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A Simple Model for Ion Solvation with Non Additive Cores

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The solvation of monoatomic ions at infinite dilution in polar solvents is considered within the context of the mean spherical approximation (MSA). The role of both ion-dipole and dipole-dipole interactions in determinign the Gibbs energy and entropy of solvation is considered in detail for the alkali metal and halide ions in water. The significance of the MSA parameters with respect to local interactions of water molecules wiht the ions and each other is discussed

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A Simple Model for Ion Solvation with Non Additive Cores*

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INTRODUCTION

Ionic solvation has been the subject of current interest for at least a century.[1] Modern experimental techniques[2] and the availability of powerful computers[3] have produced real progress in the understanding of this complex problem.

It is clear that in many problems the knowledge of the very complex details of the close range interactions are more than what one needs. In the interpretation of thermodynamic and kinetic parameters averages over large domains are predominant, and therefore, simple, yet controlled theories not only provide a way of fitting data, but also useful physical insight.

The success of the Marcus theory of electron transfer kinetics[4] in solution is a good example. In this theory the polarization of the solvent is evaluated from a continuum model for the solvent, that is, the structure of the solvent is completely ignored. The recent rather spectacular calculations of Chandler and his group[5] have conclusively shown that within certain limitations, this is not unreasonable provided that the radius of the activated complex is chosen in a suitable manner. There are also other examples where this is true. It was used by many investigators in the past, but in an entirely empirical way.[6]

In a series of recent papers[7-10] we have discussed the use of the Mean Spherical Approximation (MSA) in combination with a very simple asymmetric force model, which has a spherical repulsive core. The excellent correlations for the thermodynamic and kinetic parameters for a large number of solvents are more than mere coincidence. We believe that they are due to the fact that the MSA is not only a simple theory, but it also has some remarkable variational properties, that were discovered quite recently. Liquid state theories like the MSA and the HNC can be derived as variational problems of the free energy functional, which is written in terms of the Ornstein-Zernike direct correlation function. This view was introduced by Rosenfeld[11-13] for systems of hard objects in general, and hard spheres in particular. In that work the relation between the grand potential, the direct correlation function and the scaled particle theory was clearly shown. This analysis was extended to the case of charged hard spheres in general, and to the primitive model of electrolytes in particular.[14,15] It can be shown that the thermodynamics and

the pair correlation functions can be derived from a simple model in which the ions are replaced by charged shells and the dipoles by charged dipolar shells. We have shown that the direct correlation function in the MSA is just the electrostatic energy of the shells. Solving the MSA is thus equivalent to an electrostatics problem.

In the limit of high density and charge the Gibbs energy and the internal energy should diverge to the same order in the coupling parameter (charge/temperature ratio) while the entropy should diverge at a slower rate and therefore the Gibbs energy and the internal energy coincide in this limit. The mean spherical approximation (MSA) and the hypernetted chain approximation (NHC) satisfy these bounds, discovered by Onsager some fifty years ago. (This is not true for the Debye Hückel theory, where the entropy also diverges). Therefore, in this limit, the HNC and the MSA Gibbs energy, and its derivatives, coincide. This is a very gratifying feature, because the HNC, which is the more accurate theory, is in general difficult to solve numerically, while the MSA is analytical in most cases, and of a rather simple form.

In the asymptotic limit the excess electrostatic energy is identical to the exact Onsager lower bound, which is achieved by immersing the entire hard core system in an infinite neutral and perfectly conducting (liquid metal) fluid.[14] In the case of the primitive model of electrolytes, this is equivalent to smearing the charge on the surface of the ion. It was also shown[14,16] that the direct correlation function is equal to the interaction potential of two "smeared" ions of radius R_i, R_j where R_i is the radius of ion i plus some screening length.

The Onsager process of introducing the infinite conductor, naturally decouples all the different components in the system which may differ in size, shape, charge distribution and relative orientation in space. As a result, the variational free energy functional in the high coupling limit diagonalizes, and the mathematical solution of the asymptotic problem is given in term of the geometrical properties of the individual particles in the system.

The MSA Gibbs energy provides an appropriate functional from which the charge part of the direct correlation function is obtained by functional differentiation.

There is an actual numerical test case that proves the electrostatic analogy of the MSA. The very high charge and density limit for the one component plasma (point ions in a neutralizing background) was investigated using the HNC equation by Ng[17], in a tour de fourcer numerical calculation. The same results were obtained by Rosenfeld et al. using the analytical solution of the MSA.[18]

A second point is the use of spherical cores to represent non spherical objects. This also depends on the properties of interest. For the equation of state, it works even for very non spherical objects. There are numerous examples of sphericalization in the literature of molecular fluids. A notable example is given in the recent work of Williams et al.[19] The median diameter of a non spherical object yields a surprisingly good equation of state, not only for hard dumbbells but also for real gases at extremely high pressures.[20,21] Other examples are found in the extensive studies of Nezbeda and his group[22,23] on the structure of molecular liquids.

