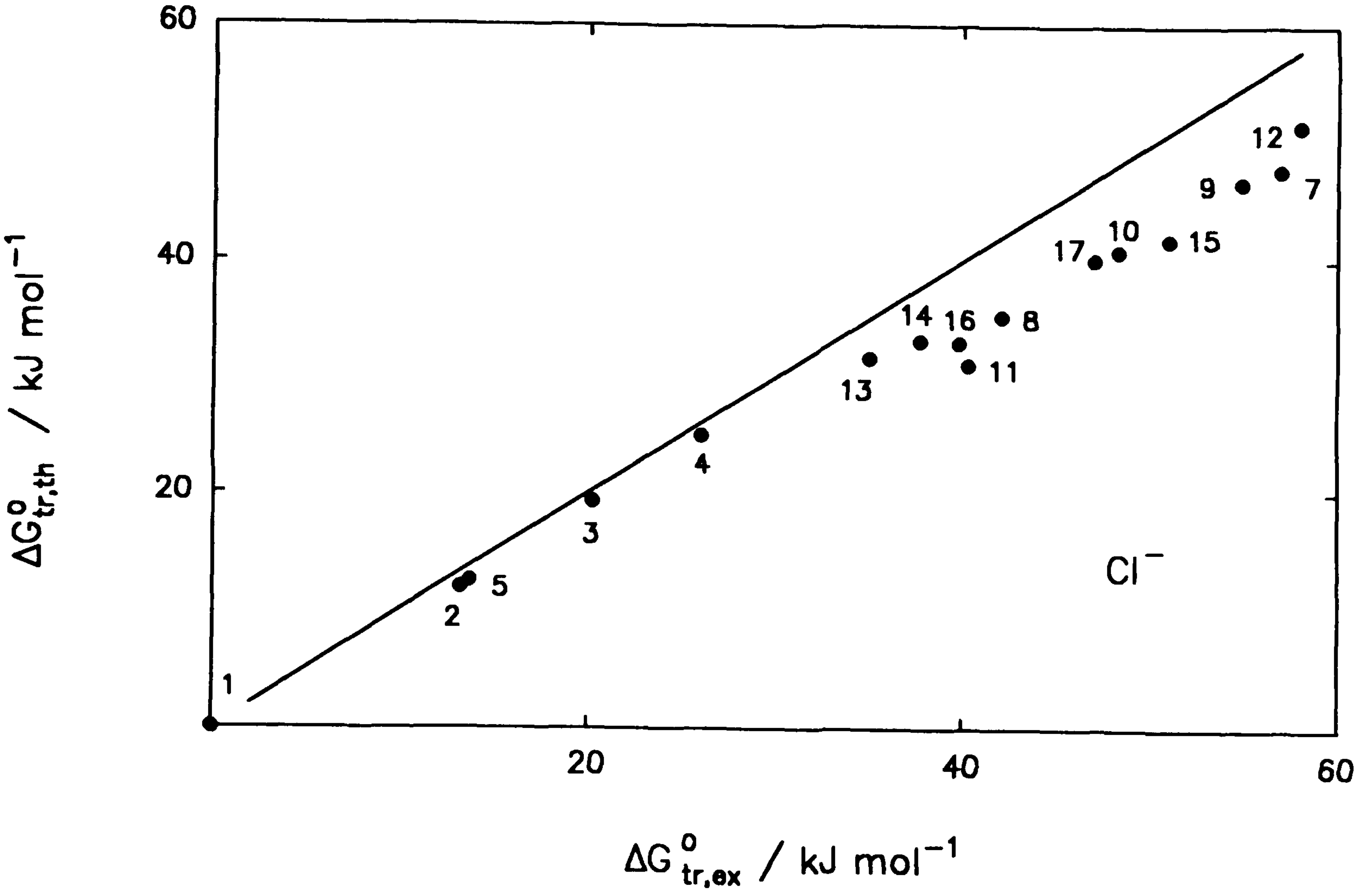

60
40
20
20
40
60
1
2
5
3
4
13
14
16
8
11
17
10
15
9
12
7
Cl⁻
$\Delta G^{o}_{tr,th}$ / kJ mol^{-1}
$\Delta G^{o}_{tr,ex}$ / kJ mol^{-1}

