Molecular Association and the Dielectric Constant of a Solution

By Ko KIMURA and Ryoichi FUJISHIRO

(Received May 12, 1961)

It may be expected that much useful information about the intermolecular force is obtained by an examination of the dielectric behavior of solutions. Only a few studies based on this point of view have been carried out because of the difficulty of taking into account the contributions of both the long- and short-range intermolecular forces to the dielectric constant of a solution. Buckingham and Raas1) tried to examine the short-range intermolecular force between solutes by the help of the dielectric virial coefficients of solutions. They showed that, to some extent, the dielectric virial coefficients gave valuable information about the intermolecular configuration as well as the intermolecular force. The results obtained by them agree fairly well with spectroscopic data, but some questions still remain about the application of the virial expansion method2) of the total dielectric polarization of a gas to solutions.

In this report, the dimerization of a nitrocompound in carbon tetrachloride will be discussed in detail, because De Maine et al.3) suggested from spectroscopic measurements the dimerization of nitromethane due to the charge transfer force in solutions. Unfortunately, the dielectric constants of the concentrated solutions, as well as the pure liquid of nitromethane, varied with time during the measurements. This was probably due to the isomerization of nitromethane to methylnitrite4). Hence, this article describes the dimerization of nitrobenzene (instead of nitromethane) in carbon tetrachloride, which dimerization is estimated on the basis of some assumptions from the observed dielectric constant of the solution.

---

1) A. D. Buckingham and R. E. Raas, *Trans. Faraday Soc.*, **55**, 377 (1959).

2) A. D. Buckingham and J. A. Pople, ibid., **51**, 1029 (1955).

3) P. A. D. De Maine, M. M. De Maine and A. G. Golbe, ibid., **53**, 427 (1957).

4) G. Geiseler und M. Rätzsch, *Z. physik. Chem.* [*N. F.*], **26**, 131 (1960).

Experimental

The apparatus for the dielectric measurement has already been described elsewhere[5]. The dielectric cell used in this work was of a Sayce-Briscoe type, the electric capacity of which was about 5 pF. All material were purified according to standard methods[6].

Experimental Results

The dielectric constant of the mixture of nitrobenzene and carbon tetrachloride has already been measured by some authors[7], but we repeated the measurement in order to examine the temperature dependence of the dielectric constant of the solution. The observed results are shown in Table I.

TABLE I. THE DIELECTRIC CONSTANTS ε OF SOLUTIONS

Mol. fraction of nitrobenzene x	ε(25°C)	ε(40°C)	x	ε(60°C)
0	2.23	2.20	0	2.17
0.0610	3.52	3.39	0.0160	3.26
0.1277	5.06	4.83	0.1277	4.57
0.2712	8.82	8.32	0.2712	7.74
0.3613	11.39	10.68	0.3613	9.88
0.4712	14.76	13.79	0.4890	13.23
0.6995	22.45	20.85	0.5997	16.30
0.7966	26.04	24.15	0.7323	20.18
0.8467	27.95	25.87	0.8382	23.46
1	34.16	31.47	1	28.76

Discussion

Determination of the Formation Constant of the Nitrobenzene Dimer in the Solution from the Observed Dielectric Data.—We can roughly estimate the formation constant K of the nitrobenzene dimer in the solution from the observed dielectric constant on the assumption that the difference between the observed dielectric constant and the calculated one obtained by the use of Scholte's model[8] is due to molecular association. We regard the monomer and the dimer of nitrobenzene as spheroidal in form and consider the spheroidal cavity of the molecular dimension in the dielectric. The surroundings of the spheroidal cavity are replaced as usual by the continuum of the macroscopic dielectric constant. The point dipole is located along the long axis. The dipole moment of the dimer is zero or twice the monomer moment according to the antiparallel or the parallel orientation of two dipoles. The long and short axes of the spheroids for the monomer and for the dimer are determined by the atomic distances and van der Waals radii of constituent atoms of a nitrobenzene molecule. Those for the monomer are easily obtained, whereas those for the dimer can not be obtained without assuming a tentative configuration for the dimer. In order to make the observed dielectric constant agree with the calculated one, only the parallel orientation of two dipoles is allowed for the configuration of the dimer. Therefore, we calculated the formation constant in each concentration by assuming some plausible configuration for the dimer with the parallel orientation of two dipoles. The most probable configuration of the dimer would indicate a small dependence of K on concentrations. Formulas required for this calculation are derived in quite the same way as in a paper already published[9].

