ION SOLVATION. APPLICATION OF COMBINED DISCRETE AND CONTINUUM MODELS

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Thermodynamic functions for the solvation systems ion–solvent (ion = Li^+, Be^{2+}, Na^+, Mg^{2+}, and Al^{3+}; solvent = H_2O, CH_3CN, DMSO, and DMF) are calculated on the basis of combined continuum and discrete models. For the mixed systems water–ion–solvent, the mole fraction of solvent is included in the calculation.

The current trend in the theory of solvation phenomena is towards establishing a link between the concepts of a solvent as a structured medium and as a continuum. The former extreme is represented by the model of a supermolecule while the latter by, for example, the Born model[1]. In the present work, we have attempted to apply a modified Hoijtink's method[2] of obtaining the energy of solvation by a quantum chemical calculation based on the supermolecule model.

THEORETICAL

Thermodynamic quantities for a system ion–solvent can be determined by using either a continuum or a discrete solvent model. In the first case, we treat the solvent as a homogeneous isotropic medium outside a sphere of ion radius. According to this model, the energy required to bring an ionic charge in a continuous manner from infinity to the surface of the sphere is the free enthalpy of ion solvation. In the other approach, known as the microscopic model, solvent molecules are regarded as particles of defined size and charge distribution, coordinatively disposed around an ion so as to form a geometrical configuration. The energy of solvation or hydration is then given as the sum of the coulombic, induction, dispersion and repulsion energies.

Combination of the two approaches, as made for example by Hoijtink[2], yields the following relation for the Gibbs energy of solvation

$$\Delta G = -\left(\sum_{\mu} \frac{Q_\mu^2}{2r_\mu} + \sum_{\mu<\nu}\sum \frac{Q_\mu Q_\nu}{r_{\mu\nu}}\right)\left(1 - \frac{1}{\varepsilon_r}\right), \qquad (1)$$

where Q_μ is the charge on atom μ, r_μ is the effective (van der Waals') atomic radius, $r_{\mu\nu}$ is the separation between atoms μ and ν, and ε_r is the effective permittivity of solvent. Using the Gibbs–Helmholtz equation, we obtain for ΔH

$$\Delta H = -\left(\sum_\mu \frac{Q_\mu^2}{2r_\mu} + \sum_{\mu<\nu}\sum \frac{Q_\mu Q_\nu}{r_{\mu\nu}}\right)\left[1 - \frac{1}{\varepsilon_r} - \frac{T}{\varepsilon_r^2}\left(\frac{\partial \varepsilon_r}{\partial T}\right)_p\right]. \tag{2}$$

The differential quotient $(\partial\varepsilon_r/\partial T)_p$ can be obtained either from the literature or from the temperature dependence of dielectric constant[3].

A similar relation can be derived for the change of entropy. Recalling, however, the well-known relations $\Delta G = \Delta H - T\Delta S$ and $\Delta G = -RT\ln K$, it is apparent that a full thermodynamic description of a chemical system can be obtained from merely the knowledge of the Gibbs energy and enthalpy changes and temperature. For this reason, the entropic contribution has been omitted from further treatment.

The quantities Q_μ and Q_ν can be obtained by a quantum-chemical calculation based on Mulliken's population analysis[4]. If we know the Mulliken electronic charge Z on an atom of nucleus charge A, we obtain the total charge on the atom from the relation

$$Q_\mu = A_\mu - Z_\mu\,. \tag{3}$$

TABLE I

Thermodynamic functions for the complexes ion–solvent calculated from Eqs (*1*) and (*2*). Column *a* gives energies of solvation in kJ/mol, and column *b* the enthalpies of solvation in kJ/mol. Values in parentheses are experimental[10]

	Water		Acetonitrile		Dimethyl sulphoxide		Dimethylformamide	
Ion	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
Li^+	−543 (−511)	−552 (−523)	−314	−328	−126	−130	−364	−379 (−541)
Be^{2+}	−5 196 (−2 442)	−5 287	−4 360	−4 506	−2 962	−3 054	−3 435	−3 573
Na^+	−465 (−411)	−474 (−418)	−480	−497	−243	−251 (−446)	−444	−462 (−451)
Mg^{2+}	−3 118 (−1 906)	−3 173 (−1 828)	−2 917	−3 017	−2 618	−2 700	−2 643	−2 751
Al^{3+}	−9 622 (−4 616)	−9 792	−8 359	−8 646	−6 822	−7 036	−7 622	−7 930

The above expressions were used to calculate the thermodynamic functions for 1 : 1 complexes. The computation was performed using a modified POPMIN sub-routine of the *ab initio* GAUSSIAN 70 program[5]. The same routine was employed to execute *ab initio* quantum-chemical calculations for the systems ion–solvent. Interactions of Li^+, Be^{2+}, Na^+, Mg^{2+}, and Al^{3+} with water, acetonitrile, dimethylformamide, and dimethyl sulphoxide were investigated. The geometries of solvent molecules were used as published in the literature[6], and were kept fixed during optimization of the geometries of the complexes. The calculation was performed using the non-empirical *ab initio* SCF method with minimal STO-3G base of wave functions. The results obtained are given in Table I. It is seen that the method greatly overestimates energy values for systems with cations in higher oxidation states (Be^{2+}, Al^{3+}). For the other cations, the results are within the accuracy of quantum-chemical calculations.