The analytical solution of the MSA for mixtures of ions and dipoles with a non spherical sticky potential was obtained some time ago[24-26] for the case of a sphere with a point dipole and a sticky potential of dipolar symmetry, which represents the specific non electrostatic interactions. In this work it was shown that the contribution of the sticky potential was merely a shift in the polarization parameter, λ. This work has been continued to include short ranged potentials of higher (tetrahedral) symmetry.[27]

In this spirit we have recently analyzed the solvation thermodynamics of monoatomic monovalent ions in water and in a number of polar solvents.[7,10,28] The basic idea comes from the observation that to a first approximation the corrections due to the molecular nature of the solvent result in a change in the screening length from $1/r$ to $1/r + \lambda\sigma_i/r \ \sigma_s$, the shift being different for each ion, according to its size; because of geometrical packing considerations the number of solvent molecules that can be the first neighbors of a given ion, i, vary according to the ratio σ_i/σ_s. Consider now a realistic model of the solvent, with a soft repulsive core, and of non-spherical shape. Then, the distance of closest approach of a certain ion should be very different for the anion-solvent pair and the cation-solvent pair, even if the unsolvated anion and cation are of the

same size. The correct statical mechanical model for such a situation is the mixture with non-additive cores discussed in the literature.[29] A simple way of accounting for this is to assume that at low concentration the effective radius of the solvent is

$$r_{si} = r_s + \Delta_{si} \tag{1}$$

The Model

In the MSA for a system of spherical ions and dipoles of arbitrary size[30], the Gibbs energy of solvation in the limit of infinite dilution is[31]

$$G_{id} = -\frac{N_o(z_ie_o)^2}{8\pi\,\varepsilon_0}\left(1-\frac{1}{\varepsilon_s}\right)\frac{1}{r_i+\delta^o} \tag{2}$$

Here, z_i is the valence of the ion, e_o, the fundamental charge, ε_s, the static dielectric constant of the solvent, ε_0, the permittivity of free space, r_i, the radius of the ion, and N_o, the Avogadro constant. δ^o is equal to r_s/λ, where r_s is the radius of the solvent (the effective radius) and the MSA polarization parameter, λ is calculated from the dielectric constant of the pure solvent ε_s using the Wertheim relationship[32]

$$\lambda^2\,(\lambda+1)^4 = 16\,\varepsilon_s \tag{3}$$

Although this value of the polarization parameter may be appropriate for estimating dipole-dipole interaction energy, it gives poor estimates of the Gibbs solvation energy when this is assumed to equal G_{id}.[7,10,28] Therefore, and in view of the above discussion we change eq. (2) to

$$G_{id}(C^+) = -\frac{N_o\,(z_ie_0)^2}{8\pi\varepsilon_0}\left(1-\frac{1}{\varepsilon_s}\right)\frac{1}{(r_i+\delta_c)} \tag{4}$$

where

$$\delta_c = \frac{r_s+\Delta_{sc}}{\lambda} \tag{5}$$

and for cations, and similarly, for monovalent monoatomic anions

$$G_{id}(A^-) = -\frac{N_o\,(z_ie_0)^2}{8\pi\varepsilon_0}\left(1-\frac{1}{\varepsilon_s}\right)\frac{1}{(r_i+\delta_A)} \tag{6}$$

where

$$\delta_A = \frac{r_s + \Delta_{sA}}{\lambda} \tag{7}$$

This separation and parameterization produces a much more sensible and physical model of G_{id} for ions in a number of solvents.

The second contribution to the Gibbs solution energy comes from repulsive dipole-dipole interactions[25,33] and is given by the equation

$$G_{dd} = \frac{(z_i e_0)^2 (\epsilon_s - 1)^2}{64 \pi \, \epsilon_0 \epsilon_s \, (r_i + \delta_i)^2} \left[\frac{4r_i + \delta_i \left(\frac{3\lambda + 2}{\lambda + 1}\right)}{\epsilon_s + \frac{\lambda(\lambda + 3)}{2(\lambda + 1)^2}} \right] \tag{8}$$

This expression may be simplified considerably when one considers the range of values typical for λ. For water whose dielectric constant is 78.3 at 25 °C, λ is equal to 2.65. The corresponding value of the ratio $\lambda(\lambda+3)/2(\lambda+1)^2$ which appears in the denominator of the term in square brackets in eq. (8) is 0.56. This is negligible with respect to the value of ϵ_s and may be neglected. The ratio appearing in the numerator of this term, namely, $(3\lambda+2)/(\lambda+1)$ is equal to 2.7. Thus, the expression for G_{dd} may be rewritten as

$$G_{dd} = \frac{N_0 (z_i e_0)^2}{64 \pi \, \epsilon_0} \left(1 - \frac{1}{\epsilon_s}\right)^2 \frac{(4r_i + 2.7 \, \delta_i)}{(r_i + \delta_i)^2} \tag{9}$$