When we use 0, 1 and 2 as suffixes expressing the nonpolar solvent, the monomer and the dimer, respectively, we obtain the following formula:

$$\varepsilon-1=4\pi\left[\sum_{i=1}^{2} N_i \frac{\varepsilon}{\varepsilon+(1-\varepsilon)A_i}\left\{\frac{\mu_i^2}{(1-\alpha_i g_i)^2 3kT}+\frac{\alpha_i}{1-\alpha_i g_i}\right\}+N_0\frac{\varepsilon(n_0^2-1)}{2\varepsilon+n_0^2}a_0^3\right] \qquad (1)$$

in which the notations are the same as those used in the previous paper[9]. In calculating N_1 and N_2 from Eq. 1, polarizability α_2 was assumed to be twice α_1, both α_1 and α_2 being isotropic, and volume change on mixing was ignored. When N_1 and N_2 are calculated from Eq. 1 by means of the observed dielectric constant, the formation constant is easily obtained,

$$K=\frac{N_2}{N_1^2}\cdot\frac{\boldsymbol{N}}{10^3}\ (\text{l./mol.}) \qquad (2)$$

in which $\boldsymbol{N}$ is the Avogadro number. Table II shows some of the calculated results of K for the two plausible configurations of the dimer at different temperatures. When the ratio a_2/b_2 for the dimer is equal to 1, the variation of K with concentrations is comparatively small. This ratio a_2/b_2 for the dimer corresponds to a configuration such as that in which constituent dipoles of the dimer take a parallel orientation and in which one of them lies upon another one. The value of K is very small compared with that for hydrogen bonding and is kept almost constant at

---

[5] K. Kimura and R. Fujishiro, This Bulletin, 32, 433 (1959).

[6] A. Weissberger et al., "Organic Solvents", Interscience Publishers, Inc., New York (1955).

[7] T. Hanai et al., *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 17 (1959); N. N. Pal, *Phil. Mag.*, (7) **10**, 265 (1930).

[8] T. G. Scholte, *Physica*, **15**, 437 (1949).

[9] K. Kimura and R. Fujishiro, This Bulletin, 32, 1237 (1959).

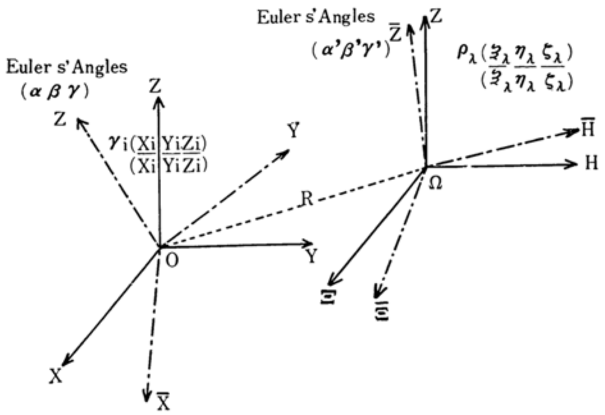

Fig. 1. The coordinate systems.

