Dielectric Constants of Binary Mixtures; 1,2-Dichloroethane and Nonpolar Solvents

By Ryoichi FUJISHIRO and Ko KIMURA

(Received May 25, 1959)

The molecular structure of 1, 2-dichloroethane has been studied in detail by many authors[1]. This molecule has steric isomers arising from the internal rotation and the equilibrium between these isomers in solutions is determined by the intramolecular interaction in the dichloroethane molecule and by the intermolecular interaction with solvent molecules. For example, the greater part of the dichloroethane molecules exists as the *gauche* form in the liquid state, whereas the dilution by adding nonpolar solvents causes decrease of the fraction of the *gauche* form. This is particular interest and worth being examined from various standpoints, that is, the dielectric and the thermodynamic behaviors of mixtures.

The thermodynamic behavior of such mixtures has already been discussed from the measurements of heats of mixing[2], and the excessive enthalpy was explained to some extent by considering the equilibrium between the steric isomers. The dielectric behavior of mixtures of dichloroethane with nonpolar solvents, however, has not been studied in detail except in the low concentration range of dichloroethane.

In this report the dielectric properties of mixtures of dichloroethane with nonpolar solvents such as carbon tetrachloride,

---

[1] S. Mizushima, "Structure of Molecules and Internal Rotation", Academic Press, New York (1954).

[2] K. Amaya and R. Fujishiro, This Bulletin, 31, 90 (1958).

cyclohexane, benzene and carbon disulfide, will be examined experimentally over all the concentrations and discussed on the basis of the Onsager theory and the theory extended by Fujishiro[3] and Scholte[4].

Outlines of the Theory

According to Onsager, we select the spheroidal cavity of the molecular dimension and put a point dipole in the center of this cavity. The surroundings of the spheroidal cavity are replaced by the continuum of the macroscopic dielectric constant. When the long and the short axes of the spheroid are $2a$ and $2b$, respectively, and the dipole is located along the long axis, the local field $\vec{f}$[5] is given by

$$\vec{f}=\vec{G}+\vec{R}=\varepsilon/[\varepsilon+(1-\varepsilon)A]\vec{E}+g\vec{m} \tag{1}$$

where $\vec{G}$, $\vec{R}$ and $\vec{E}$ express the cavity, the reaction and the external fields, respectively, and $\vec{m}$ is the electric dipole moment in dielectrics in the presence of an external field. A is the constant determined by the geometric shape of the cavity and has the following expression[6],

$$A=\frac{ab^2}{2}\int_0^\infty \frac{\mathrm{d}\xi}{(\xi+a^2)^{3/2}(\xi+b^2)}$$

g is called the factor of the reaction field and is given by

$$g=\frac{3}{ab^2}\cdot\frac{A(1-A)\cdot(\varepsilon-1)}{\varepsilon+(1-\varepsilon)A}$$

When we assume the optical polarizability of dichloroethane to be isotropic, $\vec{m}$ is generally related to both $\vec{\mu}$ and $\vec{f}$ by the formula,

$$\vec{m}=\vec{\mu}_v+\alpha\vec{f} \tag{2}$$

μ_v and α being the electric dipole moment and the optical palarizability of the *gauche* form of dichloroethane, respectively. From Eqs. 1 and 2, we obtain

$$\vec{f}=\frac{g}{1-\alpha g}\vec{\mu}_v+\frac{\varepsilon}{\varepsilon+(1-\varepsilon)A}\cdot\frac{\vec{E}}{1-\alpha g} \tag{3}$$

Then the average dipole moment $\overline{m}$ is written as follows:

$$\begin{aligned}\overline{m}&=\langle\vec{m}\cdot\vec{e}\rangle\\ &=\int_\Omega(\vec{m}\cdot\vec{e})e^{-U/kT}\mathrm{d}\Omega\Big/\int_\Omega e^{-U/kT}\cdot\mathrm{d}\Omega\\ &=\frac{\varepsilon}{\varepsilon+(1-\varepsilon)A}\left\{\frac{\alpha}{1-\alpha g}\right.\\ &\quad\left.+\frac{1}{(1-\alpha g)^2}\cdot\frac{\mu_v^2}{3kT}\right\}E\end{aligned} \tag{4}$$