For the purpose of calculations relating to systems involving mixed solvents, an attempt was made to describe quantitatively the influence of the relative proportion of mixed solvent components. Interactions of the above ions with the mixtures acetonitrile–water, dimethyl sulphoxide–water and dimethylformamide–water were investigated over the whole range of the mole fractions. This was done by introducing

TABLE II

Thermodynamic functions of the complexes acetonitrile–ion–water calculated from Eqs (*6*) and (*7*). The first row for each mole fraction gives Gibbs energies of solvation in kJ/mol and the second row, the enthalpies of solvation in kJ/mol

Mole fraction		Ion				
CH_3CN	H_2O	Li^+	Be^{2+}	Na^+	Mg^{2+}	Al^{3+}
0	1·0	−412	−3 621	−476	−2 904	−7 305
		−467	−3 772	−512	−3 164	−7 551
0·2	0·8	−392	−3 544	−451	−2 847	−7 243
		−438	−3 731	−486	−3 084	−7 494
0·4	0·6	−353	−3 465	−424	−2 796	−7 186
		−402	−3 654	−459	−2 994	−7 448
0·6	0·4	−303	−3 396	−407	−2 741	−7 112
		−354	−3 589	−436	−2 915	−7 395
0·8	0·2	−267	−3 312	−384	−2 690	−7 063
		−314	−3 503	−418	−2 810	−7 313
1·0	0	−219	−3 246	−365	−2 615	−6 950
		−271	−3 423	−394	−2 764	−7 212

an expression whereby the dielectric constant of each solvent entered the calculation in proportion to its mole fraction in the mixture. Thus, ε_r was replaced by

$$z = x_1(\varepsilon_r)_1 + x_2(\varepsilon_r)_2 \tag{4}$$

and the differential quotient by

$$z' = x_1 \left(\frac{\partial \varepsilon_r}{\partial T}\right)_1 + x_2 \left(\frac{\partial \varepsilon_r}{\partial T}\right)_2 , \tag{5}$$

where x_1 and x_2 are the mole fractions of the mixed solvent components, $(\varepsilon_r)_1$ and $(\varepsilon_r)_2$ are their dielectric constants, and $(\partial \varepsilon_r/\partial T)_1$ and $(\partial \varepsilon_r/\partial T)_2$ the respective differential quotients.

However, these modifications did not result in any significant improvement. Compared with the preceding calculations, they introduced a dependence on the mole fractions of solvents, but failed to give a reasonable approximation at the ends of the composition range. This was because the quantum-chemical calculation had been made for a system uncorrected for the molar ratio of the two solvents involved.

TABLE III

Thermodynamic functions of the complexes dimethyl sulphoxide–ion–water calculated from Eqs (*6*) and (*7*). The first row for each mole fraction gives Gibbs energies of solvation in kJ/mol and the second row, the enthalpies of solvation in kJ/mol

Mole fraction		Ion[a]			
DMSO	H_2O	Li^+	Na^+	Mg^{2+}	Al^{3+}
0	1·0	−424	−482	−2 416	−6 342
		−452	−501	−2 512	−6 512
0·2	0·8	−397	−464	−2 260	−6 261
		−428	−485	−2 326	−6 427
0·4	0·6	−372	−438	−2 110	−6 165
		−402	−467	−2 247	−6 315
0·6	0·4	−356	−417	−2 041	−6 016
		−377	−449	−2 165	−6 193
0·8	0·2	−324	−396	−1 906	−5 814
		−351	−424	−2 078	−6 024
1·0	0	−308	−371	−1 826	−5 701
		−332	−403	−1 993	−5 896

[a] No convergence was reached in the *ab initio* calculation for Be^{2+}.

In order to improve the results, it was necessary to make also the charge distribution dependent on the relative proportions of mixed solvent components. Therefore, the charges on the atoms of both solvents were corrected for the values of the mole fractions.

Eq. (*1*) was then modified as follows:

$$\Delta G = -\left(\sum_{\mu} \frac{Q_\mu^2 x_\mu}{2r_\mu} + \sum_{\mu<\nu}\sum \frac{Q_\mu Q_\nu \sqrt{x_\mu x_\nu}}{r_{\mu\nu}}\right)\left(1 - \frac{1}{z}\right), \qquad (6)$$

where

$$x_j = \begin{cases} x & \text{for} \quad j = 1, \ldots, k \\ 1 - x & \text{for} \quad j = k + 1, \ldots, n \\ 1 & \text{for} \quad j = n + 1 \end{cases}$$

$j = \mu$ or ν is the serial number of an atom in a supersystem with $n + 1$ atoms, of which k atoms make up a molecule of one solvent, $n - k$ atoms a molecule of the other solvent, and the cation is given the index number $j = n + 1$.