TABLE II. THE FORMATION CONSTANT K OF THE DIMER

Monomer $a/b=1.72$ Dimer $a/b=1.74$		Monomer $a/b=1.72$ Dimer $a/b=1$			
x	K (25°C)	K (40°C)	K (25°C)	x	K (60°C)
0.1277	0.016	0.0077	—		
0.2712	0.019	0.0078	0.0087	0.2712	0.0074
0.3613	—	0.0082	—		
0.4712	0.027	0.009	0.0093	0.4890	0.0094
0.6995	—	0.010	—		
0.7966	—	0.011	—	0.7323	0.011
0.8467	0.050	0.011	0.011		
1	0.068	0.012	0.012	1	0.012

any temperature between 25°C and 60°C. The latter result means that the heat of the formation of the dimer is of the same order of magnitude as $\boldsymbol{kT}$. These results may probably be attributable to the electrostatic force by considering the large dipole moment of the solute molecule. In the next two sections, discussion will be given over mainly to electrostatic force.

Intermolecular Electrostatic Energy and the Sign of $\langle\cos\varphi_{12}\rangle$.—Let it be supposed that two dipoles form an angle φ_{12} in vacuo. The average value of $\langle\cos\varphi_{12}\rangle$ is given by

$$\langle\cos\varphi_{12}\rangle=\frac{\int\cos\varphi_{12}\,\mathrm{e}^{-U/kT}\,\mathrm{d}\omega}{\int\mathrm{e}^{-U/kT}\,\mathrm{d}\omega} \tag{3}$$

where ω is a solid angle and U is the electrostatic potential energy. If the coordinate systems depicted in Fig. 1 are used, and coordinates of a charge e_i and those of a charge e_λ are r_i (x_i, y_i, z_i) in the O-coordinate system and ρ_λ $(\xi_\lambda, \eta_\lambda, \zeta_\lambda)$ in the Ω-coordinate system, respectively, U is given by the following formula[10],

$$\begin{aligned}U=&-\frac{1}{R^3}\sum_{i,\lambda}e_ie_\lambda(2z_i\zeta_\lambda-x_i\xi_\lambda-y_i\eta_\lambda)\\&+\frac{1}{2R^4}\sum_{i,\lambda}e_ie_\lambda\{r_i^2\zeta_\lambda-\rho_\lambda^2z_i\\&+(2x_i\xi_\lambda+2y_i\eta_\lambda-3z_i\zeta_\lambda)(z_i-\zeta_\lambda)\}+\cdots\end{aligned} \tag{4}$$

The first term of the above formula corresponds to the dipole-dipole interaction energy, the second term to the dipole-quadrupole interaction, and so on. Generally speaking, non-electrostatic forces such as dispersion and repulsive forces must be included in the function U. However, if these non-electrostatic forces are assumed to have spherical symmetry, they have no effect on the averaging process over ω. In calculating the right hand side of Eq. 3, it is convenient to introduce rotating coordinate systems $\bar{X}$, $\bar{Y}$, $\bar{Z}$ of the origin O and $\bar{\Xi}$, $\bar{H}$, $\bar{Z}$ of the origin Ω. The direction of a dipole located at the origin O and that of another dipole located at the origin Ω are taken along the axes $\bar{Z}$ and $\bar{Z}$, respectively. Angles (α, β, γ) or $(\alpha', \beta', \gamma')$ express Eulerian angles of the axes $\bar{X}$, $\bar{Y}$, $\bar{Z}$ to X, Y, Z or those of the axes $\bar{\Xi}$, $\bar{H}$, $\bar{Z}$ to Ξ, H, Z. When we express the coordinates of e_i and e_λ by the rotating coordinate systems, coordinates of e_i $(\bar{x}_i, \bar{y}_i, \bar{z}_i)$ and e_λ $(\bar{\xi}_\lambda, \bar{\eta}_\lambda, \bar{\zeta}_\lambda)$ do not vary with the averaging process. Hence, the average value is obtained by carrying out integration over Eulerian angles only. If we introduce the following transformation matrix,

$$T=\begin{pmatrix}\cos\alpha\cos\gamma-\sin\alpha\sin\gamma\cos\beta, & -\cos\alpha\sin\gamma-\sin\alpha\cos\gamma\cos\beta, & \sin\alpha\sin\beta\\ \sin\alpha\cos\gamma+\cos\alpha\sin\gamma\cos\beta, & -\sin\alpha\sin\gamma+\cos\alpha\cos\gamma\cos\beta, & -\cos\alpha\sin\beta\\ \sin\gamma\sin\beta & \cos\gamma\sin\beta & \cos\beta\end{pmatrix} \tag{5}$$