The symbols $\vec{e}$ and U are a unit vector in the direction of the external field and the potential energy of the system in the presence of the external field, respectively. Then the dielectric constant of a mixture containing N_1 molecules of 1-compound, N_2 molecules of 2-compound and so on per cc., is given by the following formula,

$$\varepsilon-1=4\pi\textstyle\sum_z\cdot N_z\overline{m}_z/E \tag{5}$$

If we take the mixture containing N_g molecules of the *gauche* form of dichloroethane, N_t molecules of the *trans* form ($N_d=N_g+N_t$) and N_s molecules of a nonpolar solvent per cc., we obtain from Eqs. 4 and 5

$$\begin{aligned}\varepsilon-1=4\pi\Big[&N_g\cdot\frac{\varepsilon}{\varepsilon+(1-\varepsilon)A}\left\{\frac{1}{(1-\alpha g)^2}\cdot\frac{\mu_v^2}{3kT}\right\}\\ &+N_d\cdot\frac{\varepsilon}{\varepsilon+(1-\varepsilon)A}\cdot\frac{\alpha}{1-\alpha g}\\ &+N_s\frac{\varepsilon}{2\varepsilon+n_s^2}a_s^3(n_s^2-1)\Big]\end{aligned} \tag{6}$$

In the derivation of this equation, we used the following assumption and relation:

(i) A or α for the *trans* form is equal to that for the *gauche* from, though this assumption is not strictly correct.

(ii) Assuming that a solvent molecule is spherical, A for the solvent molecule may be substituted by the value 1/3 for the spherical cavity, and the polarizability of the solvent molecule is replaced by the Lorentz-Lorenz relation,

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

n and a being the refractive index and the radius of the spherical solvent molecule, respectively. Strictly speaking, as there is the contribution of atomic polarization to α, it is expressed by the Clausius-Mossotti relation instead by that of Lorentz-Lorenz. However, the atomic polarization is generally equal to only a few per cent of the electronic polarization. Hence we have conventionally used the latter relation.

Now, as the dielectric constant of the

---

[3] R. Fujishiro, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **65**, 352 (1949).

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

[5] H. Fröhlich, "Theory of Dielectrics", Oxford University Press, London (1949).

[6] C. G. Bötter, "Theory of Electric Polarisation", Elsevier Publishing Co., Houston (1952).

mixture itself is concerned not only with N_d, but also with N_g in the mixture as already shown in Eq. 6, we need to know the ratio N_g/N_d in the equilibrium state of the mixture. Factors determining the equilibrium are the intramolecular energy difference ΔE between the *gauche* and the *trans* forms of dichloroethane, the free energy ΔG for the electrostatic stabilization of the polar *gauche* form in the dielectrics, and the intermolecular dispersion energy between dichloroethane and solvent molecules. As is well known, ΔG is given by

$$\Delta G=\frac{1}{2}\cdot\frac{g}{1-\alpha g}\mu_v{}^2 \tag{7}$$

So far as the dispersion energy is concerned, it is natural to consider that the interaction of the *gauche* form of dichloroethane with a solvent molecule is approximately equal to that of the *trans* form. Thus, one interaction parameter w instead of two may be introduced as follows:

$$w=w_{ds}-\frac{1}{2}(w_{dd}+w_{ss})$$

where w_{ij} is the ordinary dispersion energy between i and j molecules and d or s expresses dichloroethane or a solvent. Then the configurational partition function[7] may be written as

$$Z=2^{N_g}\phi_d{}^{N_d}\phi_s{}^{N_s}\frac{(N_d+N_s)!}{N_t!\,N_g!\,N_s!}\exp\left(\frac{-Xw}{\boldsymbol{k}T}\right)\times\exp\left\{\frac{-N_g(\Delta E-\Delta G)}{\boldsymbol{k}T}\right\} \tag{8}$$

where ϕ_d and ϕ_s represent the internal partition functions of dichloroethane and a solvent molecule respectively, and X is the number of dichloroethane solvent pairs. As the chemical potential of the *gauche* form of dichloroethane is equal to that of the *trans* form in the equilibrium state, we write

$$\frac{\partial\ln Z}{\partial N_g}=\frac{\partial\ln Z}{\partial N_t} \tag{9}$$

Hence the ratio of N_g/N_t is easily derived by using Eqs. 8 and 9 as follows:

$$N_g/N_t=2\exp\left\{\left(-\Delta E+\Delta G+N_g\cdot\frac{\partial\Delta G}{\partial N_g}\right)\Big/\boldsymbol{k}T\right\} \tag{10}$$

The value ε and at the same time the ratio N_g/N_t are determined at any composition and temperature by the method of "trials and errors" from Eqs. 6, 7 and 10.

