The Dielectric Constant of 1,4-Dioxane

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The possibility of a significant contribution of the atomic polarization to the dielectric constant of the polyatomic molecule was discussed by Van Vleck.[1] The experimental evidences were obtained by Sutton et al.[2], for the substances considered as nonpolar stereochemically. Their conclusions were based upon the following facts:

1) The molecular polarization of the gaseous substance was independent of the temperature over a wide range.

2) The value of the molecular polarization for the gaseous substances agreed with that obtained by the solution method.

3) The molecular polarization obtained by the solution method was independent of the solvent used.

In the present work we shall propose new criteria for determining whether the molecular polarization is due to the atomic polarization plus electronic polarization.

A) If the value of the molecular polarization in the pure liquid state does not depend upon the temperature.

B) If the molecular polarization in the solution states is dependent neither on concentration nor on the species of solvent.

C) If the molecular polarization in the solid state does not depend upon the temperature.

D) If the obtained values in the various states are consistent with each other.

Then we may conclude that the molecular polarization is simply the sum of the atomic polarization and electronic polarization except in very special cases.*

We shall apply these criteria to the 1, 4-dioxane, and shall conclude that we cannot exclude the explanation that the dioxane molecule has only nonpolar form and the observed molecular polarization consists of the atomic and of the electronic polarizations.

The dielectric constant of dioxane in the gaseous state was measured by M. Kubo.[3] The molecular polarization was calculated in the usual way. The obtained value is about 5 cc. greater than the electronic polarization. It was concluded that the difference between the molecular polarization and the electronic polarization is due partly to the orientation polarization of the dioxane molecules in the polar form (or "boat" form) which exist in a small amount in the nonpolar form (or "chair" form). An alternative possibility that the difference is due entirely to atomic polarization of the molecule in the nonpolar form, was considered by the author to be less likely, for he believed that the atomic polarization is equal to about 10% of the electronic polarization.

The statement that the atomic polarization is approximately equal to 10% of the electronic polarization was not proved theoretically[1] but was merely guessed from analogy to the case of compounds,[4] which, however, have only one bond of an appreciable moment or have a rigid structure. If the vibrations of a molecule are harmonic and are not influenced by a neighbouring molecule, then the atomic polarization is independent of the temperature and of the states (gas, liquid, solution, solid). On the other hand, if we find that the molecular polarization of a substance depends neither upon the temperature over a wide range nor upon the state, we can conclude that the molecule of the concerned substance is nonpolar and the molecular polarization is due to the atomic and electronic polarizations. (It may happen that exceptions exist.)

To determine whether the molecular polarization of the dioxane is due to the atomic and electronic polarization, we have measured the dielectric constant of the substance in the liquid state and the solid state. Also the dielectric constants of the dioxane solutions of various concentrations in various solvents (hexane, heptane, cyclohexane and benzene) are measured.

The measurement of the dielectric constant in the solid state is very important to determine if the substance is polar or nonpolar. The dielectric constants of most of the polar substances suddenly decrease to lower values

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[1] J.H. Van Vleck, "Theory of Electric and Magnetic Susceptibilities", (1932) p. 51, 68. Oxford, Clarendon Press.

[2] I.E. Coop and L.E. Sutton, *J. Chem. Soc.*, **1938**, 1269.

* It must be noted that the inverse statement is not always valid. It may happen that the atomic polarization is dependent upon the temperature and upon the states.

[3] M. Kubo, *Sci. Pap. Inst. Phys. Chem. Res.* (*Tokyo*), **30**, 238 (1936).

[4] M. Kubo, *Sci. Pap. Inst. Phys. Chem. Res.*, **29**, 122 (1936).

when they go from the liquid state to the solid state. Some substances behave similarly at the transition point in the solid state[5]. Consequently, if we measure the dielectric constant of the substance concerned in the solid state from melting point to a much lower temperature, we can determine if the substance is polar or nonpolar.

Our plan is to measure the dielectric constant of dioxane in the liquid state and in the solid state, and to measure those of solutions, to calculate the molecular polarization using Clausius-Mosotti relation, and to see whether it is constant or not.

