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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Effect of Solvent upon the Moment of a Molecule Containing Movable Dipoles

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Previous work has shown that the dipole moment of ethylene chloride in solution in hexane[1] and in heptane[2] and in the vapor state[3] increases with rising temperature because the increasing rotational energy of the two halves of the molecule overcomes more and more the effect of the potential energy between the two —CH_2Cl's, which tends to orient the chlorines in a *trans* position of zero moment. It was found, however, that, in benzene, the apparent moment of ethylene chloride was considerably higher and independent of temperature.[1] Similar behavior was found in the case of ethylene bromide.[4] As these phenomena are intimately connected with the problem of the energy of rotation within a molecule and of the molecular condition in liquids, it has seemed desirable to obtain information as to the behavior of ethylene chloride in a variety of solvents.

Preparation of Materials

Ethylene Chloride.—Material from the Eastman Kodak Company was purified as in previous work;[2] b. p. 83.5–83.7°; n_D^{20} 1.44476.

Heptane.—Normal heptane from the Ethyl Gasoline Corporation was fractionated once; n_D^{20} 1.38771.

Benzene.—The material was treated as in earlier work.[5]

Carbon Tetrachloride.—Merck reagent was dried over fused calcium chloride and fractionated; b. p. 76.4°; n_D^{20} 1.46023.

Carbon Disulfide.—Merck reagent, which did not darken mercury in two hours, was dried over fused calcium chloride and anhydrous copper sulfate and distilled; b. p. 46.0° (754 mm.); d_4^{20} 1.2622.

Ether.—Anesthesia grade material was treated with acid permanganate solution, with sodium chloride and sodium hydroxide solution, washed with water, dried over fused calcium chloride, and distilled; b. p. 34.5° (752 mm.); d_4^{20} 0.7134.

Chloroform.—Merck reagent was dried over calcium chloride and fractionated; b. p. 61.1–61.2°; d_4^{20} 1.4892.

Method of Determination

The dielectric constants, ϵ, and densities, d, were measured with the apparatus used in previous work,[6] the former being determined at a wave length of approximately 600 meters. The polarization, P_2, of the ethylene chloride was calculated by means of the equations $P_{12} = (\epsilon - 1)(c_1M_1 + c_2M_2)/(\epsilon + 2)d$ and $P_{12} = c_1P_1 + c_2P_2$, in which P_{12} is the polarization of the mixture and P_1 that of the pure solvent, and c_1, c_2 and M_1, M_2 are the mole fractions and molecular weights of the two components. When a third component was used c_3M_3 was added to $c_1M_1 + c_2M_2$ in the numerator on the right of the first equation and the term c_3P_3 was added on the right of the second equation. The polarization of ethylene chloride at infinite dilution, P_∞, was obtained in the usual manner by extrapolation to $c_2 = 0$. However, in the dilute solutions, the variation of polarization with concentration appeared to be smaller than the experimental error, so that P_∞ was commonly obtained as the average of the P_2 values for the dilute solutions. The dipole moment μ was calculated by subtracting from P_∞ the polarization of the solid $P_E + P_A = 23.9$ determined by Dr. C. S. Hitchcock[7] and using the equation $\mu = 0.0127 \times 10^{-18} \sqrt{(P_\infty - 23.9)T}$, in which T is the absolute temperature. The moments thus obtained for ethylene chloride are given in Table I, the solvent used being given at the head of each column of moment values.

In the ethylene chloride–ether solutions as the

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(1) Meyer, *Z. physik. Chem.*, [B] **8**, 27 (1930).

(2) Smyth, Dornte and Wilson, THIS JOURNAL, **53**, 4242 (1931).

(3) Zahn, *Phys. Rev.*, **38**, 521 (1931).

(4) Smyth and Kamerling, THIS JOURNAL, **53**, 2988 (1931).

(5) Smyth and Walls, *ibid.*, **54**, 1854 (1932).

(6) Smyth, Morgan and Boyce, THIS JOURNAL, **50**, 1536 (1928); Smyth and Morgan, *ibid.*, **50**, 1547 (1928); Dornte and Smyth, *ibid.*, **52**, 3546 (1930).

(7) *Cf.* Smyth and Hitchcock, *ibid.*, **54**, 4631 (1932).

temperature fell below 0°, an apparent conductance developed and the polarization decreased instead of increasing in the normal manner. Indeed, the polarization decreased slightly even from 20 to 0°, and the apparent conductance became so great that, in the case of a solution containing as much as 0.2031 mole fraction of ethylene chloride, the bridge could not be balanced at −60°. Apparently, a slow change occurred in this latter solution with decreasing temperature, for, while the bridge could be balanced as the temperature was lowered to −20 and −40°, the conductance was too great for balancing when the temperature was raised from −60 to −40 and −20°. The moment values are not given below −20° and those at −20° and above are doubtless affected by what appears to be anomalous dispersion, presumably as the result of compound formation. It was deemed desirable, therefore, to measure an equimolecular mixture of ethylene chloride and ether in carbon tetrachloride. The last column in Table I gives the values of the apparent moment calculated for the ethylene chloride molecule in a mixture containing 0.0604 mole fraction of ethylene chloride, 0.0601 of ether, and 0.8795 of carbon tetrachloride. The moment of ether in a solution containing 0.150 mole fraction of ether in carbon tetrachloride was determined as 1.22 at −20°, 1.22 at 0° and 1.20 at 20°, the polarization being close to those found by other investigators for solutions in benzene.[8] In order to calculate the apparent moment values for ethylene chloride in the mixture, the moment of ether was assumed to be 1.22 throughout.

