



OFFICE OF NAVAL RESEARCH
Grant No. N00014-90-J-1263
RCT Project 4133002---05
Technical Report #19

APPLICATION OF THE MEAN SPHERICAL APPROXIMATION TO
DESCRIBE THE ENTROPY OF SOLVATION OF SPHERICAL
IONS IN POLAR SOLVENTS

by

W. R. Fawcett* and L. Blum**

Prepared for Publication in the
J. Chem. Soc. Faraday

DTIC
ELECTE
FEB 16 1993
S E D

*Department of Chemistry, University of California
Davis, CA 95616

and

**Department of Physics, University of Puerto Rico
P.O. Box 23343
Río Piedras, P.R. 00931-3343, USA

Reproduction in whole or in part is permitted for
any purpose of the United States Government

*This document has been approved for public release
and sale; its distribution is unlimited

*This statement should also appear in Item 10 of Document Control
Data - DD Form 1473. Copies of form available from cognizant
contract administrator.

93-02829

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION AVAILABILITY OF REPORT		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report #19			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Physics Department University of Puerto Rico		6b. OFFICE SYMBOL (If applicable)		7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State, and ZIP Code) Río Piedras Puerto Rico 00931-3343			7b. ADDRESS (City, State, and ZIP Code)		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Chemistry Office of Naval Research		8b. OFFICE SYMBOL (If applicable) Code 472		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER RCT Project 4133002---05	
8c. ADDRESS (City, State, and ZIP Code) Arlington Virginia 22217-5000			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO	PROJECT NO	TASK NO
			WORK UNIT ACCESSION NO		
11. TITLE (Include Security Classification) Application of the Mean Spherical Approximation to describe the Entropy of Solvation of Spherical Ions in Polar Solvents					
12. PERSONAL AUTHOR(S) W.R. Fawcett and L. Blum					
13a. TYPE OF REPORT Paper		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) 1-15-93	
15. PAGE COUNT 5					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
The entropy of solvation of monoatomic ions in polar solvents is considered within the context of the mean spherical approximation which is used to estimate the experimentally observed quantities in 15 different polar solvents. The role of ion-dipole interactions in determining both the Gibbs energy and entropy of solvation is assessed. It is shown that the temperature variation of the polarization parameter, which characterizes short-range electrostatic interactions, plays an important role in determining the magnitude of the entropy. Not only does this temperature coefficient depend on whether the ion is a cation or an anion, but also on the charge on the ion. The model developed here, together with the parameters extracted from experimental data for monoatomic ions, is applied to estimate the entropic change associated with a simple spherical redox system, namely, ferrocenium cation-ferrocene, which has been used as a model reaction for considering solvent effects on thermodynamic parameters.					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Robert Nowak			22b. TELEPHONE (Include Area Code) (203) 696-4410		22c. OFFICE SYMBOL ONR 472

Application of the Mean Spherical Approximation to Describe the Entropy of Solvation of Spherical Ions in Polar Solvents

W. Ronald Fawcett
 Department of Chemistry
 University of California
 Davis, CA 95616
 and
 Lesser Blum
 Department of Physics
 P.O. Box 23343
 University of Puerto Rico
 Rio Piedras, PR 00931-3343

Accession For	
NTIS	CRA&I ☒
DTIC	TAB ☒
Unannounced ☐	
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

DTIC QUALITY INSPECTED 3

Abstract

The entropy of solvation of monoatomic ions in polar solvents is considered within the context of the mean spherical approximation which is used to estimate the experimentally observed quantities in 15 different polar solvents. The role of both ion-dipole and dipole-dipole interactions in determining both the Gibbs energy and entropy of solvation is assessed. It is shown that the temperature variation of the polarization parameter, which characterizes short range electrostatic interactions, plays an important role in determining the magnitude of the entropy. Not only does this temperature coefficient depend on whether the ion is a cation or an anion, but it also depends on the charge on the ion. The model developed here together with the parameters extracted from experimental data for monoatomic ions is applied to estimate the entropic change associated with a simple spherical redox system, namely, ferrocenium cation/ferrocene, which has been used as a model reaction for considering solvent effects on thermodynamic parameters.

Introduction

In a recent paper¹, we considered the variation in Gibbs solvation energy of monovalent monoatomic ions with the nature of the solvent using a non-primitive model of the electrolyte solution in the mean spherical approximation (MSA).²⁻⁵ In the limit of infinite dilution, the MSA requires only two parameters to describe the Gibbs solvation energy, namely, the dielectric constant of the pure solvent, ϵ_s , and a polarization parameter, λ . The latter quantity is usually calculated from the Wertheim equation⁶ which is derived from a model of the pure solvent in which the molecular dipole moment is the only electrical property considered. In our comparison of the experimental data with theoretical predictions, we showed that it is necessary to consider other molecular parameters, such as higher order moments and the solvent molecule's polarizability. Stated more chemically, the "stickiness" of ion-dipole interactions is quite important in determining the magnitude of the solvation free energy. When one assumes the MSA result for the Gibbs energy for ion-dipole interactions and calculates the value of the polarization parameter, λ , one finds that the experimental value is rather different from that predicted by the Wertheim equation. Furthermore, values for anions are quite different from those estimated for cations. This result is not surprising since the mechanism of solvation for the two types of ions is generally recognized to be different. Another important result of the earlier study was that the ratio of the parameter, λ , to the effective solvent diameter, σ_s for cations is linearly related to an empirical parameter describing the solvent's basicity, namely, the donor number. At the same time, the corresponding ratio for anions is linearly related to an empirical parameter describing the solvent's acidity, namely, the Dimroth-Reichardt parameter, E_T .