The simplified expression has the advantage that the parameter λ does not appear on its own but only in δ_i. This fact is important in applying the expression to experimental data. Finally, on the basis of previous work[25], only a fraction θ of the dipole-dipole term is used in estimating the Gibbs energy of solvation so that the final expression for G_s becomes

$$G_s = G_{id} + \theta \, G_{dd} \tag{10}$$

The expressions for the corresponding entropies are obtained from the temperature derivatives of the above Gibbs energies. For the ion-dipole term, the result for a cation is

$$S_{id}(C^+) = \frac{N_0(z_ie_0)^2}{8\pi\,\varepsilon_0}\left[\frac{1}{\varepsilon_s^2}\frac{d\varepsilon_s}{dT}\frac{1}{(r_i+\delta_c)} - \frac{1}{(r_i+\delta_c)^2}\left(1 - \frac{1}{\varepsilon_s}\right)\frac{d\delta_c}{dT}\right] \tag{11}$$

where $d\delta_c/dT$ is the temperature derivative of δ_c which is obtained from the temperature derivative of λ_c. Comparing eqs. (4) and (11), it is easily shown that

$$S_{id}(C^+)\left(1 - \frac{1}{\varepsilon_s}\right) = -\frac{G_{id}(C^+)}{\varepsilon_s^2}\frac{d\varepsilon_s}{dT} - \frac{8\pi\,\varepsilon_0 G_{id}^2(C^+)}{N_0(z_ie_0)^2}\frac{d\delta_c}{dT} \tag{12}$$

The corresponding expression for an anion is

$$S_{id}(A^-)\left(1 - \frac{1}{\varepsilon_s}\right) = -\frac{G_{id}(A^-)}{\varepsilon_s^2}\frac{d\varepsilon_s}{dT} - \frac{8\pi\,\varepsilon_0 G_{id}^2(A^-)}{N_0(z_ie_0)^2}\frac{d\delta_A}{dT} \tag{13}$$

From these equations it follows that two additional parameters are required to estimate the entropy of solvation of a salt, namely, the temperature derivatives of the polarization parameters for the cation and anion.[10,28]

From the expression for G_{dd}, one obtains the following equation for the corresponding entropy:

$$S_{dd} = G_{dd}\left[\frac{2}{\varepsilon_s^2}\frac{d\varepsilon_s}{dT}\Big/\left(1 - \frac{1}{\varepsilon_s}\right) + \frac{2.7\,\delta_i}{\lambda}\frac{d\lambda}{dT}\Big/(4r_i + 2.7\,\delta_i) - \frac{2\delta_i}{\lambda}\frac{d\lambda}{dT}\Big/(r_i + \delta_i)\right] \tag{14}$$

The derivative $d\lambda/dT$ may be found from the Wertheim equation from which one obtains

$$\frac{d\lambda}{dT} = \left[\frac{\lambda(1+\lambda)}{3\lambda+1}\right]\frac{1}{2\varepsilon_s}\frac{d\varepsilon_s}{dT} \tag{15}$$

Assuming that the fraction θ is independent of temperature, the resulting expression for the entropy of solvation is

$$S_s = S_{id} + \theta\,S_{dd} \tag{16}$$

This model is now examined with respect to data for monoatomic monovalent ion solvation in water.

Results and Discussion

In order to apply the above model to experimental data one must choose radii for the ions and an extrathermodynamic assumption for extracting single ion solvation energies from experimental values for the salts, namely, the alkali metal halides. Two sets of ionic radii give good fits between experiment and theory[10], namely, the values given by Pauling[34] and those extracted from neutron and X-ray diffraction experiments.[35] The Pauling values are used here simply because they are more familiar. The extrathermodynamic assumptions used to separate experimental quantities into those for cations and anions were examined in detail for aqueous systems by Conway.[36] Values of the Gibbs energy and entropy of solvation for the alkali metal cations and halide anions estimated by Conway are summarized in Table 1 together with the Pauling radii for these ions.

In our previous analysis of the Gibbs solvation energy[7,10], the contribution of dipole-dipole interactions was ignored ($\theta = 0$ in eq. (10)). Analysis of the data for the alkali metal halides showed that the best values of δ_c and δ_A (eqs. (4) and (6)) assuming Pauling radii for the ions were 82.4 and 18.0 pm, respectively.[10] *The quality of the fit between theory and experiment is really excellent,* the standard deviation for the calculated values being 1.5 kJ mol^{-1}, that is, significantly less than 1 percent. This result is illustrated in Fig. 1 in terms of a plot of -G_s against $1/(r_i+\delta_i)$. It is apparent that the values of G_s fit very well on a straight line in the region where data exist but that the slope of the best straight line through these data is slightly higher (75.2 kJ nm mol^{-1}) than that predicted by theory (69.45 kJ nm mol^{-1}). As a result, an ion with infinite radius is predicted to have a Gibbs solvation energy of 35.7 kJ mol^{-1} when this simple model is applied. This can be attributed to the failure to account for dipole-dipole interactions which constitute a positive contribution to G_s.