TABLE I

DIPOLE MOMENT (× 10^{18}) OF ETHYLENE CHLORIDE IN DIFFERENT SOLVENTS

Solvent = t, °C.	n-C_7H_{16}	C_6H_6	CS_2	CCl_4	$CHCl_3$	$(C_2H_5)_2O$	$\begin{cases}0.0601(C_2H_5)_2O\\0.8795\ CCl_4\end{cases}$
−70			1.22				
−50			1.27		1.25		
−30			1.30		1.29		
−20				1.33		1.26	1.70
−10	1.31		1.34		1.32		
0				1.36		1.37	1.76
10	1.38	1.77	1.37		1.35		
20				1.37		1.44	1.86
30	1.43	1.77	1.40		1.40		
40				1.41			1.84
50	1.49	1.76			1.42		
60				1.45			
70	1.53	1.74					
90	1.57						

As previous work had shown the marked difference of behavior of ethylene chloride in heptane and in benzene, measurements were made in a solvent varying from pure heptane to pure benzene. As the variation of the polarization of ethylene chloride with concentration had been shown to be slight or negligible in the more dilute solutions, the value of P_2 in a dilute solution was taken as P_∞, and the value of the moment calculated directly from it. Except in the first solution in the mixed solvent, where 0.05224 mole was used, approximately 0.1 mole of ethylene chloride was used for every mole of solvent. Table II gives at the top of each column of moment values the fraction of this mole which is benzene.

Discussion of Results

In Table I, the value at −10° in heptane is identical with that found by Smyth, Dornte and Wilson,[2] but, with rising temperature, the values increase a little more rapidly than do those found in the earlier investigations. It is believed that greater care in the prevention of bubble formation between the condenser cylinders makes the present values more accurate. Their continued rise as the boiling point is approached is in accord with theory. The mean value 1.76 for the solutions in benzene agrees as well as can be expected with the value 1.71 obtained from Meyer's measurements by subtracting 23.9 from the polarization in order to calculate the moment and is lower than the approximate value 1.9 given by van Arkel and Snoek.[9] The value 1.37 at 20° in carbon tetrachloride is in agreement with the approximate

TABLE II

DIPOLE MOMENT (× 10^{18}) OF ETHYLENE CHLORIDE IN BENZENE–HEPTANE MIXTURES

t, °C.	M. f. C_6H_6 in solvent = 0	0.05187	0.1957	0.4391	0.6013	0.8179	1.000
−10	1.31	1.31	1.41	1.50	1.60		
10	1.38	1.35	1.46	1.53	1.61	1.68	1.77
30	1.43	1.39	1.47	1.54	1.63	1.69	1.77
50	1.49	1.43	1.46	1.53	1.60	1.70	1.76
70	1.53	1.48	1.48	1.52	1.59	1.69	1.74
90	1.57	1.52					

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(8) Lange, *Z. Physik*, **33**, 169 (1925); Williams, *Physik. Z.*, **29**, 176 (1928); Rolinski, *ibid.*, **29**, 658 (1928).

(9) Van Arkel and Snoek, *Z. physik. Chem.*, [B] **18**, 159 (1932).

value 1.3 given by van Arkel and Snoek for room temperature, and the values in ether are slightly lower than those, 1.39–1.51, found by Mizushima and Higasi.[10] No mention is made by these investigators of anomalous dispersion such as that observed in the present investigation. In very dilute solutions measured on an apparatus involving loosely coupled circuits, it might not have been apparent.

It seems probable that the apparent moments found in ether solution are low because of anomalous dispersion and the smallness of their difference from the values in heptane, carbon disulfide, carbon tetrachloride and chloroform is, therefore, not significant. The much higher moment values obtained for ethylene chloride when it is mixed with an equimolecular quantity of ether in dilute solution in carbon tetrachloride point to compound formation between the ether and the ethylene chloride molecules. This compound formation is presumably responsible for the anomalous dispersion in the binary mixtures of ethylene chloride and ether. In the dilute solution of the complex in carbon tetrachloride, the interaction between the complex molecules may be sufficient to lower the polarization and thus give relatively lower values for the apparent moment of ethylene chloride at lower temperatures. It might be concluded that the attachment of an ether molecule to a chlorine in the ethylene chloride molecule so reduced the effect of the potential energy between the C–Cl dipoles in the two halves of the molecule that they could depart much farther from a *trans* position and so give a higher mean dipole moment. As the ether moment is probably much less affected than that of ethylene chloride, it is reasonable to suppose that the moment of the molecule of the latter in the complex is not far from 1.85. This value differs by no more than its probable error from the value 1.76 found in benzene solution.

