$$\mathrm{EA}[(SO_2)_2] - \mathrm{EA}[SO_2] = D[SO_2^- \cdots SO_2] - D[SO_2 \cdots SO_2] = \sim 0.8 \quad \mathrm{eV},$$

where EA[ ] denotes the electron affinities of the dimer and the monomer, and D[ ] denotes the dissociation energies of the ionic and the neutral dimers into the indicated products.

We wish to thank A. W. Castleman, Jr. and M. T. Bowers for helpful discussions. We gratefully acknowledge the support of the National Science Foundation under Grant CHE-8511320. Acknowledgment is also made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

[a] Present address: University of California at Santa Barbara, Santa Barbara, CA.

[b] Present address: University of California at Berkeley, Berkeley, CA.

[1] R. G. Keesee and A. W. Castleman, Jr., J. Phys. Chem. Ref. Data **15**, 1011 (1986).

[2] R. G. Keesee, N. Lee, and A. W. Castleman, Jr., J. Chem. Phys. **73**, 2195 (1980).

[3] J. J. Breen, K. Kilgore, K. Stephan, R. Hofmann-Sievert, B. D. Kay, R. G. Keesee, T. D. Mark, and A. W. Castleman, Jr., Chem. Phys. **91**, 305 (1984).

[4] M. R. Nimlos and G. B. Ellison, J. Phys. Chem. **90**, 2574 (1986).

[5] K. H. Bowen, G. W. Liesegang, R. A. Sanders, and D. R. Herschbach, J. Phys. Chem. **87**, 557 (1983).

[6] R. V. Hodges and J. A. Vanderhoff, J. Chem. Phys. **72**, 3517 (1980).

[7] H. -S. Kim and M. Bowers, J. Chem. Phys. **85**, 2718 (1986).

[8] A. W. Castleman, Jr., C. R. Albertoni, Kurt Marti, D. E. Hunton, and R. G. Keesee, J. Opt. Soc. A **3**, 102 (1986).

[9] J. V. Coe, J. T. Snodgrass, C. B. Freidhoff, K. M. McHugh, and K. H. Bowen, J. Chem. Phys. **83**, 3169 (1985).

[10] J. V. Coe, J. T. Snodgrass, C. B. Feidhoff, K. M. McHugh, and K. H. Bowen, Chem. Phys. Lett. **124**, 274 (1986).

[11] J. V. Coe, J. T. Snodgrass, C. B. Freidhoff, K. M. McHugh, and K. H. Bowen, J. Chem. Phys. **87**, 4302 (1987).

[12] J. V. Coe, J. T. Snodgrass, C. B. Freidhoff, K. M. McHugh, and K. H. Bowen, J. Chem. Phys. **84**, 618 (1986).

[13] H. Haberland, H.-G. Schindler, and D. R. Worsnop, Ber. Bunsenges. Phys. Chem. **88**, 270 (1984).

COMMENTS

Comment on: "Water–water and water–ion potential functions including terms for many-body effects," T. P. Lybrand and P. Kollman, J. Chem. Phys. 83, 2923 (1985), and on "Calculation of free energy changes in ion–water clusters using nonadditive potentials and the Monte Carlo method," P. Cieplak, T. P. Lybrand, and P. Kollman, J. Chem. Phys. 86, 6393 (1987)

Bruce J. Berne and Anders Wallqvist
Department of Chemistry, Columbia University, New York, New York 10027

(Received 26 October 1987; accepted 25 February 1988)

In a recent series of papers[1] the interaction energy of an assembly of water molecules and ions is computed taking into account many-body polarization effects. It is assumed that the system consists of point polarizable centers and charges. Each charge then induces dipoles on the polarizable spheres which contribute to the electrostatic energy. In the above papers this polarization energy is taken to be

$$E_{\mathrm{pol}} = -\frac{1}{2}\sum_j \alpha_j \mathbf{E}_j \cdot \mathbf{E}_j, \tag{1}$$

where $\mathbf{E}_j$ is the total electric field at site j:

$$\mathbf{E}_j = \mathbf{E}_j^{(0)} + \sum_k \mathbf{T}_{jk} \cdot \alpha_k \mathbf{E}_k, \tag{2}$$

where the term with the superscript (0) represents the electric field at the site j arising from all of the unscreened charges; that is, the unscreened Coulomb field and the second term on the right-hand side represents the part of the electric field at site j due to all of the induced dipoles at other sites. The tensor $\mathbf{T}$ is the standard dipole propagator.

Unfortunately, Eq. (1) is incorrect. The correct polarization energy is[2]

$$E_{\mathrm{pol}} = -\frac{1}{2}\sum_j \alpha_j \mathbf{E}_j \cdot \mathbf{E}_j^{(0)}. \tag{3}$$

The difference between Eq. (1) used by Kollman *et al.*[1] and the correct expression given by Eq. (3) is that the larger unscreened Coulomb field appears in the last position instead of the total field. Equation (1) will give incorrect predictions of the solubility, and solvent structure around ions as well as the interaction between water molecules.

It should be recognized that Eq. (1) is simply wrong and should never be interpreted as arising from a "different physical model." Equation (3) is the correct equation for

 0021-9606/88/128016-02$02.10

classical point polarizable molecules. It is important that future simulations use the correct expression.