The same data were re-examined on the basis of eq. (10) using the expression for G_{dd} given by eq. (9). The fit was carried out so that the resulting estimates of G_{id} and G_{dd} would go to zero for an ion of infinite radius. The resulting best values of δ_c and δ_A were much smaller than those obtained by the simpler analysis, and are recorded in Table 2. The corresponding estimates of G_{id} are plotted against $1/(r_i+\delta_i)$ in Figure 2. As expected these estimates are larger in magnitude

than the experimental values of G_s also plotted on the same graph. Both plots are linear in $1/(r_i+\delta_i)$ and have zero intercepts within the experimental standard deviation. Estimates of θG_{dd} for the same nine ions are also plotted in this figure. For the cations, this quantity varies from a high of 41.2 kJ mol^{-1} for Li$^+$ to a low of 22.7 kJ mol^{-1} for Cs$^+$, and is approximately eight percent of the magnitude of G_{id}. In the case of the anions it represents a slightly higher fraction of the total Gibbs energy and varies from a high of 42.7 kJ mol^{-1} for F$^-$ to a low of 30.8 kJ mol^{-1} for I$^-$ ion. The values of θG_{dd} are also approximately linear in $1/(r_i+\delta)$ with an intercept corresponding to zero for an infinitely large ion. The value of δ used in estimating G_{dd} is that estimated on the basis of the Wertheim equation, namely, 51.6 pm. When the contributions, G_{id} and θG_{dd} are added one obtains estimates of G_s which agree with those obtained from experimental data to within a few kJ mol^{-1}. Values of the parameters used in our calculations including the fraction θ are summarized in Table 2.

A successful model for ionic solvation must also be able to estimate correctly the entropy of solvation. In order to make this calculation one must have estimates of the temperature derivatives of the parameters δ_c, δ_A and λ. The latter was calculated using eq.(15) which gives a value of -2.48×10^{-8} K^{-1} for $d\lambda/dT$ on the basis of the dielectric properties of water. Assuming r_s, the radius of a water molecule, is equal to 137 pm the corresponding value of $d\delta/dT$ is 0.048 pm K^{-1}. Values of δ_c and δ_A were determined from the single ion estimates of S_s given by Conway.[13] In the case of cations on the basis of eqs. (12) and (16), one may write

$$Y = \frac{d\delta_c}{dT} X \tag{17}$$

where

$$X = -\frac{8\pi \, \varepsilon_0 G_{id}^2(C^+)}{N_0(z_i e_0)^2} \tag{18}$$

and

$$Y = S_s(C^+) \left(1 - \frac{1}{\varepsilon_s}\right) + \frac{G_{id}(C^+)}{\varepsilon_s^2} \frac{d\varepsilon_s}{dT} + \theta S_{ss} \tag{19}$$

$S_c(C^+)$ being the solvation entropy of the cation. Similar equations can be written for anions using eqs. (13) and (16). A plot of Y against X for both ions is shown in Fig. 3. These data were fit to a straight line passing through zero (one parameter fit) as shown, the resulting slope which equals both $d\delta_S/dT$ and $d\delta_A/dT$ being 0.032 pm K^{-1}. It is important to note that the present analysis suggests that these temperature coefficients are equal in contrast to our previous conclusion based on an analysis which ignored dipole-dipole interactions. The estimated error in the slope is not large being about 4%. It should also be noted that the magnitude of $d\delta_C/dT$ and $d\delta_A/dT$ is about 65 percent of that found on the basis of the Wertheim equation (eq. (15)).

Using the above coefficients values of S_{id} were estimated for the alkali metal and halide ions and are plotted in Fig. 4 together with estimates of S_{dd} and experimental values of S_s against the experimental Gibbs solvation energy G_s. It is clear that the entropy of solvation is approximately a quadratic function of the Gibbs energy as suggested by the MSA model. The ion-dipole contribution to the solvation entropy is clearly the larger varying from -161 J K^{-1}mol^{-1} for Li$^+$ to -55 J K^{-1}mol^{-1} for Cs$^+$; in the case of the anions, this contribution is -145 J K^{-1}mol^{-1} for F$^-$ and -65 J K^{-1}mol^{-1} for I$^-$. The positive dipole-dipole contribution is generally less than ten percent of that from ion-dipole interactions. The estimate of S_s agrees with the experimental value quite well except for the heavier halide ions. Thus, in the case of I$^-$ ion, the estimate of S_s is higher in magnitude by 20 kJ mol^{-1}. This may be a result of some oversimplification used in the present analysis, especially the assumption that $d\delta_C/dT$ and $d\delta_A/dT$ are equal. Nevertheless, the agreement between theory and experiment is really quite good and demonstrates that the MSA provides a simple and powerful model for ion solvation in water.

