

THE EFFECT OF THE SOLVENT ON DIPOLE MOMENT

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ABSTRACT. The dielectric constant of dilute solutions of propyl bromide, propyl iodide, butyl chloride, butyl bromide and butyl iodide is measured in each of the solvents hexane, heptane, carbon tetrachloride, benzene and toluene by the method of resonance. The results are used to calculate the apparent electric moment in solution using the Debye equation and volume fractions.

The various empirical and theoretical relations are found suitable for representing the results. The customary extrapolation to $\epsilon=1$ for calculating μ_{gas} has failed to give consistent results. Extrapolating to $\epsilon=1.7$ the values obtained from the various relations are not only self-consistent but also agree with the experimentally determined value in the vapour state.

The formula of Goss is found to give a better agreement than the rest.

The effect of the solvent in the measurements on dipole moment was brought into prominence by the results of Müller (1933) on the polarization of chlorobenzene in a number of solvents. It was then realised that electric moments estimated from measurements on dilute solutions needed reconsideration and the problem was studied from both theoretical and practical points of view in an effort to discover a relationship between the apparent moment in solution and the real moment in the gaseous state. It is usual to extrapolate to $\epsilon=1$ to obtain the moment in the gaseous state. Davar and Paranjpe (1941) observed that extrapolation to $\epsilon=1.7$ gave a better agreement between the values derived from the various empirical equations. The present work was undertaken to re-examine the validity of the various solvent effect equations and of the suggestion of Davar and Paranjpe to extrapolate to $\epsilon=1.7$ instead of to $\epsilon=1$.

The apparent electric moment of propyl bromide, propyl iodide, butyl chloride, butyl bromide and butyl iodide was measured in each of the solvents hexane, heptane, carbon tetrachloride, benzene and toluene. Sugden (1937) has determined the electric moment in the vapour state of the solutes and his values are useful for comparison with our experimental results.

The apparatus and the procedure are the same as in the previous work on this subject carried out in this laboratory, except that in the present work a tri-tet crystal-controlled oscillator was used.

Tables Ia and Ib give the experimental results.

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TABLE Ia

	Propyl Bromide			Propyl Iodide		
	∞P_2	∞P_{E_2}	μ_{sol}	∞P_2	∞P_{E_2}	μ_{sol}
Hexane ...	111.2	24.0	2.07	102.2	25.1	1.94
Heptane ...	109.5	21.0	2.06	100.4	25.2	1.92
Carbon Tetrachloride ...	104.9	24.0	1.99	98.7	27.9	1.86
Benzene ...	102.3	23.4	1.97	98.6	29.3	1.84
Toluene ...	98.9	23.2	1.93	95.8	27.7	1.83

TABLE Ib

	Butyl Chloride			Butyl Bromide			Butyl Iodide		
	∞P_2	∞P_{E_2}	μ_{sol}	∞P_2	∞P_{E_2}	μ_{sol}	∞P_2	∞P_{E_2}	μ_{sol}
Hexane ...	109.3	24.8	2.03	114.6	25.6	2.09	111.1	29.2	2.00
Heptane ...	108.9	25.3	2.02	114.2	30.4	2.03	110.8	30.4	1.98
Carbon Tetrachloride ...	103.3	25.3	1.95	108.6	28.4	1.98	109.6	33.0	1.94
Benzene ...	102.3	25.6	1.94	107.4	27.5	1.98	106.2	32.3	1.93
Toluene ...	100.4	25.5	1.92	105.8	27.5	1.96	105.8	32.4	1.90

∞P_2 stands for molar polarization of the solute at infinite dilution.

∞P_{E_2} stands for electronic polarization (molar refraction) of the solute at infinite dilution.

μ_{sol} stands for the electric moment in solution.

In calculating the molecular polarization we used Van Arkel and Snoek's (1934) modification based on volume fractions. In this method it is not necessary to determine the density of the solution at different concentrations and the observations and calculations are considerably simplified. Polarization at infinite dilution was calculated on the assumption of Sugden's relation. The electronic polarization, P_{E_2} , was calculated from the measurement of refractive index using a Pulfrich refractometer (Na-D lines). The electric moment of the solute was calculated from

$$\mu = 0.01273 \sqrt{(\infty P_2 - \infty P_{E_2})T} \text{ Debye units,}$$

T being the absolute temperature of the solution.

The discussion of our experimental results will be considerably facilitated by dividing the discussion under three headings, viz. (1) empirical relations for correcting the solvent effect, (2) theoretical considerations of factors not included in the Debye equation and (3) the empirical relations of Goss.

I. EMPIRICAL RELATIONS FOR CORRECTING THE SOLVENT EFFECT

The following empirical relations have been tried :—

$$\frac{P_0^{\text{sol}}}{P_0^{\text{gas}}} = 1 - 0.075 (\epsilon - 1)^2 \quad (\text{Müller, 1933, 1934})$$

$$P_2 = A \pm B \frac{\epsilon - 1}{\epsilon + 2} \quad (\text{Sugden, 1934})$$

$$P_2 = K_1 + \frac{K_2}{\epsilon} \quad (\text{Jenkins, 1934})$$

$$P_2 = \frac{a}{\sqrt{\epsilon}} \quad (\text{Davar and Paranjpe, loc. cit.})$$

Tables II and III give the values of P_0^{gas} and μ_{gas} calculated from our observations on the assumption of Müller's relation.