Fig 4

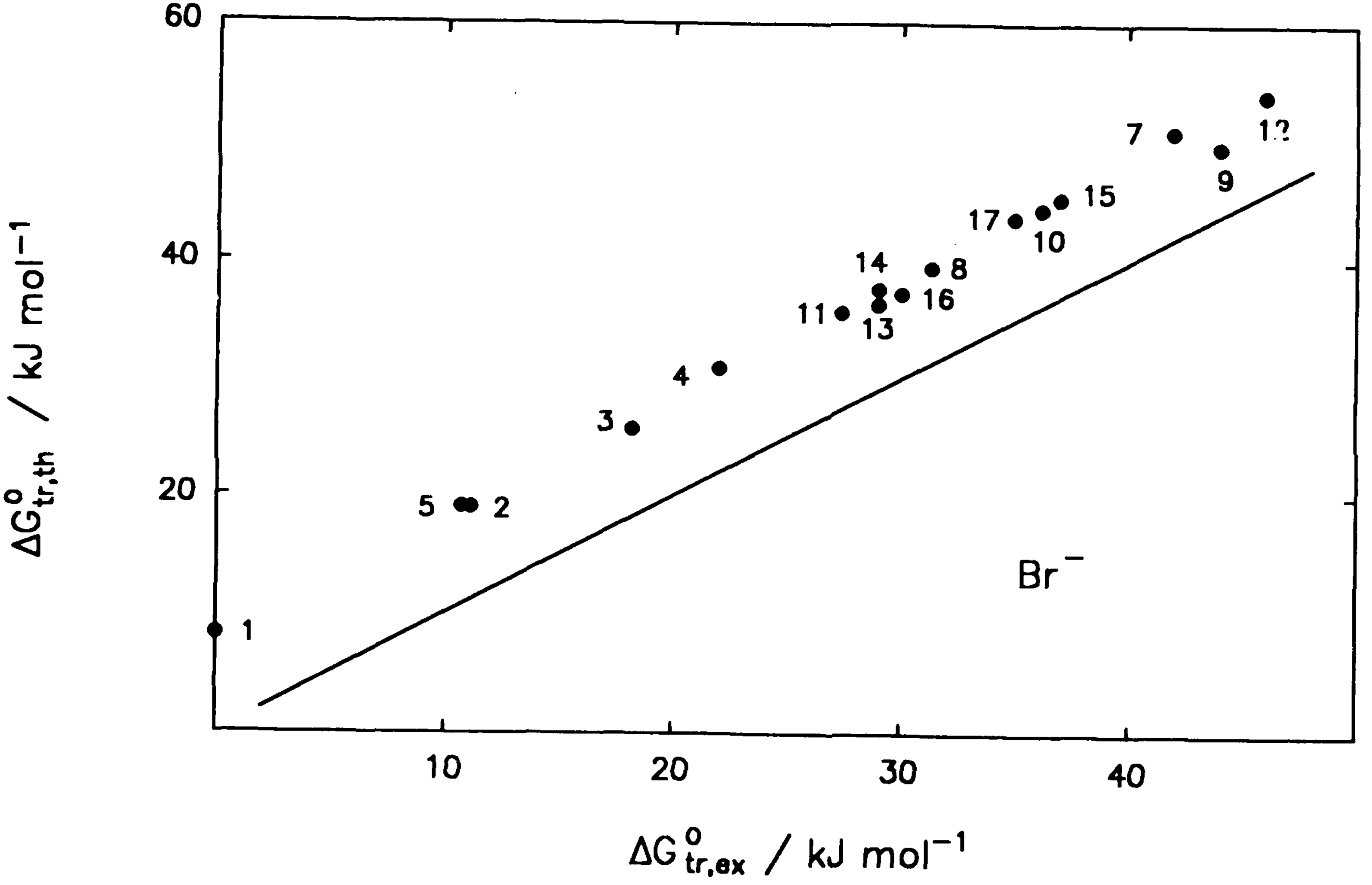

60
40
20
10
20
30
40
$\Delta G^{o}_{tr,th}$ / kJ mol^{-1}
$\Delta G^{o}_{tr,ex}$ / kJ mol^{-1}
Br$^-$
1
2
3
4
5
7
8
9
10
11
12
13
14
15
16
17