Experimental

In order to compare the theoretical results with the experimental ones, we measured the dielectric constants of the mixture of dichloroethane and nonpolar solvents such as carbon tetrachloride, cyclohexane, benzene and carbon disulfide. The apparatus[8] for the measurement of the dielectric constant was already described and the capacity of a dielectric cell used in this experiment was about 5 pf. All materials were purified according to the standard method[9].

Comparison of the Theoretical Results with the Observed Values

Fig. 1 shows the theoretical curves of the dielectric constants plotted against the mole fraction of dichloroethane for the dichloroethane-carbon tetrachloride mixture at 25 and 60°C. In this calculation the following values are used;

$\mu=2.55$ D, $\alpha=0.838\times10^{-23}$ cc.
E[10]$=1.27$ kcal./mol.

	$n_s{}^2$	v_d (molecular volume of dichloroethane)	v_s (molecular volume of carbon tetrachloride)
25°C	2.124	1.325×10^{-22}	1.612×10^{-22}
60°C	2.072	1.375×10^{-22} cc.	1.676×10^{-22} cc.

All the calculations were carried out on the assumption that there is no volume change on mixing, i.e., $N_dv_d+N_sv_s=1$. This

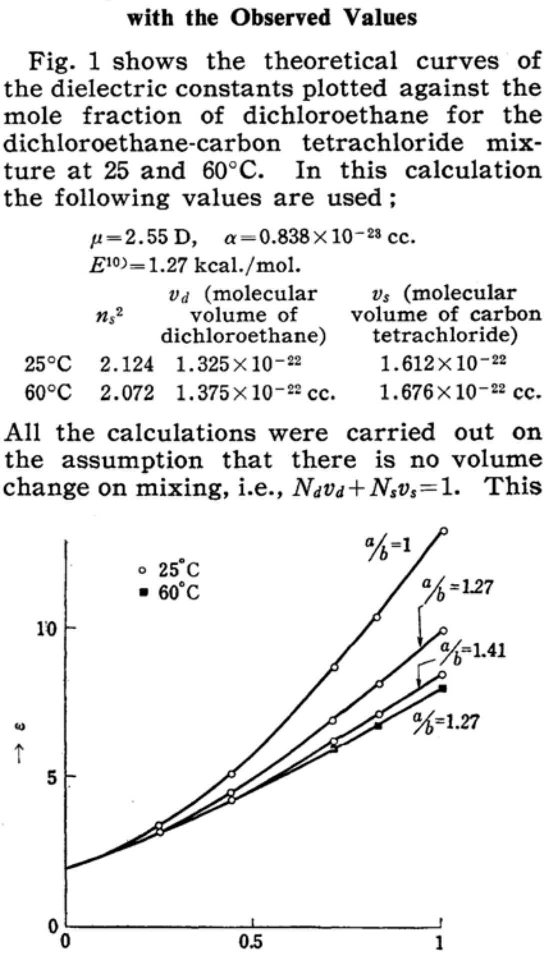

Fig. 1. The calculated dielectric constants of the mixture; dichloroethane-carbon tetrachloride.

---

[7] The detailed description was given in a previous paper. See reference 2.

[8] I. Nakagawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 1353 (1958); K. Kimura and R. Fujishiro, This Bulletin, **32**, 433 (1959).

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

[10] A. Wada, *J. Chem. Phys.*, **22**, 198 (1954).

assumption was confirmed to be reasonable by the measurements of densities of the mixture.

