

Calculation of the Solvation Energy of Dipolar Molecules

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An analytical expression for the solvation energy of dipolar molecules is developed. The model used is a prolate spheroid, with the charges at the foci. Calculated solvation energies are compared with numerical data obtained previously from a model in which the effect of dielectric saturation was included.

The purpose of the present communication is to develop an analytical expression for the solvation energy of dipolar molecules, and to compare energies of solvation calculated from this expression with numerical data obtained previously from a model in which the effect of dielectric saturation was included.¹

The solvation energy can be calculated as an integral over the total solvent volume surrounding the dipolar molecule.²

$$\begin{aligned} w &= \frac{1}{8\pi} \int (\mathbf{E}\mathbf{D} - D^2) dv \\ &= \frac{1}{8\pi} \int (\epsilon^{-1} - 1) D^2 dv \end{aligned} \quad (1)$$

where ϵ is the dielectric permeability, \mathbf{D} is the dielectric induction and \mathbf{E} is the electric field created by the charge distribution in the molecule. Since a dipolar molecule has no net charge, it is reasonable to assume that the field even close to the molecules is relatively unimportant. Therefore, dielectric saturation effects can be neglected, and ϵ can be considered to be a constant ϵ_0 , equal to the value in the bulk of the solution.

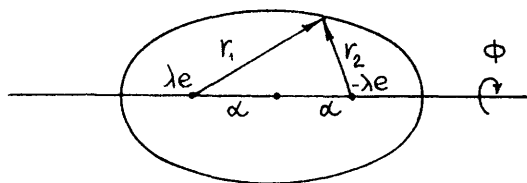


FIG. 1

We describe the dipolar molecule as a prolate spheroid in which the distance between the foci is 2α . The charges λe and $-\lambda e$ are situated at the foci (fig. 1). The calculations are carried out in prolate spheroidal coordinates ξ , η and ϕ ,³ which assume the following values in the integration region outside the prolate spheroid

$$1 < \xi_0 \leq \xi < \infty \quad (2)$$

$$-1 \leq \eta \leq 1 \quad (3)$$

$$0 \leq \phi \leq 2\pi \quad (4)$$

where

$$\xi_0 = (r_1 + r_2)/2\alpha \quad \text{and} \quad \eta = (r_1 - r_2)/2\alpha. \quad (5)$$

Expressing D^2 and dv in the coordinates ξ , η and ϕ ¹

$$D^2 = \frac{4\lambda^2 e^2}{\alpha^4} \frac{1}{(\xi^2 - \eta^2)^4} \{ \eta^2 (3\xi^2 + \eta^2) + \xi^2 - \eta^2 \} \quad (6)$$

$$dv = \alpha^3 (\xi^2 - \eta^2) d\xi d\eta d\phi \quad (7)$$

we obtain the following expression for the solvation energy

$$w = \frac{\lambda^2 e^2}{\alpha} \left(\frac{1}{\epsilon_0} - 1 \right) \int_{-1}^1 dy \int_{\xi_0}^{\infty} d\xi (\xi^2 - \eta^2)^{-3} (3\xi^2 \eta^2 + \eta^4 + \xi^2 - \eta^2) \\ = \frac{\lambda^2 e^2}{\alpha} \left(\frac{1}{\epsilon_0} - 1 \right) f(\xi_0) \quad (8)$$

where

$$f(\xi_0) = \frac{\xi_0^2 + 1}{4\xi_0(\xi_0^2 - 1)} - \frac{\xi_0^2 - 1}{4\xi_0^2} \ln \frac{\xi_0 + 1}{\xi_0 - 1}. \quad (9)$$