In order to describe the thermodynamics of ion solvation further, one should be able to estimate the entropy of solvation. Such a calculation requires knowledge of the temperature derivatives of both the dielectric constant of the solvent and the polarization parameter, λ . According to the Wertheim equation, these quantities are related, but on the basis of our previous results, there is good reason to anticipate that the experimentally relevant value of $d\lambda / dT$ is quite different.

In the present paper, the available experimental data for the entropy of solvation of monoatomic monovalent ions in polar solvents are examined within the context of the MSA. Values of the temperature coefficient $d\lambda / dT$ are extracted and the ability of the model to account for variation in entropy with ionic size is considered. The significance of the results is then considered with respect to other available experimental data related to ionic solvation.

The Model

In the MSA for a system of spherical hard ions and dipoles of different sizes, the following expression is derived^{4,5} for the ion-dipole contribution to the Gibbs energy of solvation in the limit of infinite dilution:

$$G_{id} = - \frac{N_0 (z_i e_0)^2}{8\pi \epsilon_0 r_i} \left(1 - \frac{1}{\epsilon_s} \right) \frac{1}{(1 + \xi_i)} \quad (1)$$

Here, z_i is the value of the ion, e_0 , 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_0 , the Avogadro constant. The dimensionless parameter, ξ_i , which depends on the solvent and the ion, is given by

$$\xi_i = r_s / (\lambda r_i) \quad (2)$$

where r_s is the radius of the solvent dipole and λ , the MSA polarization parameter. The latter parameter is often calculated from the dielectric constant ϵ_s by the Wertheim relationship

$$\lambda^2 (\lambda + 1)^4 = 16 \epsilon_s \quad (3)$$

A second contribution to the Gibbs solvation energy comes from the repulsive dipole-dipole interactions, and is given by the equation

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

This expression may be simplified considerably when one considers the range of values typically found for the parameter, λ . For solvents with dielectric constants varying between 1 and 200, λ varies between 1 and 3.2 according to the Wertheim equation. A more realistic range for λ when one considers the values needed to fit experimental data for Gibbs solvation energies¹ is between 1 and 9. The corresponding change in the ratio $R = \lambda(\lambda + 3) / 2(\lambda + 1)^2$ which appears in the denominator of term in square brackets in eq. (4) is from 0.50 to 0.54. Not only is the change in R small, but R is small with respect to the static dielectric constant for polar solvents ($\epsilon_s > 20$) and therefore may be neglected. In a similar way, the ratio appearing in the numerator of the term in

square brackets, namely, $(3\lambda+2)/(\lambda+1)$ varies between 2.5 and 29 in the same range. Using the average value, 2.7, the expression for G_{dd} may be rewritten as

$$G_{dd} = \frac{(z_i e_0)^2}{64\pi \epsilon_0 r_i} \left(1 - \frac{1}{\epsilon_s}\right)^2 \frac{(4+2.7 \xi_i)}{(1+\xi_i)^2} \quad (5)$$

It is easily shown that estimates of G_{dd} based on eq. (5) differ from those based on eq. (4) by only a few percent in the worst cases. Moreover, the simplified expression has the advantage that the parameter λ does not appear on its own but only in the ratio ξ_i . This fact is important in applying the expression to experimental data. Finally, on the basis of previous work⁵, only a fraction θ of the dipole-dipole term is used in estimating the standard Gibbs energy of solvation so that the final expression for the Gibbs energy of solvation becomes

$$\Delta G_s^0 = G_{id} + \theta G_{dd} \quad (6)$$

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

$$S_{id} = \frac{N_0 (z_i e_0)^2}{8\pi \epsilon_0 r_i} \left[\frac{1}{\epsilon_s^2} \frac{d\epsilon_s}{dT} - \frac{1}{(1+\xi_i)} - \frac{1}{(1+\xi_i)^2} \left(1 - \frac{1}{\epsilon_s}\right) \frac{1}{r_i} \frac{d\delta_s}{dT} \right] \quad (7)$$

where $\delta_s = r_s / \lambda$ depends only on the solvent and $d\delta_s / dT$ is its temperature derivative.

