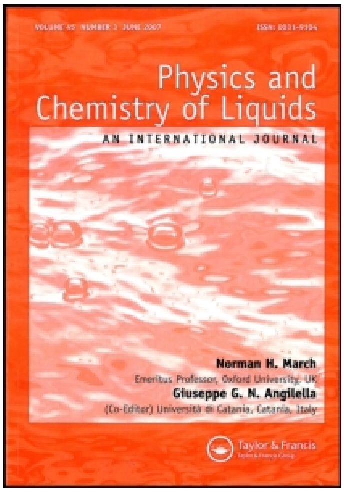

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ELECTROSTATIC INTERACTION OF LIQUID MOLECULE WITH SURROUNDINGS

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The deformation of a spherical molecule due to its own reaction field is studied theoretically. The spheroidal shape thus obtained is used to calculate the cohesion energy of polar liquids and also their molecular dipole moments. The latter values are found to be in better agreement with moments measured in the gas phase than those obtained earlier. Relevance of the model in molecular theory of liquids is pointed out.

KEY WORDS: Polarization, solution shells, continuum model.

1 INTRODUCTION

The study of problems involving interaction between liquid molecules presents some basic difficulties. Firstly, each molecule is directly surrounded by several others (for instance, the first, second etc solvation shells). Secondly, it is not possible to assume that the molecules lie at well defined positions. In these calculations, therefore, an elaborate statistical treatment or at least some minimization of energy with respect to molecular configuration becomes necessary. Exact expressions[1] for the various solvation thermodynamic quantities can thus be derived in the case of dilute solutions.

In practice, however, accurate computational methods for evaluating the various statistical quantities become rather costly. Some approximate methods have been, therefore, developed. These are the discrete model[2-5], the continuum model[6-8] and the discrete-continuum model[2,4,5,9]. All the three models have been used to calculate the dispersion and repulsion parts of interaction energy between the molecules.

Construction of a discrete model of the solvent for calculating the electrostatic part is more difficult because the respective positions of the molecules play an important role in such evaluations. In fact, it is cumbersome to take into account the interaction of molecules and the microscopic structure of the material by the methods of statistical mechanics. This part has been, therefore, usually calculated by treating the solvent as an infinite continuum dielectric.

Such studies have been usually based on the Onsager model[10] which neglects the effect of short range forces acting on a molecule, assumed spherical and located in a continuum formed by the rest of the molecules. Subsequent improvements have centred round the shape of the molecule under reference. Thus, Scholte[11] assumed it to be ellipsoidal for polar liquids while Abbott and Bolton[6] considered that the prolate spheroid was a closer mathematical approximation in many cases. The latter also concluded that since other factors were still ignored, the theory yielded results which were as satisfactory as expected from classical electrostatics alone. More recently Huron and Claverie[3] have proposed a numerical method in order to extend the calculations to a cavity with an arbitrary shape.

2 FORMULATION

Following Bell[12] the dipole in a molecule, may be considered in the present treatment as an ideal dipole in the centre of a spherical cavity. The dipole field polarizes the surrounding matter. The inhomogeneous polarization of the continuum gives rise to the reaction field at the dipole. The reaction field in turn, produces electric stresses on the cavity continuum interface which tend to distort the spherical shape and thus change the potentials, both inside and outside the cavity. Consequently, the reaction field itself may undergo a modification.

Consider a spherical cavity of radius 'a' surrounded by a liquid of dielectric constant ε. With a non-polarizable point dipole of moment μ (along the positive Z-axis) situated at the centre, the potentials outside (φ_1) and inside (φ_2) may be written as[13]

$$\varphi_1 = \frac{3}{2\varepsilon + 1}\frac{\mu}{r^2}\cos\theta \qquad r > a \tag{1}$$

$$\varphi_2 = \frac{\mu}{r^2}\cos\theta - \frac{2(\varepsilon - 1)}{2\varepsilon + 1}\frac{\mu}{a^3} r\cos\theta \qquad r < a. \tag{2}$$

The second term in the expression for φ_2 is the reaction potential. The reaction field may, hence, be expressed as[13]

$$\mathbf{R} = f\boldsymbol{\mu} \tag{3}$$

where the scalar constant f is given by

$$f = \frac{1}{a^3}\frac{2(\varepsilon - 1)}{2\varepsilon + 1}. \tag{4}$$

The polarization of the continuum, however, produces electric stresses at the interface and the spherical shape may be accordingly deformed. The resulting changes in $\mathbf{R}$ can be calculated, at least for small deformations, by assuming that the deformed interface is represented by

$$r = a_0 + \sum_{n=1}^{\infty} a_n P_n(\cos\theta) \tag{5}$$

where a_n is the deformation parameter for the nth mode and 'a_0' is the equilibrium radius of the surface under reference. Consequently, the perturbed potentials, φ'_1 and φ'_2 can be approximately written as:

$$\varphi'_1 = \varphi_1 + \mu \sum_{n=0}^{\infty} a_m(A'_m r^m + B'_m r^{-m-1})P_m(\cos\theta) \quad r > a_0 \tag{6}$$

$$\varphi'_2 = \varphi_2 + \mu \sum_{m=0}^{\infty} a_m(C'_m r^m + D'_m r^{-m-1})P_m(\cos\theta) \quad r < a_0. \tag{7}$$