TABLE 1

ξ_0	$f(\xi_0)$	$-W_{\max}/(10\lambda)^2$	$-W_{\max-G,U}/(10\lambda)^2$			$-W_{\min}/(10\lambda)^2$
			$\lambda e = 0.1e$	$\lambda e = 0.55e$	$\lambda e = 0.75e$	
1.050	9.66	11.3	13.95	11.23	10.94	25.3
1.261	1.54	1.80	3.173	2.401	2.271	4.04
1.471	0.695	0.81	1.295	1.104	1.039	1.82
1.682	0.392	0.458	0.652	0.618	0.585	1.025
1.897	0.250	0.282	0.371	0.368	0.359	0.655
2.104	0.176	0.206	0.231	0.231	0.229	0.462
2.314	0.128	0.150	0.151	0.151	0.151	0.335
2.525	0.094	0.110	0.104	0.104	0.104	0.246
2.737	0.073	0.0854	0.073	0.073	0.073	0.191
2.956	0.057	0.0666	0.053	0.053	0.053	0.139
3.157	0.0455	0.0531	0.040	0.040	0.040	0.119
3.368	0.0385	0.0450	0.031	0.031	0.031	0.105
3.578	0.0305	0.0357	0.024	0.024	0.024	0.080
3.789	0.0260	0.0304	0.019	0.019	0.019	0.068
4.000	0.0222	0.0250	0.015	0.015	0.015	0.058

Table 1 contains the values of $f(\xi_0)$ for the same values of ξ_0 as used previously.¹ In the numerical calculations of w eqn (1) was applied, accounting for the dependence of ϵ on the electric field by the relation^{4, 5}

$$\epsilon = n^2 + \frac{\epsilon_0 - n^2}{C^{\frac{1}{2}} E} \operatorname{arctg} C^{\frac{1}{2}} E \quad (10)$$

where ϵ_0 is the bulk dielectric constant of the solvent, n the optical refractive index and C a constant taken as $1.08 \times 10^{-8} \text{ cm}^2 (\text{e.s.u.})^{-2}$. Eqn (10) shows that ϵ can vary from $n^2 = 1.78$ to $\epsilon = \epsilon_0 = 78.5$ depending on the field strength, and correspondingly the factor $(\epsilon^{-1} - 1)$ under the integral sign can vary from -0.44 to -0.987 . Using the limiting values of ϵ , the corresponding limiting values of the solvation energy W_{\min} and W_{\max} can be obtained from eqn (8) and (9). W_{\min} corresponds to the complete

absence of dielectric saturation, whereas W_{\max} corresponds to dielectric saturation in the whole solvent volume. These values are shown in table 1 for $2\alpha = 2.50 \text{ \AA}$. It follows from eqn (1), that if dielectric saturation exists in the region closest to a dipolar molecule, then this saturation should decrease sharply with increasing dimensions of the prolate spheroid (increasing ξ_0). Therefore, W is expected to be well described by eqn (8), putting $\varepsilon = \varepsilon_0 = 78.5$. This should also be reflected in the proportionality between W and λ^2 , since the dependence of ε on the field strength becomes negligible. In fact, the numerical calculations do show, e.g., for $2\alpha = 2.50 \text{ \AA}$ and $\xi_0 \geq 2.3$ —which is close to the value for real molecules—that W/λ^2 does not depend on λ^2 in the interval $0.01 < \lambda^2 < 0.56$. This strongly indicates that dielectric saturation can be neglected in the calculation of solvation energies of dipolar molecules, and that eqn (8) is applicable to the estimation of W . On the other hand, a comparison of the solvation energies $W_{\text{M-G,L}}$ of ref. (1) with W_{\min} and W_{\max} —e.g., for $2\alpha = 2.50 \text{ \AA}$, and $\lambda = 0.1, 0.55, 0.75$ —shows that $W_{\text{M-G,L}}$ does not tend towards W_{\min} with increasing ξ_0 , and even becomes bigger than W_{\max} (table 1). It therefore appears that the calculations of ref. (1) should be reconsidered.

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⁵ K. J. Laidler and J. S. Muirhead-Gould, *Trans. Faraday Soc.*, 1966, **62**, 953.