Comparing eqs. (1) and (7), it is easily shown that

$$S_{id} \left(1 - \frac{1}{\epsilon_s}\right) = - \frac{G_{id}}{\epsilon_s^2} \frac{d\epsilon_s}{dT} - \frac{8\pi \epsilon_0 G_{id}^2}{N_0 (z_i e_0)^2} \frac{d\delta_s}{dT} \quad (8)$$

It follows that the ion-dipole contribution to the entropy is related to the corresponding Gibbs energy through parameters which depend only on the nature of the solvent. Rewriting the expression for the dipole-dipole contribution to the Gibbs solvation energy as

$$G_{dd} = \frac{\pi \epsilon_0 r_i}{(z_i e_0)^2 N_0} G_{id}^2 (4 + 2.7 \xi_i) \quad (9)$$

the expression for the corresponding entropy is

$$S_{dd} = - \frac{\pi \epsilon_0 r_i}{(z_i^2 e_0) N_0} G_{id} S_{id} (4 + 2.7 \xi_i) + \frac{2.7 \pi \epsilon_0 r_i}{(z_i^2 \epsilon_0) N_0} G_{id}^2 \frac{d\delta_s}{dT} \quad (10)$$

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

$$\Delta S_s^0 = S_{id} + \theta S_{dd} \quad (11)$$

This model for ion solvation is now examined with respect to available experimental data for monovalent monoatomic systems in the polar solvents.

Results and Discussion

Extensive data are available for the Gibbs energy and enthalpy of transfer of monoatomic monovalent ions in water and other polar solvents, a recent compilation having been given by Marcus et al.⁷ These data may then be combined with data for the Gibbs energy and enthalpy of solvation of the same ions in the reference solvent water⁸ to obtain an estimate of the standard entropy of solvation, ΔS_s° . Thus,

$$T\Delta S_s^\circ = \Delta H_{tr}^\circ + \Delta H_{aq}^\circ - (\Delta G_{tr}^\circ + \Delta G_{aq}^\circ) \quad (12)$$

where ΔG_{tr}° and ΔH_{tr}° are Gibbs energy and enthalpy of transfer of a given ion, and ΔG_{aq}° and ΔH_{aq}° , the corresponding solvation quantities in water. It is important to remember that the data are for single ions, and therefore involve an extrathermodynamic assumption. The assumption used, known as the TATB assumption⁷⁻⁹, is that the thermodynamics parameters for solvation of two large ions, namely, the tetraphenyl arsonium cation and tetraphenylborate anion, are equal.

The estimation of the entropy of solvation involves one extra parameter with respect to those needed to estimate the corresponding Gibbs energy. In the latter case, the parameters are r_i , ϵ_s , λ and r_s . In our previous analysis of the Gibbs energy data, the parameter λ was not determined from the dielectric constant of the solvent using eq. (3) but instead, the ratio $\delta_s = r_s / \lambda$ was estimated directly from the experimental data using eq. (1) and assuming a negligible contribution from dipole-dipole interactions ($\theta = 0$ in eq. (6)). In the present paper we wish to illustrate the extent to which values of δ_s depend on the manner in which this parameter is estimated. At first, we consider only the static dielectric constant data for a collection of polar solvents together with gas phase solubility data from which effective radii for solvent molecules have been extracted. These data are summarized in Table I for 20 polar solvents both protic and aprotic. It is readily apparent that the parameter λ estimated on the basis of the Wertheim equation does not vary greatly, specifically, from 2.01 for acetone to 3.15 for N-methyl formamide on the basis of the solvents considered. The estimates of δ_s vary over a wider range, from 52 pm for water to 124 pm for n-propanol. This result is obviously due to the changes in solvent size. As will be seen

below, the values of δ_s estimated in this fashion result in poor estimates of the Gibbs solvation energy. In particular, the estimate of G_{id} on the basis of eq. (1) using the values of δ_s from Table I yield equal values of this quantity for cations and anions of the same radius. On the other hand, it is well known from experiment that this is not the case. Thus, the value of ΔG_s^0 for fluoride ion is much larger in magnitude than that of potassium ion in spite of the fact that their Pauling radii are approximately equal.^{8,9}

The temperature derivative of the parameter λ may be estimated from the temperature dependence of the dielectric constant. On the basis of the Wertheim equation the relationship between these quantities is

$$\frac{d\lambda}{dT} = \left[\frac{\lambda(1+\lambda)}{3\lambda+1} \right] \frac{1}{2\epsilon_s} \frac{d\epsilon_s}{dT} \quad (13)$$

The corresponding value of $d\delta_s / dT$ is given by

$$\frac{d\delta_s}{dT} = r_s \left(\frac{d\lambda}{dT} \right)^{-1} \quad (14)$$

Values of the latter parameter calculated on the basis of experimental data for the dielectric properties of pure solvents are also presented in Table I. This parameter also changes considerably from a low of 0.048 pm K⁻¹ for water to a high of 0.187 pm K⁻¹ for n-propanol.

The experimental data for the Gibbs energy and entropy of solvation of the alkali metal cations and halide anions were examined with and without consideration of the contribution from dipole-dipole interactions. As discussed previously¹, a good fit to the Gibbs energy data can be made assuming that ΔG_s^0 is equal to G_{id} . Then, the parameter $d\delta_s / dT$ can be determined from the experimental data using a rearranged form of eq. (8). Since the experimental entropy of solvation ΔS_s^0 is equal to S_{id} when $\theta = 0$, it follows that

$$\Delta S_s^0 \left(1 - \frac{1}{\epsilon_s} \right) + \frac{\Delta G_s^0}{\epsilon_s^2} \frac{d\epsilon_s}{dT} = - \frac{8\pi \epsilon_0}{N_0 (z_i e_0)^2} (\Delta G_s^0)^2 \frac{d\delta_s}{dT} \quad (15)$$

The quantity on the left hand side of this equation may be calculated directly from experimental data and is identified as the local contribution to the entropy of solvation $\Delta S_s^0(\text{loc})$ as discussed below.