The constants A'_m, B'_m etc. may be evaluated by applying the boundary conditions. Since at large distances from the cavity ($r \to \infty$), φ'_1 must vanish, A'_m is seen to be zero. Also, the terms involving D'_m in Eq. (7) account for the change in potential due to charges within the cavity. In the present case, the only source is the permanent dipole $\boldsymbol{\mu}$ whose contribution is included in the expression for φ_2. It, therefore, follows that $D'_m = 0$. It may be mentioned that the terms involving C'_m give rise to the additional reaction potential.

At the interface of the deformed cavity, Eq. (5), $\varphi'_1 = \varphi'_2$ and $\varepsilon(\partial\varphi'_1/\partial n) = (\partial\varphi'_2/\partial n)$ ($\partial\varphi'/\partial n$ represents the normal component of the electric field). With these boundary conditions and for small departures from sphericity ($a_n < 1$) of the cavity, assumed incompressible ($a_0 \approx a$), the constants B_m and C_m are given by

$$B'_m = \frac{3a^{m-2}}{a_m(m\varepsilon + \varepsilon + m)} \frac{(\varepsilon - 1)}{(2\varepsilon + 1)} \left[\frac{-3m(m+1)}{(2m+3)} a_{m+1} + \frac{m(1-m)}{(2m-1)} a_{m-1} \right] \tag{8}$$

$$C'_m = \frac{3a^{-(m+3)}}{a_m(m\varepsilon + \varepsilon + m)} \frac{3(\varepsilon - 1)}{(2\varepsilon + 1)} \left[\frac{(m+1)}{(2m+3)} (2m\varepsilon + 2\varepsilon - m)a_{m+1} \right.$$
$$\left. + \frac{m}{2m-1} (2m\varepsilon + 2\varepsilon + m + 1)a_{m-1} \right] \tag{9}$$

The reaction potential for the deformed cavity is therefore found to be

$$\varphi'_R = -\frac{2(\varepsilon - 1)}{2\varepsilon + 1} \frac{\mu}{a^3} r\cos\theta + \mu \sum_{m=0}^{\infty} a_m C'_m r^m P_m(\cos\theta) \tag{10}$$

3 ELECTRIC ENERGY OF THE DIPOLE

The energy of an ideal dipole in its own reaction field is given by

$$W = -\tfrac{1}{2}\boldsymbol{\mu}\cdot\mathbf{R} \tag{11}$$

This equation is independent of the particular shape of the cavity and hence it can be used for calculating W for the deformed cavity as well. Thus, for the spherical cavity

$$W = -\frac{(\varepsilon - 1)}{(2\varepsilon + 1)} \frac{\mu^2}{a^3} \tag{12}$$

which, however, is altered to W' as a result of the deformation such that

$$W' = -\tfrac{1}{2}\boldsymbol{\mu}\cdot\mathbf{R} = -\tfrac{1}{2}\boldsymbol{\mu}\cdot(\nabla\varphi'_R) \tag{13}$$

where the reaction field $\mathbf{R}'$ inside the cavity ($\mathbf{R}' = -\nabla\varphi'_R$) is given by

$$\mathbf{R}' = -\left\{\hat{r}\left[-\frac{2(\varepsilon-1)}{2\varepsilon+1}\frac{\mu}{a^3}\cos\theta + \mu\sum_{m=0}^{\infty} C'_m a_m P_m m r^{m-1}\right]\right.$$
$$\left. + \hat{\theta}\left[\frac{2(\varepsilon-1)}{2\varepsilon+1}\frac{\mu}{a^3}\sin\theta - \mu\sum_{m=0}^{\infty} a_m C'_m P'_m \sin\theta r^{m-1}\right]\right\} \tag{14}$$

Combination of Eqs. (13) and (14) leads to

$$\bar{W}' = W + \tfrac{1}{2}\mu^2 \sum_{m=0}^{\infty} a_m C'_m r^{m-1}(mP_m P_1 + P'_m \sin^2\theta) \tag{15}$$