TABLE II
 P_0^{gas} calculated from Müller's relation

	Propyl Bromide	Propyl Iodide	Butyl Chloride	Butyl Bromide	Butyl Iodide
Hexane	92.57	81.80	89.66	94.55	87.07
Heptane	92.	80.60	89.51	89.69	86.06
Carbon Tetrachloride	91.05	79.68	87.70	90.17	86.20
Benzene	89.60	78.78	87.11	90.75	86.17
Toluene	87.89	79.08	86.98	90.96	85.21
Mean	90.75	79.98	88.19	91.24	86.14
Observed values in vapours (Sugden)	94.45	82.55	90.97	94.45	88.40

TABLE III
 μ_{gas} calculated from Müller's relation

	Propyl Bromide	Propyl Iodide	Butyl Chloride	Butyl Bromide	Butyl Iodide
Hexane	2.13	2.00	2.10	2.15	2.06
Heptane	2.13	1.99	2.09	2.10	2.05
Carbon Tetrachloride	2.11	1.98	2.07	2.10	2.05
Benzene	2.09	1.96	2.07	2.11	2.05
Toluene	2.07	1.97	2.06	2.11	2.04
Mean	2.11	1.98	2.08	2.11	2.05
Observed values in vapours (Sugden)	2.15	2.01	2.11	2.15	2.08

Tables IV and V give similar values calculated on the assumption of other relations. In each table we give Sugden's values as determined in the vapour state for ready reference.

TABLE IV

P_2^{gas} calculated from empirical relations
(extrapolation $\epsilon=1$)

	Propyl Bromide	Propyl Iodide	Butyl Chloride	Butyl Bromide	Butyl Iodide
Sugden's relation	146.4	115.5	134.6	140.4	127.0
Davar & Paranjpe's relation	157.2	119.8	142.2	148.1	131.9
Jenkins' relation	169.3	124.7	150.5	156.6	148.6
Observed values in vapours (Sugden)	118.2	111.5	116.4	122.8	121.9

TABLE V

P_2^{gas} calculated from empirical relations
(extrapolation $\epsilon=1.7$)

	Propyl Bromide	Propyl Iodide	Butyl Chloride	Butyl Bromide	Butyl Iodide
Sugden's relation	117.8	104.1	113.8	119.3	114.5
Davar & Paranjpe's relation	118.6	104.4	114.4	119.8	114.9
Jenkins' relation	119.4	104.7	114.9	120.3	117.4
Observed values in vapours (Sugden)	118.2	111.5	116.4	122.8	121.9

It will be seen from these tables that none of the relations when extrapolated to $\epsilon=1$ give consistent results. When the extrapolation is carried out only to $\epsilon=1.7$, the values obtained from the various relations are not only self-consistent but they also agree with the experimentally determined value in the vapour state. It should be pointed out that the extrapolation to $\epsilon=1.7$ does not appear to improve the agreement in the case of propyl iodide.

II. THEORETICAL CONSIDERATION OF FACTORS NOT INCLUDED IN THE DEBYE EQUATION

All the theories of the solvent effect agree in stating that

$$\mu_s = \mu_{\text{gas}} + \mu_{\text{induced}}$$

They, however, differ from one another in considering the various factors responsible for the induced moment, μ_{induced} . Still all agree in assuming that

μ_{induced} depends on the shape of the molecule and the position of the dipole in it. The parameters in the following relations depend on these two factors, viz., the shape of the molecule and the position of the dipole:—

$$\frac{\mu_{\text{sol}}}{\mu_{\text{gas}}} = 1 + \frac{\epsilon - 1}{\epsilon + 2} C \quad (\text{Weigle, 1933})$$

$$\mu_{\text{sol}} = a + \frac{b}{\epsilon} \quad (\text{Frank, 1935})$$

where $a = (1 + A_1 + A_2) \cdot \mu_{\text{gas}}$ and $b = -(A_1 + A_2) \cdot \mu_{\text{gas}}$.

Here also μ_{gas} can be calculated for $\epsilon = 1$ and for $\epsilon = 1.7$ and again as before $\epsilon = 1.7$ gives a much better agreement (Tables VI and VII). Further, we find that an equation of the type

$$\mu_{\text{sol}} = \frac{a}{\sqrt{\epsilon}}$$

can also be applied to the experimental results.