Since it is a linear function of $(\Delta G_s^0)^2$, the parameter $d\delta_s/dT$ can be found on the basis of a one parameter linear fit. Two such plots are shown in Fig. 1 using data for the alkali metal cations in water and acetonitrile. In the case of the data for water, an excellent linear plot is found with a zero intercept. However, in the case of acetonitrile, the fit is not that good, and yields an estimate of $d\delta_s/dT$ with a standard deviation of 12 percent. When one considers that dipole-dipole interactions were neglected and that the experimental data involve an extrathermodynamic assumption, the fit of the data to eq. (15) is certainly not bad. With the exception of water, the level of error in the estimates of $d\delta_s/dT$ reported below is similar to that found for acetonitrile.

A summary of the MSA parameters found for 15 polar solvents for which ionic solvation data are available is presented in Table II. Although these parameters fall in the range of values predicted by the Wertheim equation, they are clearly quite different. The most important feature of the present analysis is that parameters for cations are different from those for anions. Such a result is not unexpected since a detailed molecular description of the interaction of a solvent molecule with a cation is different from that for an anion. For aprotic solvents this is mainly a result of the fact that the negative end of the solvent dipole is chemically soft with a complex polarizable electron cloud which interacts with cations. On the other hand, the positive end of the molecular dipole is hard in the usual chemical sense, and interacts with anions chiefly because it is the part of the molecule which is furthest away from the electronegative group. When one compares the parameters obtained from the analysis of the data for ionic solvation with those from the permittivity data for the solvents it is clear that there is no correlation between them, whether one chooses the data for cations or for anions.

The above analysis of the experimental data can be criticized on the grounds that it does not consider the role of dipole-dipole interactions. This question was considered by improving the fit of the experimental data for aqueous systems to eq. (6). In this way, it was found that the best value of θ is 0.16. However, the improvement of the fit between theory and experiment was not great when data for all solvents were considered. When dipole-dipole interactions are ignored the average standard deviation in fitting the Gibbs energy data for the alkali metal cations in 17

different solvents is 7.6 kJ mol^{-1} and that for the halide anions 8.3 kJ mol^{-1} . This amounts to an error of about 3 percent. When the term involving dipole-dipole interactions is included with θ set equal to 0.16 the standard deviation for the cationic data is 5.8 kJ mol^{-1} , and for the anions 8.6 kJ mol^{-1} . Thus, inclusion of the term in G_{dd} is not warranted on the basis of the available data. Further improvement with consideration of G_{dd} would require that the fraction θ be chosen for each solvent, thereby introducing another solvent dependent adjustable parameter. This is not justified without further analysis of the TATB assumption used to derive the results considered in the present analysis. Nevertheless, it is interesting to note that the values of δ_s derived with the assumption that $\theta = 0.16$ are linearly related to those obtained on the basis of eq. (1) (see Fig. 2). In the case of cations, the value of δ_s is lower by about 12 pm, and for anions, by about 17 pm. Thus, the correlations between $1/\delta_s$ and the donor number (DN)¹⁶ for cations, and between $1/\delta_s$ and the Reichardt acidity parameter (E_T)¹⁷ for anions, which were observed previously¹ would not be affected by the inclusion of a contribution from dipole-dipole interactions.

The success of the present analysis in describing the variation of the standard entropy of solvation with solvent nature is illustrated for the K^+ cation in Figure 3. In general, the agreement between calculated and experimental values is not bad, the calculated values tending to fall below the experimental ones for solvents in which $-\Delta S_s^0$ is large. Similar results were obtained with data for the Rb^+ and Cs^+ ions. In the case of the Na^+ ion, the estimated value of $-\Delta S_s^0$ was usually higher than the experimental value. In the case of Li^+ ion, the difference between the experimental and calculated values of $-\Delta S_s^0$ was unacceptably large. Looking at the problem from another point of view, the value of $d\delta_s/dT$ estimated from entropy of solvation data for Li^+ ion was always considerably smaller than the average value for the five alkali metal cations, and the value for Na^+ ion somewhat smaller. On the other hand, values for K^+ , Rb^+ and Cs^+ were sufficiently close that one could describe their entropic data on the basis of an average for these ions only. The failure of the MSA model to describe data for all five ions can be a result of the fact that the model as presently applied neglects dipole-dipole interactions, or that the TATB assumption does not give a good separation of the thermodynamic data for electrolytes into values for single ions. We suspect

that the latter factor is more important because of the fact that eq. (15) could be applied reasonably well to entropy data for aqueous solutions which were obtained without the TATB assumption⁸; on the other hand, results indicating a poor fit for Li^+ and Na^+ ions were obtained in other polar solvents where the TATB assumption was used to obtain single ion data⁷⁻⁹ (see Fig. 1).