The average change is energy, $\overline{\Delta W}$ is thus soon to be

$$\Delta W = \tfrac{1}{2}\mu^2 \frac{\int_{\text{vol.}} \sum_{m=0}^{\infty} a_m C'_m r^{m-1}[mP_m P_1 + P'_m \sin^2\theta]dv.}{\int_{\text{vol.}} dv.} \tag{16}$$

Since, the only non-vanishing integrals on the RHS of Eq. (16) exist for $m = 1$ and have the values $\frac{2}{3}$ and $\frac{4}{3}$ respectively, $\overline{\Delta W}$ can be calculated by finding the value of C'_1 from Eq. (9). Hence, it is found that only the second mode of deformation accounts for the average change in energy,

$$\overline{\Delta W} = \frac{3}{5}\frac{\mu^2}{a^3}\frac{(\varepsilon-1)(4\varepsilon-1)}{(2\varepsilon+1)^2}\frac{a_2}{a} \tag{17}$$

Thus for a polarizable dipole, the reaction field at the dipole, $\mathbf{R}'$ in Eq. (14), may be written as

$$\mathbf{R}'_{\text{pol}} = \frac{f'}{1 - f'\alpha}\boldsymbol{\mu} \tag{18}$$

where α is the average polarizability of the molecule. In the present case, with only the second mode of deformation contributing, the constant f' can be expressed as

$$f' = \frac{2(\varepsilon-1)}{2\varepsilon+1}\frac{1}{a^3}\left[1 - \frac{3}{5}\frac{(4\varepsilon-1)}{2\varepsilon+1}\frac{a_2}{a}\right] = \frac{H}{a^3} \tag{19}$$

The reaction field $\mathbf{R}'_{\text{pol}}$ can hence be calculated by using the Onsager's approximation

$$\frac{4\pi}{3}Na^3 = 1$$

where N is number of molecules per unit volume. In case the atomic polarization can be neglected, α can be reasonably approximated by the relation

$$\alpha = \frac{n^2-1}{n^2+2}a^3$$

where n is the index of refraction for the sodium line. In terms of the Avogadro's number N_A, density d and molecular weight M of the liquid, $\mathbf{R}'_{\text{pol}}$ can thus be written as

$$R'_{\text{pol}} = \frac{4\pi}{3}\frac{d}{M} N_A H\boldsymbol{\mu}\left[1 - \frac{2(\varepsilon - 1)}{(2\varepsilon + 1)}\left\{1 - \frac{3}{5}\frac{(4\varepsilon - 1)}{(2\varepsilon + 1)}\frac{a_2}{a}\right\}\frac{(n^2 - 1)}{(n^2 + 2)}\right]^{-1} \tag{20}$$

The electrostatic properties of the liquid dielectric determined by $\mathbf{R}'_{\text{pol}}$ can, therefore, be expected to change accordingly. Two such examples are discussed below.

4 COHESIVE ENERGY

Equation (20) can be used to calculate the contribution of the permanent dipoles to the cohesion energy of a liquid from the expression (13)

$$W' = -\tfrac{1}{2}N_A\boldsymbol{\mu}\cdot\mathbf{R}'_{\text{pol}} \tag{21}$$

Its value depends upon the shape of the molecules and has earlier been calculated[13] by taking the molecules as spherical ($W_{\text{sph.}}$). The deformation of the cavity can be, however, taken into account by combining Eqs. (20) and (21) provided the value of the deformation parameter a_2 is known. In the present work estimates of a_2 have been obtained from the approximate ratios of minor to major axes of molecules calculated with the help of data on atomic radii and interatomic distances for some polar liquids. Thus taking the length of the axis along $\boldsymbol{\mu}$ to be A and that normal to it as B, it can be shown that

$$\frac{B}{A} = \frac{1 - a_2/2a}{1 + a_2/a} \tag{22}$$

The values of W', calculated with the help of Eqs. (20) to (22) and Ref. (13) are presented in Table 1. It is seen that they vary between ten to forty per cent from those obtained for spherical molecules.

Table 1 Calculated values of dipole contribution to cohesion energy.

Compound	*Temperature (°K)*	B/A	*a_2/a estimated from B/A*	*density d gm/cm³*	M	ε	$\frac{n^2-1}{n^2+2}$	*μ (D)*	$-W_{Spherical}$ *K Cal/Mole*	$-W_{Spheroidal}$ *K Cal/Mol*
Chloroform	334	1.4	−0.21	1.41	119.4	4.23	0.2556	1.0	0.18	0.23
Iodomethane	315	0.8	0.15	2.21	141.9	6.48	0.3023	1.6	0.74	0.59
Cyanomethane	355	0.7	0.25	0.72	41.0	26.20	0.2021	3.9	5.60	3.75
Propanone	329	1.3	−0.16	0.75	58.1	17.68	0.2021	2.9	2.20	2.77
Nitromethane	374	0.9	0.07	1.03	61.0	27.75	0.2105	3.5	4.40	3.99

Table 2 Calculated values of dipole moments.