The present analysis may easily be extended to the other polar solvents considered in our previous work.[7,28] It is obvious that the values of λ for these solvents that would be obtained using the present analysis would be quite different from those reported earlier.[7,28] However, preliminary calculations indicate that they follow the same trend. Thus, the correlation observed between λ_C and the Gutmann donor number, DN[37] for the solvent, and λ_A and the Dimroth-Reichardt acidity parameter E_T[38] should be maintained. This provides an important connection

between the MSA λ and these empirical solvent parameters which are often used by chemists in assessing solvent properties.[39,40]

In conclusion, the present study has shown that the description of the variation in Gibbs energy and entropy with ion size is significantly improved when dipole-dipole interactions for the solvent molecules are taken into consideration. This is especially important when considering the entropy of solvation which is very poorly estimated by other models. The simplicity of the MSA makes it an attractive model for general use by physical chemists. Furthermore, the polarization parameter has practical significance as a measure of the solvents' ability to act as a Lewis acid or a Lewis base. In future papers, we will expand the description applied here for water to other polar solvents.

Acknowledgement

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Table 1. Pauling radii and standard thermodynamic parameters of solvation of monoatomic monovalent ions in water at 298° K

	Ion	Pauling Radius r_i, nm	Gibbs Solvation energy G_s/kJ mol^{-1}	Solvation Entropy S_s/J K^{-1} mol^{-1}
1.	Li$^+$	0.060	-487.5	-141
2.	Na$^+$	0.095	-387.6	-109.7
3.	K$^+$	0.133	-314.0	- 74.2
4.	Rb$^+$	0.148	-292.7	- 62.1
5.	Cs$^+$	0.169	-260.5	- 59.1
6.	F$^-$	0.136	-456.8	-136.8
7.	Cl$^-$	0.181	-339.7	- 79.9
8.	Br$^-$	0.195	-325.9	- 64.4
9.	I$^-$	0.216	-279.5	- 41.4

Table 2.   MSA Parameters for the Alkali Metal and Halide Ions in Water at 25 °C

Radius correction for cations, δ_c/nm	0.0692
Radius correction for anions, δ_a/nm	0.0011
Dipole-dipole fraction for cations, θ_c	0.31
Dipole-dipole fraction for anions, θ_a	0.26
Temperature derivative of radius correction for cations and anions, $d\delta/dT$/pm K^{-1}	0.032

Legends for Figures

Figure 1. Plot of the single ion Gibbs energy of solvation for the alkali metal cations (•) and halide anions (♦) against the reciprocal of the ion radius, r_i, plus the MSA parameter δ. The value of δ for cations was 82.4 pm and for anions, 18.0 pm. The solid line shows the least squares fit to these data, and the broken line the value of the ion-dipole contribution to the Gibbs energy according to eqs. (4) and (6). The numbers refer to individual ions listed in Table 1.

Figure 2. Plot of the single ion Gibbs energy of solvation, G_s, the ion-dipole contribution, G_{id}, and the dipole-dipole contribution, G_{dd}, against the reciprocal of the ion radius r_i plus the MSA parameter δ for the alkali metal cations (•, o) and halide anions (♦, ◊). The value of δ for cations was 69.2 pm, and for anions, 1.1 pm. The solid lines show the least squares fit to each set of data. The numbers refer to individual ions listed in Table 1.

Figure 3. Plot of the function, Y, (eq. (17)) against the function X (eq. (18)) for the alkali metal cations (•) and halide anions (♦). The solid line was determined by a one parameter least squares fit going through the origin. The numbers refer to individual ions listed in Table 1.