Results for the Br^- anion are shown in Fig. 4. In this case, one also finds that the estimated solvation entropies lies below the experimental values. The agreement between theory and experiment for the halide anions is somewhat better than that for the alkali metal cations. This may just be a reflection of the fact that data are generally only available for three ions, but no trend indicating that a better fit could be obtained for any one of the ions was apparent. In assessing the results for both the alkali metal and halide ions one should keep in mind the fact that the estimated error level in the entropy of solvation is usually much higher than that in either the Gibbs energy or enthalpy of solvation. As pointed out by Hefter¹⁸, the latter two quantities are often quite close to one another. Since the estimate of ΔS_s^0 is based on the difference between ΔG_s^0 and ΔH_s^0 , the relative error in the entropy can be much higher than those in the Gibbs energy and enthalpy.

On the basis of eq. (7), it is clear that the entropy of solvation can be attributed to two components, one connected with the temperature variation of the long range electrostatic interactions as expressed through the temperature coefficient of the dielectric constant, and a second due to the temperature variation of short range electrostatic interactions described by the temperature variation of the MSA parameter δ_s . Thus, the long range contribution to the entropy is given by

$$\Delta S_s^0(\text{lr}) = - \frac{\Delta G_s^0}{\epsilon_s^2} \left(1 - \frac{1}{\epsilon_s}\right)^{-1} \frac{d\epsilon_s}{dT} \quad (16)$$

and the local contribution by

$$\Delta S_s^0(\text{loc}) = - \frac{8\pi \epsilon_0}{N_o(z_i e_0)^2} (\Delta G_s^0)^2 \left(1 - \frac{1}{\epsilon_s}\right)^{-1} \frac{d\delta_s}{dT} \quad (17)$$

The latter quantity may be related to the energy associated with the formation of a hole for the solute within the solvent. One measure of this is the Hildebrand solubility parameter δ ^{9,19} which is given by

$$\delta = \left(\frac{\Delta \tilde{H}_v - R}{\tilde{V}} \right)^{1/2} \quad (18)$$

where $\Delta \tilde{H}_v$ is the molar enthalpy of vaporization of the solvent at 25 °C, $\tilde{V}$, its molar volume, and R , the gas constant. This quantity measures the cohesive energy density of the solvent, and has been used extensively to explain the solubility of non-electrolytes.¹⁹ From Fig. 5, it is clear that a reasonable correlation is obtained between the local contribution to the entropy of solvation and the solubility parameter δ , on the basis of the data for K^+ ion. However, it must be pointed out that the properties of the correlation are determined to a large extent by the data for formamide and water. No correlation would be found if one considered the aprotic solvents only. Thus, the entropy associated with hole formation for the solute is only one of the factors determining the magnitude of the contribution to the entropy from local electrostatic interactions.

It is interesting to examine the applicability of the present model to predict the entropy of solvation of divalent monoatomic ions. In our previous examination of the application of eq. (1) to data for the Gibbs energy of solvation of monoatomic cations¹, it was shown that excellent agreement between theory and experiment is found for the alkaline earth metal cations in water when the parameter ξ_i is estimated using the Pauling radius for the cation and the MSA parameter δ_s calculated from data for the alkali metal cations. However, the same value of δ_s gave low estimates of the Gibbs energy of solvation of divalent ions such as Zn^{2+} , Cd^{2+} and Pb^{2+} whose bonding to the water molecules in immediate contact with the cation involves d electrons. Thus, the value of the parameter δ_s required to achieve agreement between theory and experiment for these ions is smaller than that recorded in Table II. The experimental data for the entropy of solvation of these cations is shown as a function of their Pauling radii in Fig. 6. The solid curves show the MSA estimates based on the experimental values of the Gibbs energy of solvation of the same ions using the best value of $d\delta_s/dT$ given in Table II. Thus, according to eq. (15),

$$\Delta S_s^0(\text{MSA}) = - \frac{\Delta G^0}{\epsilon^2} \frac{d\epsilon_s}{dT} \left(1 - \frac{1}{\epsilon_s}\right)^{-1} - \frac{8\pi\epsilon_0(\Delta G^0)^2}{N_0(z_i e_0)^2} \left(1 - \frac{1}{\epsilon_s}\right)^{-1} \frac{d\delta_s}{dT} \quad (19)$$

It is apparent that a good fit of the data for the alkali metal cations to the MSA model is obtained. However, in the case of the divalent ions, the same value of $d\delta_s/dT$ leads to unreasonably high estimates of ΔS_s^0 . However, if one assumes $d\delta_s/dT$ is 0.019 pm K^{-1} , a value close to one half that used to fit the data for monovalent ions, a reasonable fit between theory and experiment is obtained. It is especially interesting that the data for both groups of cations considered seem to follow one curve, no distinction being apparent between those cations which have d electrons involved in local electrostatic interactions, and those which do not. These results demonstrate clearly that the estimates of ΔS_s^0 from the MSA model are very sensitive to the value chosen for the parameter $d\delta_s/dT$. This aspect of the MSA description needs to be examined in more detail in future work.