Experimental

The dielectric constant was measured by a resonance method. (Fig. 1.) The replaceable capacity (liquid cell, C also used for solid) was incorporated into the circuit of a Hartley oscillator (A), the signal from which was picked up in an adjacent wave-meter (B). Each electrical component was enclosed in an earthened metal box.

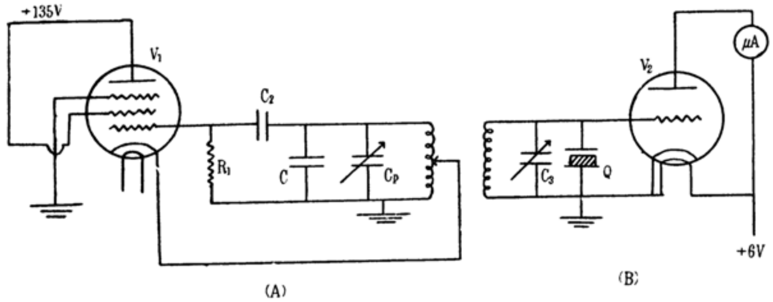

Fig. 1.

V_1: UZ-6C6
V_2: UY-76
C_P: Precision variable air condenser
C_2: Fixed condenser 60 pF
C_3: Air condenser 300 pF
Q : 2 Mc. Resonance quartz
R_1: Fixed resistance 30 kΩ
C : Liquid Cell

The resonance frequency of the wave-meter (B), when the quartz piece Q was not in the circuit, was arranged so that it would at the natural frequency of the quartz piece Q. When the frequency of the oscillator (A) was nearly the same as that of the wave-meter the anode current in the wave-meter humped, and when exactly the same it fell down. The resonance point thus indicated was very sharp.[6]

Precision Condenser C_p.—This was made by Yokogawa Electric Co. Ltd. The working range is 500 pF traversed in 25 turns. Each division (1/100 turn) corresponds to 0.2 pF. The limit of the reading is 1/10 of this division.

Liquid Cell C.—This was made up of two concentric nickel cylinders sealed into a glass vessel. This cell is similar to that used by Mizushima et al.[7] The cell constant did not change when the liquid froze. The capacity of the cell was about 24 pF.

The cell was immersed in a constant temperature bath filled with toluene, and was fixed at a definite position. Low temperatures were obtained by adding dry ice pieces to the bath. The low temperature was measured with an ether thermometer.

The densities of the liquid near room temperature were measured with an Ostwald's pycnometer. The densities of solid were measured with a dilatometer made of a glass tube having a capacity of ca. 5 cc.

The cell constant was determined using benzene as the standard whose dielectric constant was assumed to be 2.2423 at 20°C.

In order to determine the dielectric constant of a solid, it must be considered whether the thermal equilibrium was attained or not. In our experiment, however, it seems that the thermal equilibrium was attained. The reason is as follows: We have measured the dielectric constant of the solid after half an hour from the time when the temperature became constant. After two hours the dielectric constant was re-measured. (The constancy of the temperature was maintained in this time interval). The obtained values are consistent within experimental errors.

Materials used were as follows.

Dioxane.—Commercial dioxane was treated with potassium hydroxide. After distillation over potassium hydroxide, it was fractionally distilled over metallic sodium, a fraction of b. p. 101.5° C being taken.

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[5] S.O. Morgan, *Ann. New York Acad. Sci.*, XL, 357 (1940).

[6] As to the detailed description of the apparatus and procedure of the measurement; see R.J.W. Le Fèvre, "Dipole moment", Methuen's monograph on physical subjects; Methuen Co. Ltd., London (1953), p. 36.

[7] S. Mizushima, Y. Morino and K. Higasi, *Sci. Pap. Inst. Phys. Chem. Res.* (*Tokyo*), 25, 159 (1934).

Benzene.—Commercial benzene was washed with concentrated sulfuric acid, then with water, and was dried over calcium chloride. After drying over metallic sodium, it was fractionally distilled, b. p. 80°C.

***n*-Heptane.**—Commercial *n*-heptane was washed with sulfuric acid, then with water. After drying over calcium chloride, it was distilled, b. p. 97.5°C.