Fig 5

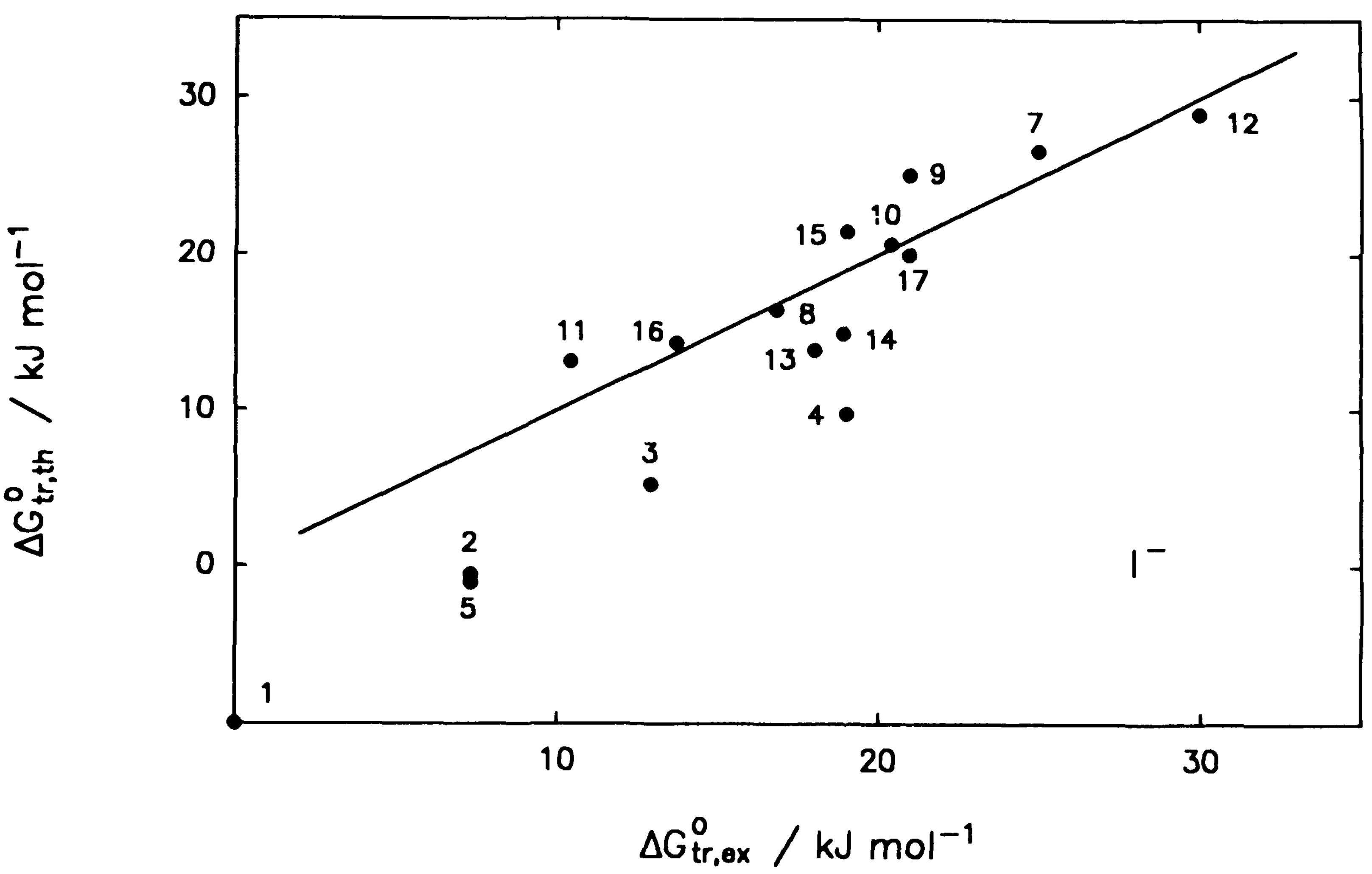

30
20
10
0
10
20
30
1
2
5
3
11
16
8
13
14
4
15
10
17
9
7
12
I⁻
$\Delta G^{o}_{tr,th}$ / kJ mol^{-1}
$\Delta G^{o}_{tr,ex}$ / kJ mol^{-1}