The present model can be used to assess results for the entropy change associated with simple redox reactions such as



which involve only one electron and no formation or breaking of bonds. The standard entropy change ΔS_R^0 associated with such an equilibrium can be estimated from the temperature dependence of its standard potential measured in a non-isothermal cell in which the temperature of the reference electrode is held constant.²⁰ Data have been collected^{20,21} for a number of inorganic redox couples in both aqueous and non-aqueous solvents and for systems involving ions of varying charges. These data also incorporate an extrathermodynamic assumption associated with the temperature dependence of the potential drop in the liquid junction between the main cell compartment whose temperature is varied, and the reference electrode compartment whose temperature is held constant. On the basis of eq. (7), the MSA expression for the standard entropy for reaction (20) is

$$\Delta S_R^0 = \frac{N_0 e_0^2 \Delta z_R^2}{8\pi\epsilon_0 r_R} \left[\frac{1}{\epsilon_s^2} \frac{d\epsilon_s}{dT} \frac{1}{(1+\xi_R)} - \frac{1}{(1+\xi_R)^2} \left(1 - \frac{1}{\epsilon_s}\right) \frac{1}{r_R} \frac{d\delta_s}{dT} \right] \quad (21)$$

where $\xi_r = \delta_s / r_R$ (22)

and $\Delta z_r^2 = z_b^2 - z_a^2$ (23)

In writing this expression, it is assumed that both reactant A and product B whose charges are z_A and z_B , respectively can be represented by spheres of equal radius r_R . The corresponding expression for the standard potential for reaction (20) estimated from the standard Gibbs energy change is

$$\mathcal{E}^0 = \frac{N_0 e_0^2 \Delta z_R^2}{8 \pi \epsilon_0 F r_R} \left(1 - \frac{1}{\epsilon_s} \right) \frac{1}{(1 + \xi_R)} \quad (24)$$

The simplest system to which the present theory can be applied is the ferrocenium cation/ferrocene reaction couple which has been suggested as a reference system for obtaining a solvent independent potential scale.^{9,22,23} This organometallic system is reasonably large and spherical with an effective radius of 0.37 nm.²⁴ However, on the basis of the MSA model (eq. (24)), the estimate of the standard potential is not independent of the nature of the solvent within the experimental precision that these quantities are usually measured (± 1 mV). In fact, the estimated change in $\mathcal{E}^0$ with respect to its value in water varies from a negative value of -25 mV in N-methylformamide to a positive value of 62 mV in nitromethane (see Table III). Choosing a reference system with a larger size does not completely eliminate the differences between $\mathcal{E}^0$ in the solvents considered. For instance, if the reacting species has an effective radius of 1 nm, the predicted values of $\mathcal{E}^0$ fall in a range from -9 mV to +23 mV with respect to the value in water. Thus, on the basis of the MSA model, the ferrocenium/ferrocene system or any similar redox couple with a larger radius does not provide an acceptable reference for a solvent independent potential scale.

Values of the standard entropy change for this reaction couple according to the Born and MSA models and from experiment are also summarized in Table III. In the case of the aprotic solvents, the MSA estimates of ΔS_R^0 are considerably better than those from the Born model and

usually within 20 percent of the experimental estimate. Considering the sensitivity of the MSA model to the assumed value of $d\delta_g/dT$, the present MSA estimates are quite good. One should also take into consideration the fact that the experimental data also contain a contribution to the entropy from ion-ion interactions, especially those resulting in ion pair formation. This contribution is expected to be very important in solvents like nitromethane where ion pairing is very strong because of the weak solvation of cations. Ion pairing was not considered in the previous analyses of solvent effects on redox reaction entropies^{20,21} which were largely based on the Born model. In fact, most of the redox couples for which values of ΔS_R^0 have been reported in non-aqueous solvents involve ions with charges greater than unity. Ion pairing is expected to play an important role in all non-aqueous solvents except the protic amides which have dielectric constants greater than that of water. In the case of the protic solvents, the MSA estimate of ΔS_R^0 is clearly too large. This may be a result of the way in which the molecule ferrocene interacts with hydrogen bonding solvents. Certainly, the estimate of the entropy based on eq. (21) considers only the effect of the charged species in the reaction couple on the net entropy change. Ferrocene has a multipole character and thus can result in local structure in protic solvents resulting in a net lowering in the net entropy change ΔS_R^0 . In the case of the simpler solvents, the Born model considered earlier^{20,21} and the MSA model used here without consideration of ion-ion interactions cannot be expected to give a realistic estimate of ΔS_R^0 for these systems. Thus, one needs in general to consider at least three contributions to the entropy change associated with simple redox couples. The first is that due to long range electrostatic interactions which can be estimated by the Born model. The second is due to short range electrostatic interactions especially those which are between ions and dipoles, and is dealt with by the MSA model presented in this paper. The third contribution is that from short range ion-ion interactions which also can be treated by the MSA when this theory is applied to systems of finite ionic strength.²⁵ Finally, in a complete description of the entropy one needs to assess the role of dipole-dipole interactions which are important near solvated charged reactants.

In summary, the present analysis has shown that a significant improvement in the estimate of the entropy of solvation of monovalent ions may be made on the basis of the MSA model presented here. This requires the introduction of one additional parameter with respect to those used to estimate the Gibbs energy, namely, the temperature derivative of the MSA parameter λ (or δ_s). The resulting estimates of the solvation entropy are extremely sensitive to the value chosen for $d\delta_s/dT$ and there is some question whether a unique value can be used to calculate ΔS_R^0 for a series of ions such as the alkali metal halides. The role of dipole-dipole interactions needs to be considered further. However, before these outstanding problems can be resolved, further attention needs to be devoted to improving the extra-thermodynamic assumptions used to separate cationic and anion contributions to experimentally measured thermodynamic parameters. This subject will be considered in detail in a future paper.