---

[10] H. Margenau and V. W. Myers, *Phys. Rev.*, **66**, 307 (1944).

TABLE III. THE STABILIZATION ENERGY DUE TO THE SURROUNDING DIELECTRIC

[A] $\rightarrow\rightarrow$, [B] $\rightleftarrows$, [C] $\rightrightarrows$, [D] $\rightarrow\leftarrow$

	$x=1$, $\varepsilon=34.16$ $\Delta G_1=-2.44$ kcal./mol.		$x=0.6995$, $\varepsilon=22.45$ $\Delta G_1=-2.38$		$x=0.2712$, $\varepsilon=8.82$ $\Delta G_1=-2.12$	
	ΔG_2	$1/2(\Delta W+\Delta G_2)-\Delta G_1$	ΔG_2	$1/2(\Delta W+\Delta G_2)-\Delta G_1$	ΔG_2	$1/2(\Delta W+\Delta G_2)-\Delta G_1$
[A]	−3.01	+0.65	−2.95	+0.62	−2.07	+0.80
[B]	0	+1.69	0	+1.62	0	+1.37
[C]	−9.46	−1.65	−9.16	−1.56	−7.81	−1.14
[D]	0	+2.70	0	+2.65	0	+2.39

we can transform the coordinate systems X, Y, Z and Ξ, *H*, *Z* to the new coordinate systems $\overline{\mathrm{X}}$, $\overline{\mathrm{Y}}$, $\overline{\mathrm{Z}}$ and $\overline{\Xi}$, $\overline{H}$, $\overline{Z}$, respectively. The function $\cos\varphi_{12}$ is expressed by the use of Eulerian angles as follows:

$$\begin{aligned}\cos\varphi_{12}=&\sin\alpha\sin\beta\sin\alpha'\sin\beta'\\&+\cos\alpha\sin\beta\cos\alpha'\sin\beta'\\&+\cos\beta\cos\beta'\end{aligned}\tag{6}$$

Substituting Eqs. 4 and 6 into Eq. 3, integration is carried out over ω. Because the denominator of Eq. 3 is always positive, the numerator decides the sign of $\langle\cos\varphi_{12}\rangle$. If we expand the numerator of Eq. 3 in power series and retain only the dipole-dipole term of U, we have

$$\begin{aligned}\int\cos\varphi_{12}\,\mathrm{e}^{-U/\boldsymbol{k}T}\,\mathrm{d}\omega=&\frac{\pi^4}{3!}\cdot\frac{1024}{25}\cdot\left(\frac{\mu^2}{R^3\boldsymbol{k}T}\right)^3\\&+\frac{\pi^4}{5!}\cdot\frac{196608}{49}\cdot\left(\frac{\mu^2}{R^3\boldsymbol{k}T}\right)^5+\cdots\\=&452+204+\cdots>0\end{aligned}\tag{7}$$

where R is determined by the density of nitrobenzene at 25°C and μ is taken to be 4.27 D. The positive sign of $\langle\cos\varphi_{12}\rangle$ agrees with the experimental results. In order to confirm the minor effect of higher multipoles, the dipole-quadrupole term was included in Eq. 7. The result is as follows:

$$\begin{aligned}\int\cos\varphi_{12}\,\mathrm{e}^{-U/\boldsymbol{k}T}\,\mathrm{d}\omega=&-\frac{\pi^4}{2!}\cdot\frac{512}{75}\left(\frac{3\mu\Theta_{zz}}{2R^4\boldsymbol{k}T}\right)^2\\&+\frac{\pi^4}{3!}\cdot\frac{1024}{25}\left(\frac{\mu^2}{R^3\boldsymbol{k}T}\right)^3\\&+\frac{\pi^4}{5!}\cdot\frac{196608}{49}\left(\frac{\mu^2}{R^3\boldsymbol{k}T}\right)^5+\cdots\\=&-80+452+204+\cdots>0\end{aligned}\tag{8}$$