Cyclohexane.—Commercial cyclohexane was dried over calcium chloride, it was then distilled. After drying over metallic sodium, it was fractionally distilled, the fraction of b. p. 81°C being taken.

Experimental Results and Discussions

In Table I are given the values of dielectric constants ε, densities d and molecular polarizations (P_M)* for dioxane in the liquid and the solid state for various temperatures. The values of P_M-P_E are also given in Table I. P_E denotes the electronic polarization, the value of molecular refraction extrapolated to infinite wave-length and amounts to 20.8 cc.

TABLE I

DIELECTRIC CONSTANT OF DIOXANE IN THE LIQUID AND THE SOLID STATE

t	ε	d	P_M(cc.)	P_M-P_E(cc.)
60	2.185	0.9911	25.2	4.4
50	2.194	1.0023	25.1	4.3
40	2.206	1.0126	25.0	4.2
30	2.220	1.0220	24.9	4.1
20	2.233	1.0321	24.9	4.1
15	2.248	1.0386	25.0	4.2
12	2.251	1.0416	24.9	4.1
m.p. 11.7				
11	2.329	1.0880	24.9	4.1
10	2.339			
0	2.329			
−10	2.331			
−20	2.331			
−30	2.329			
−40	2.329			
−50	2.329			
−60	2.329			
−70	2.329			

The values of dielectric constanst ε and of densities d for dioxane-hexane solutions at the temperature of 20° C for various molecular fractions x are tabulated in Table II. The molecular polarizations of dioxane are calculated in the usual way,[8] and are tabulated also in Table II, the values of P_M-P_E are shown in Table II.

TABLE II

DIELECTRIC CONSTANT OF DIOXANE-*n*-HEPTANE SOLUTION AT 20°C

x	ε	d	P_M(cc.)	P_M-P_E(cc.)
0.0000	1.9491	0.6870	—	—
0.2085	1.9780	0.7287	25.0	4.2
0.4359	2.0251	0.7884	25.0	4.2
0.6282	0.0786	0.8533	24.9	4.1
0.7488	2.1235	0.9026	24.9	4.1
1.0000	2.2326	1.0321	24.9	4.1

In Tables III and IV are given the above-mentioned values for dioxane-benzene and dioxane-cyclohexane solutions at the temperature of 20° C and 40° C respectively.

TABLE III

DIELECTRIC CONSTANT OF DIOXANE-BENZENE SOLUTION

x	ε	d	P_M	P_M-P_E
		$t=20°$ C		
0.0000	2.2825	0.8770	—	—
0.1874	2.2751	0.9068	24.7	3.9
0.3498	2.2751	0.9315	24.7	3.9
0.5630	2.2635	0.9640	25.0	4.2
0.7128	2.2529	0.9880	24.9	4.1
		$t=40°$ C		
0.0000	2.2423	0.8583	—	—
0.1874	2.2423	0.8862	25.4	4.6
0.3498	2.2423	0.9106	25.4	4.6
0.5630	2.2266	0.9428	25.1	4.2
0.7128	2.2193	0.9663	25.0	4.2

TABLE IV

DIELECTRIC CONSTANT OF DIOXANE-CYCLOHEXANE SOLUTION

x	ε	d	P_M	P_M-P_E
		$t=20°$ C		
0.0000	2.0483	0.7789	—	—
0.1715	2.0740	0.8093	25.9	5.1
0.3525	2.1066	0.8471	25.8	5.0
0.5476	2.1437	0.8951	25.5	4.7
0.7156	2.1872	0.9408	25.5	4.7
		$t=40°$ C		
0.0000	2.0059	0.7616	—	—
0.1715	2.0271	0.7902	25.6	4.8
0.3525	2 0579	0.8278	25.4	4.6
0.5476	2.0971	0.8749	25.3	4.5
0.7156	2.1310	0.9197	25.2	4.4

We see from Table I, that the value of molecular polarization of dioxane is constant over a wide temperature range, on solidification the value of molecular polarization does not change and maintains the same value down to −70° C. The fluctuation of the value is only about 1%, (mean value: 24.9 cc.).

From Tables II and IV, it is shown that the molecular polarization of dioxane in the

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* $P_M=\frac{\varepsilon-1}{\varepsilon+2}\frac{M}{d}$; where M is molecular weight of dioxane.