Acknowledgement

This work was supported by the Office of Naval Research and the National Science Foundation through grant CHE 90-08171.

References

1. Blum, L.; Fawcett, W.R. *J. Phys. Chem.*, in press.
2. Blum, L. *Chem. Phys. Lett.* 1974, 26, 200; *J. Chem. Phys.* 1974, 61, 2129.
3. Adelman, S.A.; Deutch, J.M. *J. Chem. Phys.* 1974, 60, 3935.
4. Garisto, F.; Kusalik, P.G.; Patey, G.N. *J. Chem. Phys.* 1983, 79, 6294.
5. Wei, D.; Blum, L. *J. Chem. Phys.* 1987, 87, 2999.
6. Wertheim, M.S. *J. Chem. Phys.* 1971, 55, 4291.
7. Marcus, Y.; Kamlet, M.J.; Taft, R.W. *J. Phys. Chem.* 1988, 92, 3613.
8. Conway, B.E. *J. Solution Chem.* 1978, 7, 721.
9. Marcus, Y. *Ion Solvation*. Wiley-Interscience, New York, (1985).
10. Karapetyan, Yu. A.; Eychis, V.N. *Physico-chemical Properties of Non-Aqueous Electrolyte Solutions*, Khimia, Moscow (1989) in Russian.
11. Mansingh, K.; Mansingh, A. *J. Chem. Phys.* 1964, 41, 827.
12. Kessler, Yu. M.; Fomicheva, M.G.; Alpatova, N.M.; Emelin, V.P. *Zhur. Strukt. Khim.* 1972, 13, 517.
13. Bréant, M. *Bull Soc. Chim. France*, 1971, 725.
14. Jannelli, L.; Azzi, A.; Lopez, A.; Salello, S. *J. Chem. Eng. Data*, 1980, 25, 77.
15. Wilhelm, E.; Battino, R. *J. Chem. Phys.* 1971, 55, 4012.
16. Gutmann, V.; Schmid, R. *Coord. Chem. Rev.* 1974, 12, 263.
17. Reichardt, C. *Solvent Effects in Organic Chemistry*; Verlag Chemie: Weinheim, 1979.
18. Hefter, G.T. *Rev. Inorg. Chem.* 1989, 10, 185.
19. Hildebrand, J.H.; Scott, R.L. *The Solubility of Non-Electrolytes*, 3rd edition, Dover, New York, 1964.
20. Sahimi, S.; Weaver, M.J. *J. Electroanal. Chem.* 1981, 122, 155; *ibid*, 1981, 122, 171.
21. Hupp, J.T.; Weaver, M.J. *Inorg. Chem.* 1984, 23, 3639.
22. Koepp, H.M.; Wendt, H.; Strehlow, H. *Z. Elektrochem.* 1960, 64, 483.

23. Popovych, O. in *Treaties on Analytical Chemistry*, Kolthoff, I.M.; Elving, P.J. editors, Part I, Vol. I, 2nd edition, Wiley, New York (1978) p. 711.
24. Krishtalik, L.I.; Alpatova, N.M.; Ovsyannikova, E.V. *Electrochim. Acta*, 1991, 36, 435.
25. Blum, L.; Vericat, F.; Fawcett, W.R. *J. Chem. Phys.*, in press.

Table I. Summary of Solvent Parameters from Dielectric Constant and Molecular Size Data

Solvent	ϵ_s^a	$-d\epsilon_s/dT^a$	r_s^b	λ^c	δ_s^d	$d\delta_s/dT^e$
		K ⁻¹	nm		pm	pm K ⁻¹
water (W)	78.3	0.360	0.274	2.65	51.6	0.048
methanol (MeOH)	32.7	0.197	0.371	2.21	83.8	0.106
ethanol (EtOH)	24.6	0.147	0.436	2.09	104.6	0.133
1-propanol (PrOH)	20.3	0.142	0.498	2.00	124.4	0.187
formamide (F)	111.0	0.720	0.345	2.85	60.6	0.079
N-methylformamide (NMF)	182.4	1.620	0.452	3.15	71.9	0.127
acetone (AC)	20.7	.098	0.476	2.01	118.4	0.120
acetonitrile (AN)	37.5	.160	0.427	2.28	93.7	0.084
propionitrile (PN)	29.6	.132	0.477	2.17	110.1	0.104
butyronitrile (BuN)	22.7	.085	0.532	2.05	129.9	0.104
benzonitrile (BzN)	25.2	.091	0.574	2.10	137.0	0.105
dimethylacetamide (DMA)	37.8	.213	0.548	2.28	120.1	0.141
dimethylformamide (DMF)	36.7	.178	0.517	2.27	114.0	0.116
dimethylsulfoxide (DMSO)	46.7	.106	.491	2.39	102.9	0.048

hexamethylphosphoramide (HMPA)	30.0	.173	0.698	2.17	160.5	0.195
nitrobenzene (NB)	34.8	.180	.574	2.24	127.8	0.139
nitromethane (NM)	35.8	.161	.431	2.26	95.5	0.090
N-methylpyrrolidone (NMP)	32.2	.140	.569	2.21	128.9	0.118
propylene carbonate (PC)	66.1	.240	.536	2.56	104.6	0.078
tetramethylene sulphone (TMS)	43.7	.115	.581	2.35	123.5	0.068

^a From the compilations of Marcus⁹ and Karapetyan and Eychis¹⁰ except in the case of butyronitrile¹¹, hexamethylphosphoramide¹², N-methyl pyrrolidone¹³, and tetramethylene sulphone¹⁴.