Compound	$\frac{B}{A}$	*a_2/a estimated from B/A*	ε	$\frac{n^2-1}{n^2+2}$	*d gm/cm*^{3}	*T* (°*K*)	μ_0 (*D*)	μ_{AB} (*D*)	μ (*Eq. 28*) (*D*)	μ_g (*D*)
Methyl Iodide	0.758	0.192	7.0	0.309	2.47	293	1.31	1.38	1.46	1.64
Methyl Chloride	0.761	0.190	14.9	0.322	1.05	223	1.54	1.78	1.81	1.86
Methyl Bromide	0.738	0.212	12.6	0.374	1.90	223	1.33	1.55	1.67	1.78
Methyl Cyanide	0.653	0.300	37.5	0.219	0.78	293	3.32	3.53	4.27	3.94

5 DIPOLE MOMENT

For a polar liquid, the polarization **P** may be thought to be made up of the induced polarization $\mathbf{P}_\alpha$ and the dipole polarization $\mathbf{P}_\mu$. Both these components can be calculated in terms of the electric fields working on individual molecules namely the internal ($\mathbf{E}_i$) and the directing ($\mathbf{E}_d$) fields. So that

$$\mathbf{P} = \frac{\varepsilon - 1}{4\pi}\mathbf{E}_0 = \mathbf{P}_\alpha + \mathbf{P}_\mu = \sum_j N_j\left[\alpha_j(\mathbf{E}_i)_j + \frac{\mu^2}{3kT}(\mathbf{E}_d)_j\right] \tag{23}$$

where the subscript j refers to the jth kind of molecule, and k is Boltzman constant. Both $\mathbf{E}_i$ and $\mathbf{E}_d$ can be expressed in terms of the cavity field $\mathbf{E}_c$ through the relations[13]

$$\mathbf{E}_i = \mathbf{E}_d + \mathbf{R} \tag{24}$$

$$\mathbf{B}_d = \frac{1}{1 - f'\alpha}\mathbf{E}_c \tag{25}$$

but their magnitudes depend upon the shape of the molecules.

For a molecule deformed into the spheroidal shape due to its own reaction field, $\mathbf{E}_c$ may be shown to be given by[14]

$$\mathbf{E}_c = \frac{3\varepsilon}{(2\varepsilon + 1)}\left[1 - \frac{6}{5}\frac{(\varepsilon - 1)}{(2\varepsilon + 1)}\frac{a_2}{a}\right]\mathbf{E}_0 = G\mathbf{E}_0 \tag{26}$$

and hence, using Eqs. (18), (24), (25) and (26)

$$\mathbf{E}_i = \frac{G\mathbf{E}_0}{1 - f'\alpha} + \frac{f'}{1 - f'\alpha}\boldsymbol{\mu} \tag{27}$$

It may be noted from Eq. (26) that for a homogeneous Maxwell field $\mathbf{E}_0$, the cavity field $\mathbf{E}_c$ is also homogeneous and is in the same direction. Similar remarks may be made for $\mathbf{E}_d$ provided an average scalar polarizability α is used.

Combining Eqs. (19), (20), (23), and (27), the dipole moment of a pure polar liquid may, therefore, be written as

$$\mu^2 = \frac{3kT}{4\pi GN}\left[1 - \frac{H(n^2 - 1)}{(n^2 + 2)}\right]^2\left[(\varepsilon - 1) - \frac{3G(n^2 - 1)}{(n^2 + 2) - H(n^2 - 1)}\right] \tag{28}$$

The dipole moments of a few non-associating liquids, calculated by Eq. (28) are given in Table 2. The values calculated by Onsager (μ_0) and Abbott and Bolton (μ_{AB})

as also their dipole moments in the gas phase (μ_g) have been included for comparison. The required data have been taken from Ref. (6).

The present treatment is seen to yield better agreement between μ and μ_g although the difference between the two ranges from two to ten percent.

6 APPLICABILITY TO MOLECULAR THEORY

The continuum model developed through the preceding formalism is a possibility which can be explored in molecular theory. One of the main difficulties in all such models is the evaluation of the cavitation term corresponding to the creation in the pure solvent of the cavity according to the solute molecule. The cavitation energy can be calculated by using macroscopic surface tension[15-21] suitably corrected for the microscopic dimensions[22] of the cavity. Since the method does not give satisfactory results, an alternative approach utilizing the scaled particle theory[23-24] has been tried. Such an evaluation has, however, to be made with adequate care[25]. The cavitation term for a molecule in its own liquid has also been calculated[2-5,9,26,27] entirely in the framework of the continuum model. These calculations with the present model would follow in a subsequent communication.

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