Fig 6

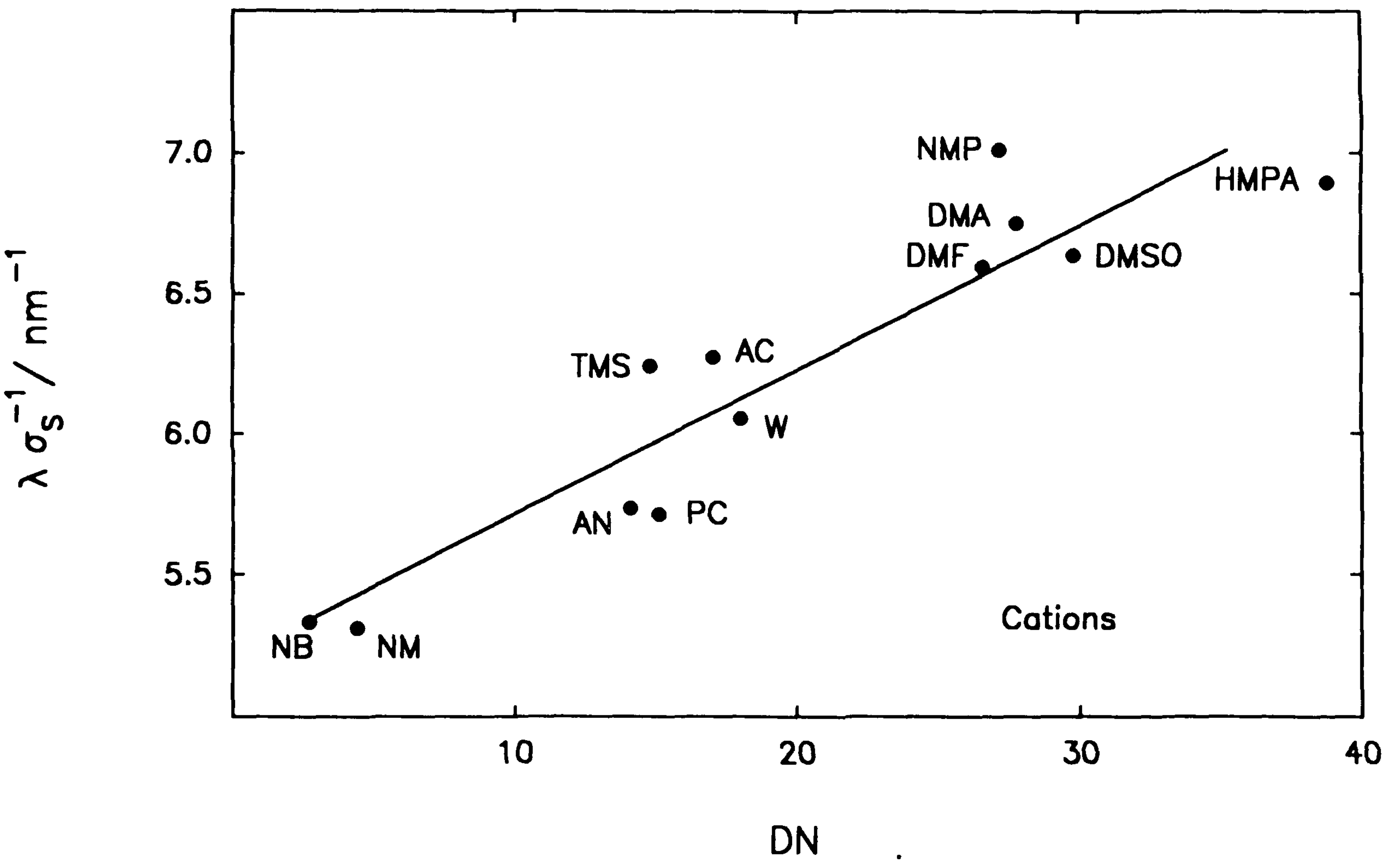
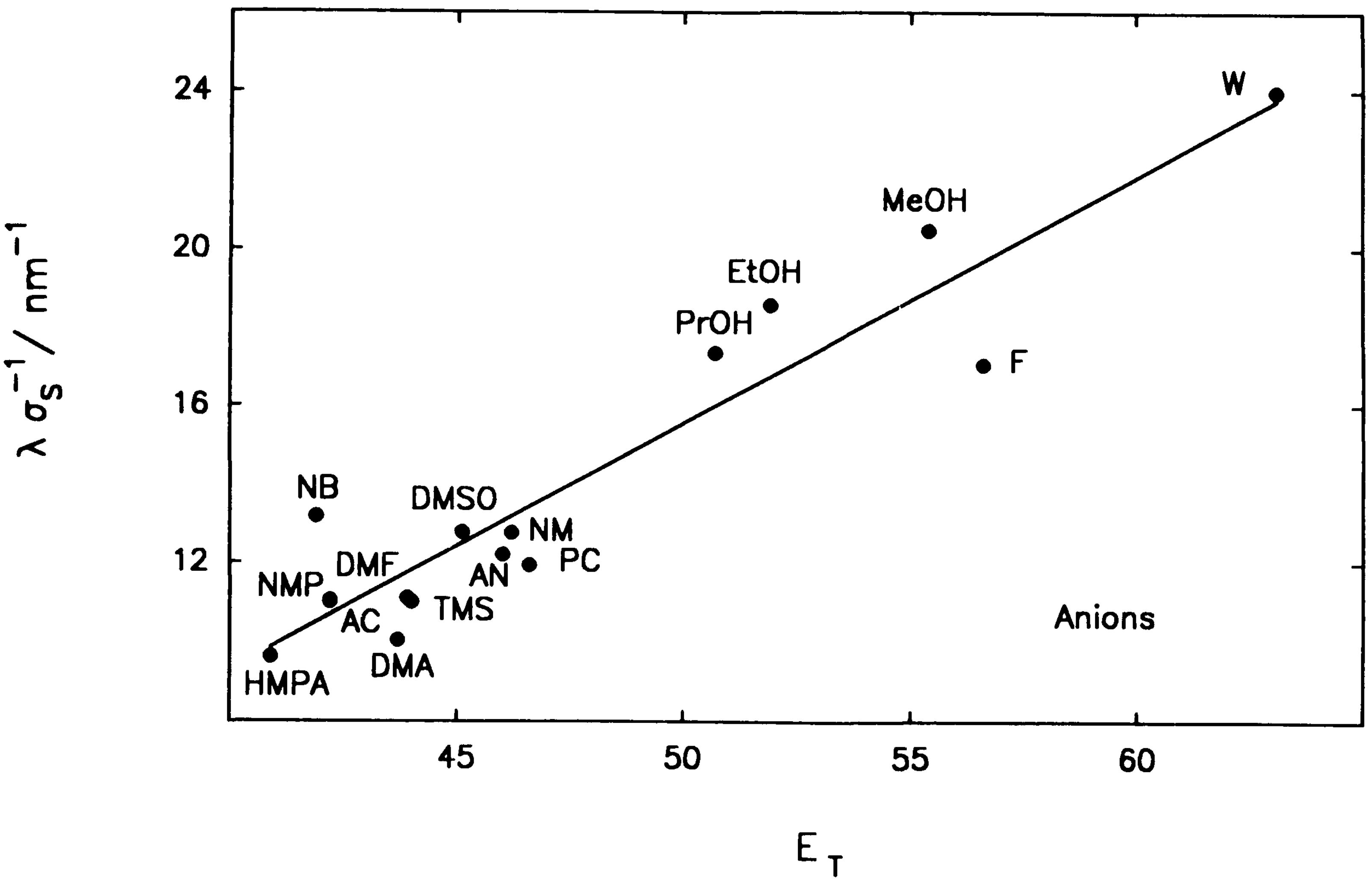
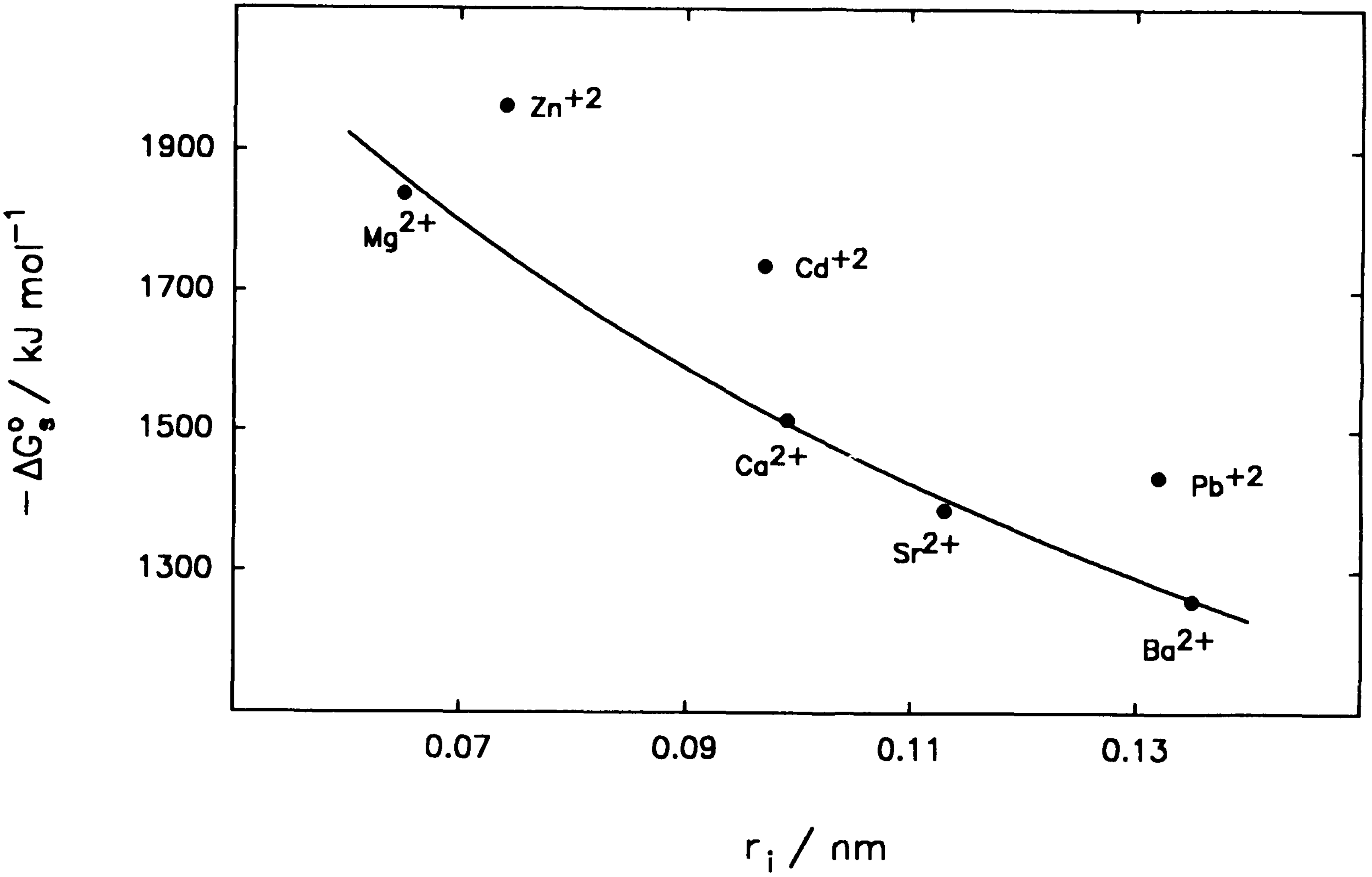

$\lambda \sigma_s^{-1} / nm^{-1}$
7.0
6.5
6.0
5.5
10
20
30
40
DN
NMP
HMPA
DMA
DMF
DMSO
TMS
AC
W
AN
PC
NB
NM
Cations

Fig 7



$\lambda\,\sigma_s^{-1}$ / nm^{-1}
24
20
16
12
45
50
55
60
E_T
Anions
W
MeOH
EtOH
PrOH
F
NB
DMSO
NM
PC
AN
DMF
NMP
TMS
AC
DMA
HMPA

Fig 8



$-\Delta G^{\circ}_{s}$ / kJ mol^{-1}
1900
1700
1500
1300
0.07
0.09
0.11
0.13
r_i / nm
Zn^{+2}
Mg^{2+}
Cd^{+2}
Ca^{2+}
Sr^{2+}
Pb^{+2}
Ba^{2+}

Fig. 9.