^b From data for gas solubilities¹⁵; when these data were not available, the solvent's radius was estimated on the basis of a linear correlation between existing estimates of molecular radii¹⁵ and the cube root of the molar volume.

^c The Wertheim polarization parameter estimated using eq. (3).

^d The ratio of $\delta_s = r_s/\lambda$ obtained for the data for λ and r_s .

^e The temperature derivative of δ_s estimated from the temperature dependence of ϵ_s (eq. (13)) and the molecular radius r_s (see eq. (14)).

Table II. Values of the MSA Parameters δ_s and $d\delta_s/dT$ estimated from the Gibbs Energy and Entropy of Solvation for Monoatomic Monovalent Ions Obtained by Fitting Experimental Data to Eqs. (6) and (11) assuming $\theta = 0$.

Solvent	Cations		Anions	
	δ_s / pm	$d\delta_s/dT$ / pm K ⁻¹	δ_s / pm	$d\delta_s/dT$ / pm K ⁻¹
water	82.6	.036	20.8	.033
methanol	82.7	.075	24.4	.022
ethanol	83.9	.074	26.9	.022
1-propanol	83.0	.056	28.8	.018
formamide	79.9	.063	29.3	.066
N-methylformamide	78.7	.062		
acetonitrile	87.2	.092	41.0	.094
dimethylacetamide	74.1	.060	49.8	.094
dimethylformamide	75.8	.072	45.0	.123
dimethylsulfoxide	75.3	.083	39.1	.101
hexamethylphosphoramide	72.5	.069	52.0	.100
nitromethane	93.8	.090	39.2	.086
N-methyl pyrrolidine	71.3	.085	45.3	.088
propylene carbonate	87.5	.095	41.9	.082
tetramethylene sulphone	80.1	.076	45.4	.111

Table III. Thermodynamic Parameters for the Ferrocinium Cation/Ferrocene Redox Couple
estimated from the Born and MSA Models together with Experimental Data

Solvent	$\Delta \mathcal{E}_{\text{tr}}^{\circ} / \text{mV}^{\text{a}}$	$\Delta S_{\text{R}}^{\circ} / \text{J K}^{-1} \text{mol}^{-1}$		
	MSA	Born ^b	MSA ^c	Expt. ^d
Water	0	11.0	21.1	-21.0
Formamide	-15	11.0	30.4	0
N-methylformamide	-25	9.1	28.8	17.0
Methanol	29	34.6	52.9	13.0
Acetone	47	42.9	58.8	67.0
Acetonitrile	38	21.4	47.1	48.0
Dimethylformamide	0	24.8	45.1	56.0
Dimethylsulphoxide	-11	9.1	36.0	52.0
Nitromethane	62	23.6	47.1	59.0
Propylene carbonate	21	10.3	39.4	46.0

^a Estimated difference between $\mathcal{E}^{\circ}$ in a given solvent and that in water using eq. (24).

^b The Born estimate may be obtained from eq. (21) when ξ_{R} and $d\delta_{\text{R}}/dT$ are set equal to zero.

^c From eq. (21).

^d Results reported in Ref. 20.

Legends for Figures

- Figure 1.** Plot of the local contribution to the solvation entropy, $-\Delta S_s^0(\text{loc})$ as defined in eq. (15) against the square of the Gibbs energy of solvation using data for the alkali metal cations in water (W) and acetonitrile (AN).
- Figure 2.** Plot of the MSA parameter δ_s determined for the alkali metal cations and halide anions with consideration of both ion-dipole and dipole-dipole interactions (eq. 6 with $\theta = 0.16$) against the same quantity considering ion-dipole interactions only (eq. 6 with $\theta = 0$).
- Figure 3.** Plot of the entropy of solvation of the K^+ cation estimated in various solvents according to the MSA theory against the corresponding experimental quantity. The definitions of the abbreviations for the solvents are given in Table I.
- Figure 4.** As in Figure 3 but for the Br^- anion.
- Figure 5.** Plot of the local contribution to the solvation entropy, $-\Delta S_s^0(\text{loc})$ for the K^+ cation in various solvents as defined in eq. (15) against the Hildebrand solubility parameter δ .
- Figure 6.** Plot of the standard entropy of solvation of various monovalent and divalent cations, ΔS_s^0 against their Pauling radii, r_i . The solid curves give the estimates for the corresponding quantity on the basis of the MSA model (eq. 17) using experimental values of ΔG_s^0 and assuming $d\delta_s/dT = 0.036 \text{ pm K}^{-1}$ for the monovalent ions and 0.019 pm K^{-1} for the divalent ions. The broken curve gives the estimates for divalent ions assuming $d\delta_s/dT$ is 0.036 pm K^{-1} .