The ratio a/b of the *gauche* form of dichloroethane is to be estimated by the use of the atomic distances and van der Waals radii of component atoms of the dichloroethane molecule. But the dichloroethane molecule is not strictly spheroidal. Only the long axis along which the dipole is located is determined uniquely, whereas the selection of the short axis is arbitrary. The ratio a/b, therefore, can take any value from 1.27 in the case of the maximum short axis to 1.57 of minimum short axis. Values of a/b used in the actual calculation are 1.27 and 1.41, the latter of which is the geometric mean of 1.27 and 1.57. For the sake of comparison the theoretical results in the case of $a/b=1$ are also shown in Fig. 1. From this figure, we may infer that the modification of the shape of the cavity leads to considerable variation of the calculated values of the dielectric constants. This means that the reaction field is overestimated in the Onsager model, i. e., $a/b=1$ and underestimated in the case of $a/b=1.41$. Fig. 2 shows the experimental results corresponding to those of Fig. 1. As seen from these figures, the most satisfactory agreement with experiments is obtained when we adopt as a/b a value 1.27 which corresponds to the allowed maximum of the short axis. This result is of particular interest from the viewpoint of the selection of the short axis. Moreover, the experimental curves representing the dielectric constants of the mixture against the mole fraction x of dichloroethane are more concave than the theoretical curves. The curvatures of the experimental curves themselves are different for different solvents as is seen later, and for different temperatures.

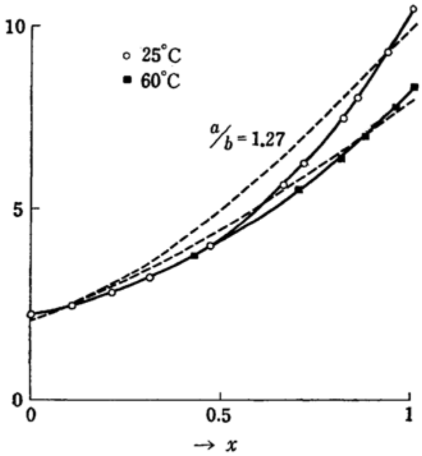

Fig. 2. Comparison of the calculated dielectric constants of the mixture, dichloroethane - carbon tetrachloride, with the observed dielectric constants. ------ Calculated, —— Observed

When we compare the theoretical values with the observed ones at 25 and 60°C, we find a better agreement with the experimental results at 60°C than at 25°C as is shown in Fig. 2 and Table I. This result is the same as that deduced from the equation for the dielectric constants of polar liquids proposed by Yasumi-Komooka[11]. Their conclusion was that a better agreement with the experimental data is obtained near the boiling point than near the melting point.

TABLE I. THE OBSERVED DIELECTRIC CONSTANTS OF THE MIXTURE; DICHLOROETHANE-CARBON TETRACHLORIDE AT 25° AND 60°C

25°C	x	ε	60°C	x	ε
	0	2.227		0	2.165
	0.098	2.501		0.248	2.879
	0.207	2.889		0.450	3.774
	0.333	3.478		0.679	5.282
	0.475	4.347		0.766	5.998
	0.667	5.875		0.851	6.823
	0.722	6.428		0.940	7.776
	0.841	7.778		1	8.492
	0.928	8.948			
	1	10.022			

On the other hand, when we examine the calculated ratio N_g/N_d, we find that it decreases more gradually in the spheroidal model than in the spherical, as is shown in Fig. 3. The calculated ratio N_g/N_d in $x=1$ at 25°C is about 0.75 which

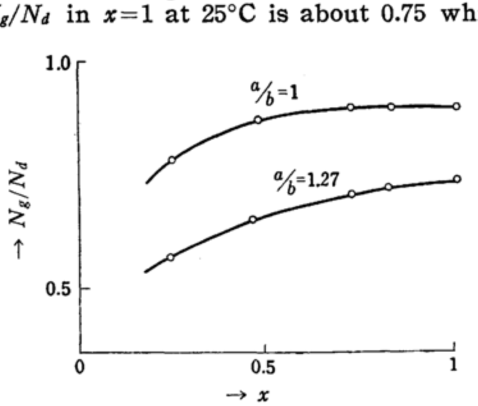

Fig. 3. The calculated ratio N_g/N_d in the mixture, dichloroethane-carbon tetrachloride at 25°C.