It seems possible that benzene molecules may form loose complexes with those of ethylene chloride, increasing the moment in the same way as do the ether complexes. The benzene ring may become loosely attached to a chlorine and lessen the effect of the interaction between this chlorine dipole and that of the chlorine in the other half of the molecule. The effect upon the moment of the ethylene chloride molecule should be much the same as that of the specific chlorine–hydrogen attachment proposed by Müller[11] and of the strong local fields about the ring suggested by van Arkel and Snoek.[9]

The behavior of the moment of ethylene chloride in the benzene–heptane mixtures given in Table II appears to be somewhat complicated. As the addition of an equivalent quantity of ether to a solution of ethylene chloride in carbon tetrachloride produced a sharp rise in the apparent moment of ethylene chloride, one may conclude that the supposed ethylene chloride–benzene compound is a loose complex, easily dissociated. With increasing concentration of benzene the proportion of ethylene chloride presumably existing in the complex increases so that the observed moment increases continuously until the solvent is pure benzene. At the same time, increasing temperature should dissociate the complex and thus tend to diminish the observed moment. This decrease due to dissociation may approximately balance the increase due to increasing rotation in the free ethylene chloride molecules. For a mole fraction of benzene in the solvent smaller than 0.3, the proportion of ethylene chloride molecules entering into complex formation appears to be too small for the dissociation of the complex with rising temperature to balance the increase in moment of the free molecules. The compensation is only approximate above this concentration, but the small differences are not appreciably greater than the experimental error.

The values found by Zahn[3] for ethylene chloride vapor rise from 1.12 at 32° to 1.54 at 270.6°, much lower than the values in solution which were determined at the same temperatures. Zahn's values for the moments of ethylene bromide and ethylene chlorobromide in the vapor state[12] also are lower than the moments determined in heptane solution.[2,4] The possession of a lower moment in the vapor state than in solution is contrary to the usual behavior observed by Müller[11] for substances containing fixed dipoles. Müller found that *p*-xylene dichloride, in which the two $-CH_2Cl$ groups occurring in ethylene chloride are separated by a benzene ring, showed a slight increase in polarization with decrease in the dielectric constant approximately as observed for most substances. The two C–Cl dipoles are so far apart in the molecule that their potential en-

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(10) Mizushima and Higasi, *Proc. Imp. Acad.* (Japan), **8**, 482 (1932).

(11) Müller, *Physik. Z.*, **34**, 689 (1933).

(12) Zahn, *Phys. Rev.*, **40**, 291 (1932).

ergy relative to one another plays a small part as compared to that in the ethylene chloride molecule. When other molecules are close to this ethylene chloride molecule, they lower the effect of the mutual potential energy of the two C–Cl dipoles, which can, therefore, depart farther from a *trans* position and give the molecule as a whole a higher moment.

If the action of the solvent were merely that of a medium which, through its dielectric constant, lowered the forces between the dipoles, thus lowering their mutual potential energy, the moment observed for ethylene chloride should increase with increasing dielectric constant of the solvent. At 10°, which is selected as a convenient temperature in the middle of the range for comparison, the dielectric constants of the solvents in which there is no evidence of compound formation are: *n*-heptane, 1.94; carbon disulfide, 2.65; carbon tetrachloride, 2.25; chloroform, 5.04. The moment values for ethylene chloride at 10° in these solvents are, respectively, 1.38, 1.37, 1.37, 1.35, differences which are within the experimental error. The dielectric constants of the first three of these liquids are approximately double that of a gas, while the dielectric constant of chloroform is approximately double that of the other three. It would seem that the mere dielectric constant of the solvent is not the determining factor. The carbon disulfide and carbon tetrachloride molecules presumably contain fairly large opposing dipoles, while the chloroform molecule has a moment of 1.05. It may be that the bulk of the sulfur and chlorine atoms is sufficient to screen these dipoles and reduce or render almost negligible their effects upon other molecules. Indeed, this is suggested by the smallness of the variation of the polarization of chloroform with concentration in solution,[6] which shows little interaction between the molecular dipoles. It may be concluded that dipoles fairly well in the interior of a molecule have no detectable effect upon the internal potential energies of adjacent molecules, although they may be responsible for a major portion of the dielectric constant of the substance containing them. However, the electric field associated with the outer part of the molecule and acting over very small distances because it falls off inversely as a high power of the distance may exert an appreciable effect upon the internal energies of immediately adjacent molecules.

Summary

The dipole moment of ethylene chloride has been determined over a range of temperature in solution in heptane, benzene, carbon disulfide, carbon tetrachloride, chloroform and ether, and in certain binary mixtures of these solvents. The measurements point to the formation of a complex between ethylene chloride and ether and are best explained in the case of the benzene solutions by the supposition of an easily dissociated complex between solute and solvent. The conclusion is drawn that a dipole well in the interior of a molecule may have no detectable effect upon the internal potential energies of adjacent molecules, although the molecular field may alter the moment of an adjacent ethylene chloride molecule.

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