The above equation is derived on the assumption that the charge distribution of a molecule and that of another one are symmetrical about the axes $\overline{\mathrm{Z}}$ and $\overline{Z}$, respectively and Θ_{zz} is presumed to be of the order of 10^{-25}. The series in Eq. 8 will converge gradually and be positive, even if the polarizability of molecules and the interaction energy between higher multipoles are taken into account. The result obtained experimentally in the previous section was confirmed theoretically.

The Dipole-Dipole Interaction Energy and the Stabilization Energy due to the Surrounding Dielectric—When two dipoles with polarizability α_1 are at distance R from each other in vacuo, the dipole-dipole interaction energy with respect to each of the four simple cases depicted in the upper part of Table III, is given by,

$$\text{[A]}\quad \Delta W_{\mathrm{A}}=-\frac{2\mu_1^2}{R^3{}_{\mathrm{A}}(1-2\alpha_1/R^3{}_{\mathrm{A}})}=-0.56\ \text{kcal./mol.}$$

$$\text{[B]}\quad \Delta W_{\mathrm{B}}=-\frac{\mu_1^2}{R^3{}_{\mathrm{B}}(1-\alpha_1/R^3{}_{\mathrm{B}})}=-1.51$$

$$\text{[C]}\quad \Delta W_{\mathrm{C}}=\frac{\mu_1^2}{R^3{}_{\mathrm{C}}(1+\alpha_1/R^3{}_{\mathrm{C}})}=1.29$$

$$\text{[D]}\quad \Delta W_{\mathrm{D}}=\frac{2\mu_1^2}{R^3{}_{\mathrm{D}}(1+2\alpha_1/R^3{}_{\mathrm{D}})}=0.53$$

If these dimers are introduced into the continuum of dielectric, there is the free energy of stabilization due to the reaction field. This energy ΔG_i (ΔG_1 for the monomer and ΔG_2 for the dimer), is

$$\Delta G_i=-\frac{1}{2}\cdot\frac{g_i\mu_i^2}{1-\alpha_i g_i}\tag{9}$$

The values of ΔG_2 for the four simple cases and those of ΔG_1 are shown in Table III in respective concentrations at 25°C. Apart from including dispersion energy, the values of $1/2(\Delta W+\Delta G_2)-\Delta G_1$ are considered as a measure of the stability of the dimer in solutions about the four configurations, although the stabilization energy ΔG_i is overestimated owing to the rough model. The most probable configuration of the dimer in solutions corresponds to the case [C]. This result of the semi-quantitative calculation thus agrees with the experimentally determined configuration of the dimer. Strictly speaking, the association of n-molecules ($n\geqq3$) will occur especially in concentrated solutions, but the dielectric behavior of solutions is, as a first approximation, interpreted in terms of dimerization.

Summary

The formation constant of the nitrobenzene dimer in carbon tetrachloride was estimated as of the order of 0.01 from the dielectric constant of the solution by the use of Scholte's model. The configuration of the dimer is probably such that one of the constituent molecules lies upon the other. The small formation constant and the configuration of the dimer suggest that there is no need to consider some special forces between molecules such as the charge transfer force. The results deduced experimentally are interpreted satisfactorily in terms of the electrostatic force.

The expenses for this work have been partly defrayed by a grant from the Ministry of Education.

Department of Chemistry
Faculty of Science
Osaka City University
Kita-ku, Osaka