Figure 4. Plot of the single ion entropy of solvation, S_s, the ion-dipole contribution, S_{id}, and the dipole-dipole contribution, S_{dd}, against the Gibbs energy of solvation G_s for the alkali metal cations (•, o) and halide anions (♦, ◊). The curves are fitted to data for S_{id} and S_{dd}. The numbers refer to individual ions listed in Table 1.
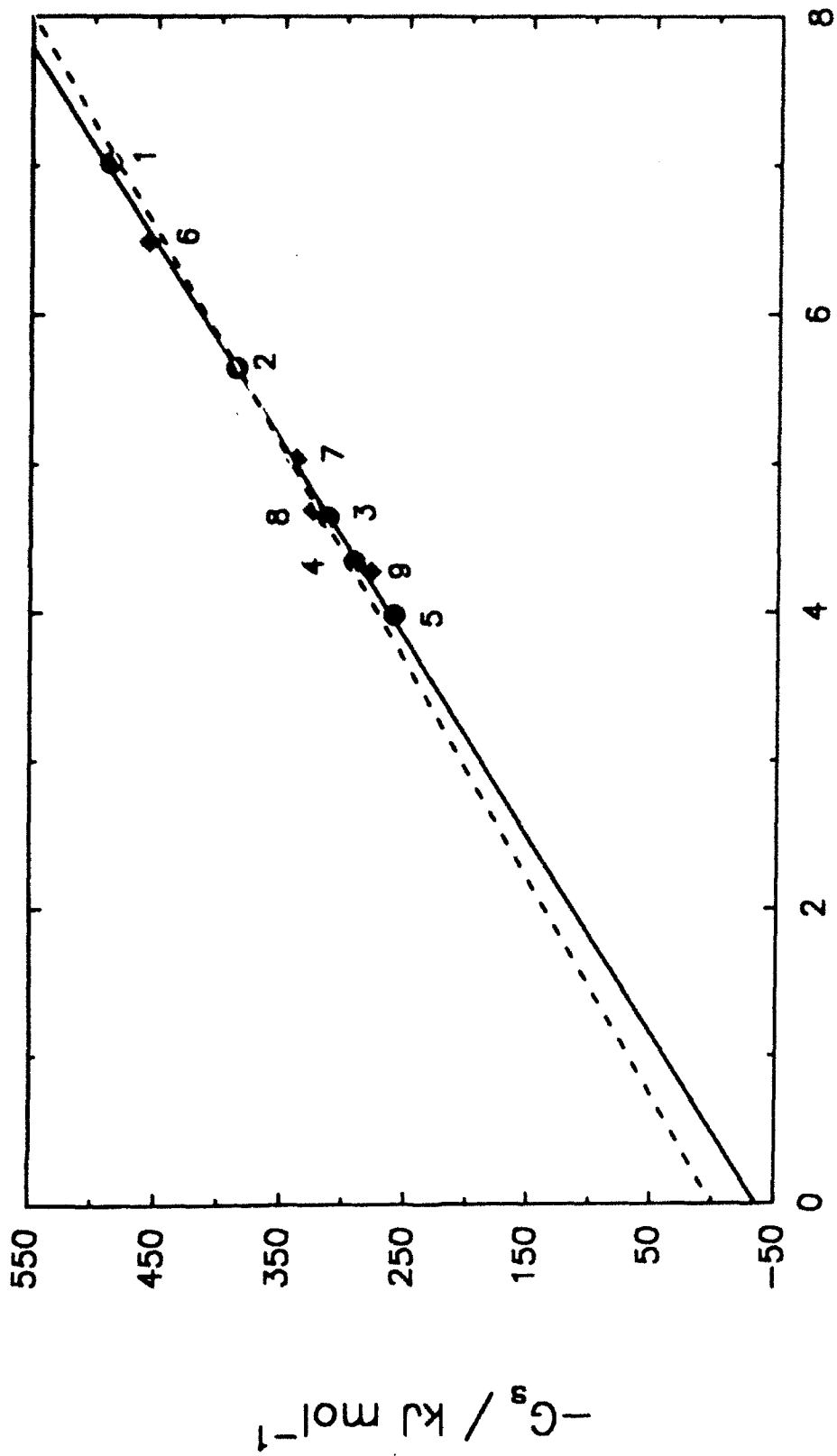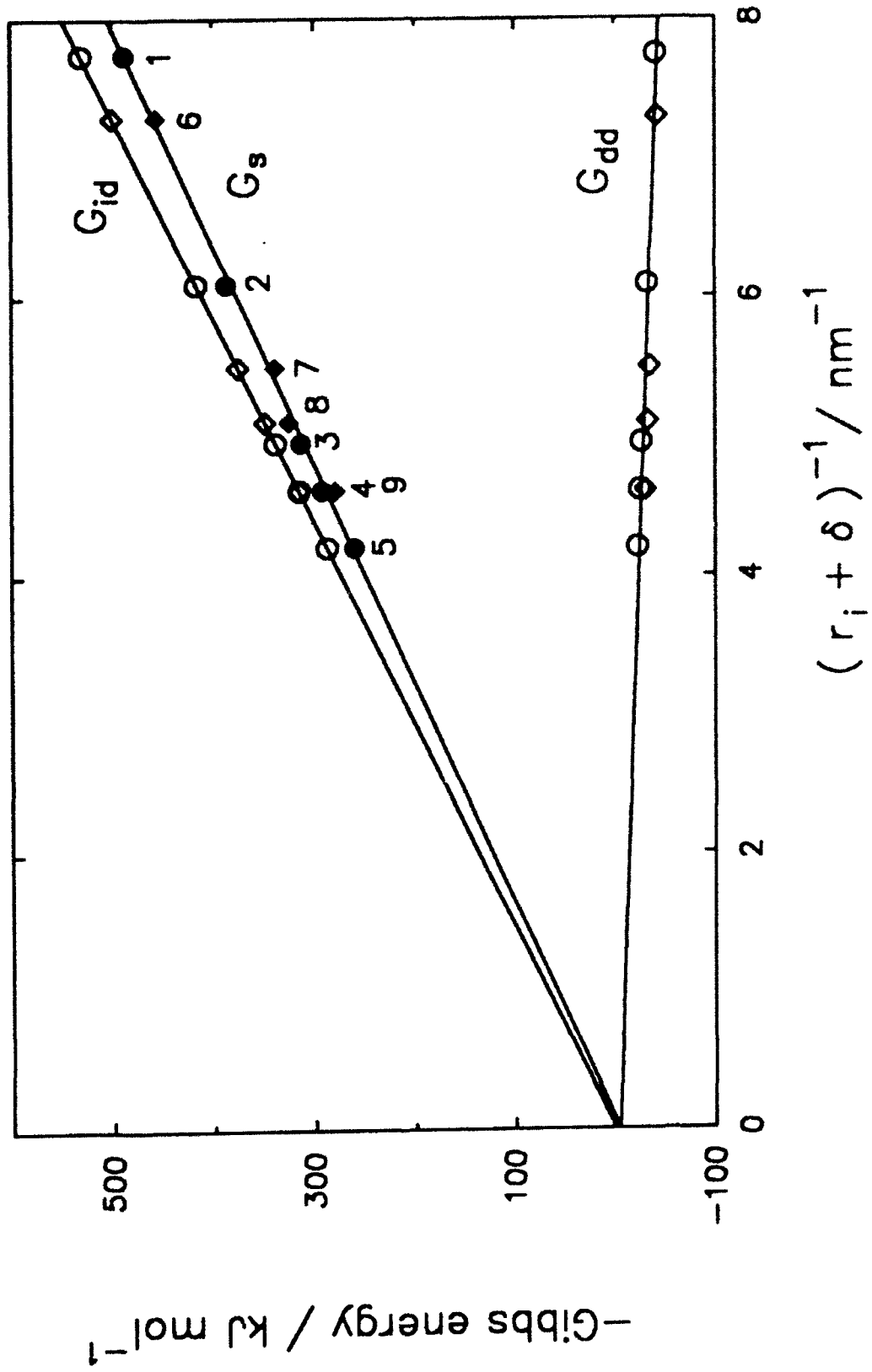
Fig 1