[1] T. P. Lybrand and P. Kollman, J. Chem. Phys. **83**, 2923 (1985); P. Cieplak, T. P. Lybrand, and P. Kollman, J. Chem. Phys. **86**, 6393 (1987).
[2] See, for example: J. A. Stratton, *Electromagnetic Theory* (McGraw–Hill, New York, 1941), Eq. (51) p. 113; L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Addisson–Wesley, Reading, Mass. 1960), Eq. (11.8), p. 54. Equation (3) is correct only if the polarizability is a scalar, and if hyperpolarizability corrections can be safely ignored.

Reply to: "Comment on 'Water–water and water–ion potential functions including terms for many-body effects,' T. P. Lybrand and P. Kollman, J. Chem. Phys. 83, 2923 (1985) and on 'Calculation of free energy changes in ion–water clusters using nonadditive potential and the Monte Carlo methods,' P. Cieplak, T. P. Lybrand, and P. Kollman, J. Chem. Phys. 86, 6393 (1987)"

Peter Kollman, Terry Lybrand,[a] and Piotr Cieplak[b]
Department of Pharmaceutical Chemistry, University of California, San Francisco, California 94143

(Received 31 December 1987; accepted 25 February 1988)

Berne and Wallqvist[1] point out that we should use Eq. (1) instead of Eq. (2) which was used in the above references to calculate polarization energies (see Ref. 1 for a definition of the terms):

$$E_{\rm pol} = -\frac{1}{2}\sum_j \alpha_j \mathbf{E}_j \cdot E_j^{(0)}, \qquad (1)$$

$$E_{\rm pol} = -\frac{1}{2}\sum \alpha_j \mathbf{E}_j \cdot \mathbf{E}_j . \qquad (2)$$

We agree that Eq. (1) instead of Eq. (2) is the correct one, as also pointed out by Rullmann and van Duijnen.[2]

We disagree with Berne and Wallqvist that our use of Eq. (2) has "given *incorrect* predictions of the solubility and solvent structure around ions as well as the interaction between water molecules," at least on the systems we have studied to date. We have repeated a number of the calculations reported in Lybrand and Kollman and have found the results reported in Table I comparing the polarization energy calculated using Eq. (1) or (2). Only in the cases of $(H_2O)_6$ and $Mg^{+2}\cdots(OH_2)_6$ are the differences between Eqs. (1) and (2) not negligible. Furthermore, the key structural insights (preference of Na^+ for lower coordination in the gas phase $-4+2$ instead of octahedral) and the tendency of H_2O's around Cl^- to cluster on one hemisphere of the ion are found with either equation. We also note that the polarization energy calculated using Eq. (2) is not necessarily smaller than with Eq. (1), since $\mathbf{E}_j^{(0)}$ may not be parallel to $\mathbf{E}_j$. Finally, we have not repeated the free energy calculations by Cieplak *et al.*, but the results in Table I suggest that the general conclusions/parameters presented in that study will remain valid.

The reason that there are no large differences in the interaction energies and structure is that: the polarization energy is only ~10%–20% of the total interaction energy and that the contribution to the electric field is dominated by the charges and permanent dipoles so that $\mathbf{E}_j$ differs from $\mathbf{E}_j^0$ by ~10% or less. Thus, the major qualitative conclusions of the papers by Lybrand *et al.* remain valid and the actual parameters derived will likely also be capable of yielding ion hydration energies in very good agreement with experiment and structures in good agreement with the results of *ab initio* quantum mechanical calculations, as found previously.

TABLE I. Comparison to total interaction energy using different equations for the polarization energy (kcal/mol).

Complex	E_T [a]	E_T [b]
$Na^+\cdots OH_2$ [c]	−23.9	−23.8
$K^+\cdots OH_2$ [c]	−17.6	−17.4
$Cl^-\cdots OH_2$ [c]	−13.0	−12.7
$H_2O\cdots H_2O$ [d]	−5.8	−5.7
$Na^+\cdots(H_2O)_6$ (4 + 2 coordination) [c]	−93.3	−93.4
$Na^+\cdots(H_2O)_6$ (octahedral coordination) [c]	−88.4	−88.8
$Cl^-\cdots(H_2O)_4$ [e,c]	−41.8	−41.8
$(H_2O)_6$ [f,c]	−41.3	−43.3
$Mg\cdots H_2O$ [c]	−78.5	−78.5
$Mg^{+2}\cdots(H_2O)_6$ [c]	−310.7	−319.3

[a] Polarization energy calculated using Eq. (2).
[b] Polarization energy calculated using Eq. (1).
[c] Complete minimizations using each quantum and negligible difference in minimum energy geometry found.
[d] Minimum energy O–O distance 2.85 Å, Eq. (2); 2.88 Å, Eq. (1).
[e] Minimum energy geometry far from tetrahedral, see discussion in Lybrand and Kollman.
[f] Cyclic hexamer geometry was very similar in both cases with R(O–O) ~2.8 Å.

[a] Current address: School of Pharmacy, University of Minnesota, Minneapolis, MN 55455.
[b] Current address: Department of Chemistry, University of Warsaw, Poland.

[1] B. Berne and A. Wallqvist, J. Chem. Phys. **88**, 8016 (1988).
[2] Rullmann and van Diujnen, Mol. Phys. (in press).