TABLE VI

μ_{gas} calculated from the equations of Weigle, Frank, and the authors
(extrapolation $\epsilon = 1$)

	Propyl Bromide	Propyl Iodide	Butyl Chloride	Butyl Bromide	Butyl Iodide
Weigle's equation	2.48	2.26	2.37	2.33	2.28
Frank's equation	2.68	2.46	2.58	2.50	2.45
Authors' equation	2.55	2.35	2.47	2.41	2.36
Observed values in vapours (Sugden)	2.15	2.01	2.11	2.15	2.08

TABLE VII

μ_{gas} calculated from the equations of Weigle, Frank, and the authors
(extrapolation $\epsilon = 1.7$)

	Propyl Bromide	Propyl Iodide	Butyl Chloride	Butyl Bromide	Butyl Iodide
Weigle's equation	2.15	1.99	2.09	2.11	2.05
Frank's equation	2.14	2.01	2.11	2.11	2.06
Authors' equation	2.14	2.00	2.10	2.11	2.06
Observed values in vapours (Sugden)	2.15	2.01	2.11	2.15	2.08

Hobbs (1939) has modified Onsager's theory of reaction field and calculated the value of ∞P_0^{sol} from the known values of P_0^{gas} . In the present work we determine P_0^{sol} experimentally and we desire to calculate P_0^{gas} . We, therefore rewrite Hobbs's equation as

$$\frac{P_0^{\text{gas}}}{P_0^{\text{sol}}} = 1 + \frac{C'\mu R}{3KT}$$

The results obtained on the assumption of this equation are given in Table VIII.

TABLE VIII

P_0^{gas} and μ_{gas} calculated from Hobbs's equation

		Propyl Bromide	Propyl Iodide	Butyl Chloride	Butyl Bromide	Butyl Iodide
P_0^{gas}	Calculated from Hobbs's equation	115.3	92.8	102.1	100.2	95.3
	Observed values in vapours (Sugden)	94.5	82.6	91.0	94.5	88.4
μ_{gas}	Calculated from Hobbs's equation	2.38	2.13	2.24	2.22	2.16
	Observed values in vapours (Sugden)	2.15	2.01	2.11	2.15	2.08

It will be seen that the values of P_0^{gas} and μ_{gas} thus calculated are much higher than those experimentally observed by Sugden for vapours. This probably means that in this calculation, following Hobbs, we have over-emphasised the effect of the reaction field.

We also tried to calculate the values of μ_{gas} by using the following equation of Higasi (1936) :

$$\frac{\mu_{\text{sol}}}{\mu_{\text{gas}}} = 1 + 3 \frac{\epsilon - 1}{\epsilon + 2} A.$$

As direct determination of the ratio of the axes of molecular ellipsoid as required by Higasi is not available for the solutes, an attempt was made to estimate it by three methods, *viz.* (1) from optical polarizabilities, (2) from molecular model and X-ray data, and (3) from the empirical relations of Goss. Values of μ_{gas} calculated with the values of this ratio obtained by these three methods showed differences among themselves and the agreement with the value of μ_{gas} observed is not satisfactory, the variations being from 5% to 10%.

III. THE EMPIRICAL RELATIONS OF GOSS

The assumptions made by Goss (1937, 1940) in his empirical relations for the solvent effect are the same as those of Raman and Krishnan, and Onsager. Goss's equation is

$$P_s = P_{s+A} + \left(\frac{\epsilon - 1}{\epsilon + 2} \right)^4 \cdot Z + \frac{Y}{\epsilon}$$

where $P_{s+A} = 1.05 [R_L]_D$, 5% of the molar refraction being added to account for the atomic polarization. Y and Z are constants.

Goss uses a graphical method to determine the value of these parameters Y and Z. He, however, uses a curvilinear extrapolation of the graph which cannot be justified. His formula and the index 4 attributed to $\frac{\epsilon - 1}{\epsilon + 2}$ seems to be reasonable. We have seen by trial and error method that index 4 gives the best agreement between the experimental values from solution and vapour data. Thus we prefer to retain Goss's equation but not his method of curvilinear extrapolation. Even here extrapolations to higher values than $\epsilon = 1$ seems to give better agreement. We observed that the values calculated from the formula of Goss without the curvilinear extrapolation give a better agreement with Sugden's data for vapours. This agreement is much better than the agreement obtained by the use of any other empirical formula.

TABLE IX

μ_{gas} calculated from different equations

$\epsilon = 1.7$ for all solvents (together)

$\epsilon = 1.81$ for carbon tetrachloride (singly)

Equations	Propyl Bromide	Propyl Iodide	Butyl Chloride	Butyl Bromide	Butyl Iodide
Müller	2.10	1.98	2.08	2.11	2.05
Jenkins	2.17	1.95	2.09	2.13	2.05
Sugden	2.15	1.94	2.08	2.12	2.02
Davar and Paranjpe	2.16	1.95	2.09	2.12	2.02
Weigle	2.15	1.99	2.09	2.11	2.05
Frank	2.14	2.01	2.11	2.11	2.06
Authors	2.14	2.00	2.10	2.11	2.06
Goss	2.14	2.00	2.10	2.13	2.08
Mean of 2 to 8	2.15	1.98	2.09	2.12	2.05
Observed values in vapours (Sugden)	2.15	2.01	2.11	2.15	2.08

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