Fig 2

Fig 3

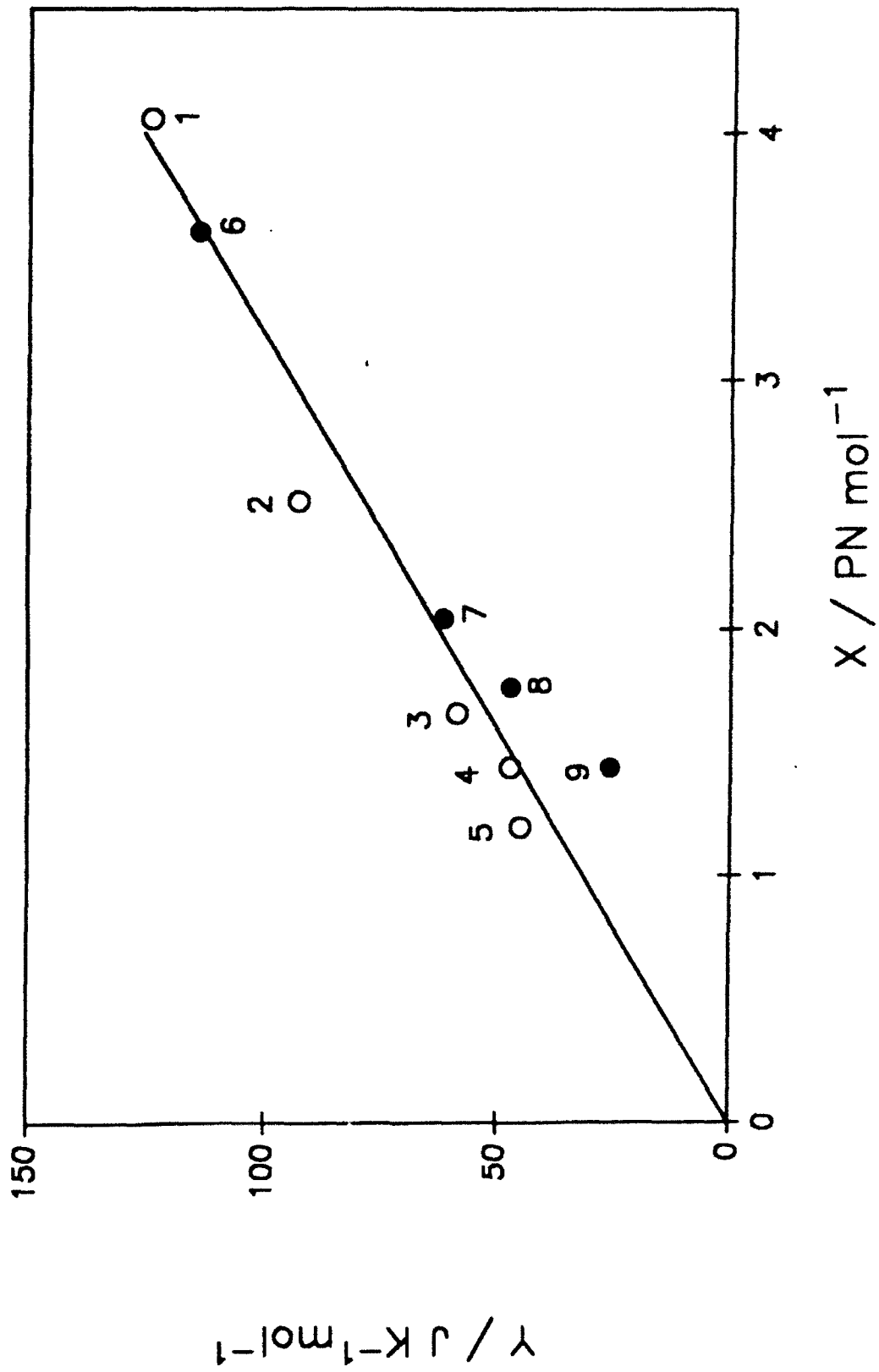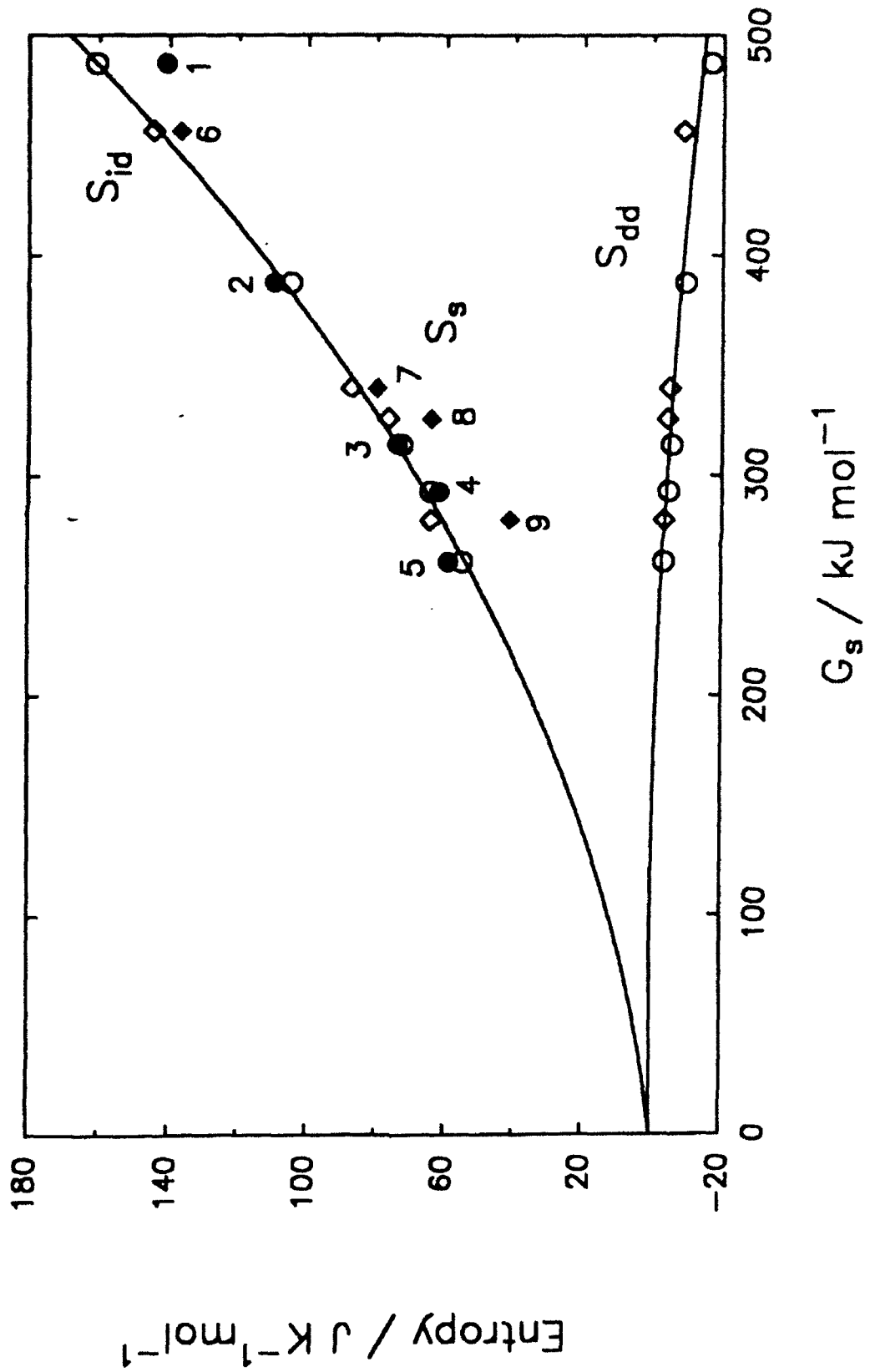Y / J K⁻¹ mol⁻¹

X / PN mol⁻¹

Fig 4.