---

[11] M. Yasumi and H. Komooka, This Bulletin, **29**, 407 (1956).

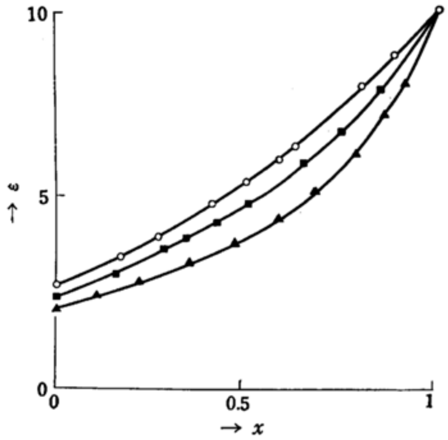

Fig. 4. The experimental results of mixtures, dichloroethane-cyclohexane —○—, dichloroethane-benzene —■— and dichloroethane-carbon disulfide —▲—.

TABLE II. THE OBSERVED DIELECTRIC CONSTANTS OF THE MIXTURES AT 25°C

Dichloroethane-cyclohexane		Dichloroethane-benzene		Dichloroethane-carbon disulfide	
x	ε	x	ε	x	ε
0	2.018	0	2.273	0	2.601
0.101	2.246	0.117	2.803	0.152	3.298
0.232	2.655	0.226	3.345	0.241	3.774
0.350	3.163	0.326	3.897	0.407	4.865
0.475	3.863	0.419	4.468	0.607	6.413
0.548	4.379	0.510	5.084	0.629	6.594
0.649	5.239	0.613	5.863	0.779	7.892
0.743	6.213	0.721	6.801	0.876	8.839
0.826	7.249	0.815	7.779	1	10.073
0.888	8.163	1	10.070		
1	10.073				

is somewhat larger than the value 2/3 measured by the spectroscopic method, but the apparent dipole moment calculated from N_g/N_d when $x \to 0$ agrees fairly well with that estimated experimentally by the use of Debye's equation for dilute solutions.

Finally, the experimental results on mixtures of dichloroethane with other nonpolar solvents at 25°C are summarized in Fig. 4 and Table II. By comparing the experimental curves representing the dielectric constants of mixtures against x with one another, it will be found that the curvatures of the curves are different for different mixtures, and diminish in the following order; cyclohexane and carbon tetrachloride > benzene > carbon disulfide. The excess enthalpy[2] of each mixture decreases in the same order, that is, cyclohexane > carbon tetrachloride > benzene, although the heats of mixing for the carbon disulfide solution have not been measured as yet. Now, the actual calculation of the dielectric constants was carried out only for the mixture dichloroethane-carbon tetrachloride. However, the concentration dependence of the dielectric constants in other mixtures may be inferred to some extent from the calculated results for the mixture dichloroethane-carbon tetrachloride. The case in which the best agreement of the theoretical results with experiments is obtained is the carbon disulfide solution, and next to it, the satisfactory agreement of the theoretical values with the experimental ones is found in the case of benzene solution. The reason why the better agreement even in this simple model is obtained in the case of the carbon disulfide and the benzene solutions is not clear, but some specific interaction may be responsible for this coincidence, considering that the thermodynamic and the spectroscopic[12] measurements suggest the anomalous behavior in the benzene solution. This interesting point may be elucidated partly by examining in detail the temperature dependence of the dielectric constants of the mixtures.

Summary

The dielectric constant for the mixture dichloroethane-carbon tetrachloride was calculated by making use of a model proposed by Onsager, Fujishiro and Scholte. The calculated values agree rather well with the experimental. The higher the temperature is, the better is the agreement. The dielectric constants of other mixtures such as dichloroethane-cyclohexane, dichloroethane-benzene and dichloroethane-carbon disulfide were also measured only at 25°C and compared with one another. The coincidence of the theoretical values with the experimental was obtained in the following order; carbon disulfide, benzene, carbon tetrachloride and cyclohexane.

The cost of this research has been partly defrayed by a grant from the Ministry of Education.

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

---

12) A. Wada and Y. Morino, *J. Chem. Phys.*, 22, 1276 (1954).