TABLE IV

Thermodynamic functions of the complexes dimethylformamide–ion–water calculated from Eqs (*6*) and (*7*). The first row for each mole fraction gives Gibbs energies of solvation in kJ/mol and the second row, the enthalpies of solvation in kJ/mol

Mole fraction		Ion				
DMF	H_2O	Li^+	Be^{2+}	Na^+	Mg^{2+}	Al^{3+}
0	1·0	−616	−3 824	−742	−2 280	−4 624
		−692	−3 981	−796	−2 345	−4 695
0·2	0·8	−594	−3 763	−705	−2 212	−4 572
		−647	−3 916	−743	−2 267	−4 618
0·4	0·6	−537	−3 645	−638	−2 174	−4 522
		−604	−3 832	−692	−2 211	−4 575
0·6	0·4	−493	−3 512	−591	−2 108	−4 465
		−565	−3 728	−627	−2 136	−4 508
0·8	0·2	−446	−3 421	−543	−2 045	−4 391
		−511	−3 610	−587	−2 094	−4 421
1·0	0	−401	−3 318	−509	−1 977	−4 327
		−472	−3 541	−532	−2 011	−4 386

Eq (*2*) was modified in an analogous manner to yield

$$\Delta H = -\left(\sum_{\mu} \frac{Q_{\mu}^{2} x_{\mu}}{2r_{\mu}} + \sum_{\mu<\nu}\sum \frac{Q_{\mu} Q_{\nu} \sqrt{x_{\mu} x_{\nu}}}{r_{\mu\nu}}\right)\left(1 - \frac{1}{z} - \frac{Tz'}{z^{2}}\right), \qquad (7)$$

where the symbols have the same meaning as above.

RESULTS AND DISCUSSION

In this work, we have used a theoretical model to represent the variation in the magnitude of solvation effects as a function of the relative proportions of solute and solvent. The solvation is understood here as a process embracing all the changes associated with the formation of an ionic solution of a given composition from ions in the gaseous state and a liquid solvent.

Results obtained from Eqs (*6*) and (*7*) are given in Tables II to IV.

The results for higher-valent ions are not so much dependent on saturated valencies as are those for 1 : 1 complexes. Although the direct incorporation of the influence of the mole fraction in the charge distribution is rather a crude modification, the values of ΔG and ΔH for all the systems are seen to follow approximately the same trend over the whole range of mixed solvent compositions. An important role is played here by the preceding *ab initio* calculation of the charge distribution, the results of which are very sensitive to the quality of the optimization of the geometry of the complex studied. Since all the preceding *ab initio* calculations were performed with an optimization step of only 0·01 nm, there appears to be some scope for further improvement of results.

An attempt to combine the discrete and continuum models on the basis of quantum mechanics has also been made by Langlet and coworkers[7], who applied their model to the problem of solvent effects on the conformation of acetylcholine in water. Their paper shows that the combined model gives essentially the same, but in absolute values more realistic, results as each model applied separately.

A phenomenological theory based on a quantum mechanical treatment of ionic and molecular solvation with continuous charge distribution has been put forward by Schmidt[8]. However, his extensive theoretical work has not as yet been broadly exploited. Beveridge and Schnuelle[9] have investigated solvent effects on the conformational stability of dissolved molecules, using a combined model based on statistical thermodynamics. For solvation of Li^+ and Na^+ in water, their results are in good agreement with those obtained in this work. Our results are, however, closer to experimental values published by Burgess[10].

REFERENCES

1. Born M.: Z. Phys. *1*, 45 (1920).
2. Hoijtink G. J.: Rec. Trav. Chim. Pays-Bas *75*, 487 (1956).
3. Landolt-Börnstein: *Kalorische Zustandgrösse*, B. II. T. 2. Springer, Berlin 1963.
4. Mulliken R. S.: J. Chem. Phys. *23*, 1833 (1955).
5. Hehre K. J., Lathan K. A., Ditchfield E., Newton M. D., Pople J. A.: Program No 236, QPCE, Indiana University, Bloomington, Indiana.
6. Sutton L. E.: *Tables of Interatomic Distances and Configuration in Molecules and Ions. Supplement.* The Chemical Society, Burlington House, London 1965.
7. Langlet J., Claverie P., Pullman B., Piazzola D., Daudey J. P.: Theor. Chim. Acta *46*, 105 (1977).
8. Schmidt P. P.: J. Chem. Soc., Faraday Trans. 2, *74*, 703 (1978).
9. Beveridge D. L., Schnuelle G. W.: J. Phys. Chem. *78*, 2064 (1974).
10. Burgess J.: *Metal Ions in Solution.* Ellis Horwood, New York 1978.

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