[8] P. Debye, "Polare Molekeln", (1929), p. 46, Leipzig.

various solutions are consistent with each other and with that for pure dioxane in the liquid and the solid state. The deviations from the mean value (25.2 cc.) are slightly greater than that for pure dioxane but does not exceed 4%.

The values obtained by M. Kubo for dioxane in the gaseous state are tabulated in Table V.

TABLE V
DIELECTRIC POLARIZATION OF DIOXANE IN THE GASEOUS STATE

T(K)	P(cc.)
328.7	26.39
352.1	26.20
412.4	25.91
478.9	25.95

The difference between the values for the gaseous state and those for the solid and the liquid state is about 1 cc.

The structure of the 1,4-dioxane molecule has been investigated by various methods. X-ray data for the structure of the molecule seem to be lacking. The electron diffraction data[9,10] showed that the molecule exists predominantly in the nonpolar "chair" form[11,12].

The dielectric constants of dioxane in the gaseous state have been measured by M. Kubo[3]. It was concluded that the molecules of dioxane exists predominantly in the "chair" form, but a small amount of the molecule exists in the polar "boat" form. This conclusion was based upon the assumption that the atomic polarization is equal to 10% of the electronic polarization.

The value of the atomic polarization of N one-dimensional oscilator is calculated[1] by the following equation, provided that the latter is harmonic.

$$ {}_AP_i = \frac{Ne_i^2}{4\pi m_i \nu_i^2} = \frac{4\pi N e_i^2}{9 f_i} \qquad (1) $$

where m_i denotes the effective mass, e_i effective charge, ν_i frequency and f_i force constant, respectively.

For the bending vibration (replacing e_i/f_i by μ_i^2/V_i) equation (1) is reduced to

$$ {}_AP_i = \frac{4\pi\mu_i^2}{9V_i} \qquad (1') $$

where μ_i is bond moment and V_i is force constant for bending.

From equation (1) or (1′) we see that the smaller the frequency (or the smaller the force constant) the greater the atomic polarization. In a complex polyatomic molecule, such as 1,4 dioxane, there exist many normal vibrations, some of which may have small frequencies. If they are infra-active, their contribution to the atomic polarization may be considerably significant.

The vibrational frequencies of the dioxane molecule have been observed[9,10], except for the infra-active vibrations of small frequencies. However, the calculation of the frequencies of skeletal vibrations has been made for the "chair" form of the molecule, and it is shown that the frequencies of infra-red active deformation vibrations are about 200 cm^{-1}.

It may be expected, that the atomic polarization of the dioxane molecule in the "chair" form exceeds 10% of the electronic polarization.

So there is no evidence that we cannot attribute the observed difference between the molecular polarization and the electronic polarization entirely to the atomic polarization of the dioxane molecule in the nonpolar "chair" form.

In the following paper the theoretical calculation of the value of the atomic polarization for the dioxane molecule in the nonpolar "chair" form will be given.

We are grateful to Prof. San-ichiro Mizushima for his kind advice and encouragement throughout this work. Our thanks are also due to the Ministry of Education for a grant in aid of this research.

Summary

The dielectric constant of pure dioxane was measured in the liquid and the solid state.

The dielectric constants of dioxane solutions dissolved in various solvents were also measured.

Using Clausius-Mosotti relation, the molecular polarization of dioxane was computed. The computed value was dependent neither upon the state (solid liquid, solution) nor upon the temperature, and agreed almost exactly with the value obtained from the measurement for the gaseous substance.

The difference between the molecular polarization and the electronic polarization is ca. 4 cc. It seems natural to attribute this value to atomic polarization.

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[9] L.E. Sutton and L.O. Brockway, *J. Am. Chem. Soc.*, **57**, 473 (1935).

[10] O. Hassel, *Fra. Fysik. Verden*, **7**, 1648 (1947).

[11] D. A. Ramsay, *Proc. Roy. Soc. S. A.* **190**, 562 (1947).

[12] S.C. Burket and R.M. Badger, *J. Am. Chem. Soc.*, **72**, 4397 (1950).