CLXXXV.—*The Electrical Energy of Dipole Molecules in Solution, and the Solubilities of Ammonia, Hydrogen Chloride, and Hydrogen Sulphide in Various Solvents.*

By Ronald P. Bell.

Born (*Z. Physik*, 1920, **1**, 45) has calculated the electrical energy of an ion in a continuous medium of given dielectric constant, assuming the ion to be a conducting sphere. As a simplifying assumption, the difference of the electrical energies for two different media can be identified with the reversible work connected with the transference of an ion from one medium to another. Such considerations have been applied to the partition of ions between two media (Scatchard, *J. Amer. Chem. Soc.*, 1925, **47**, 2098; LaMer and Goldman, *ibid.*, 1931, **53**, 473; Bjerrum and Larsson, *Z. physikal. Chem.*, 1927, **127**, 358; Bjerrum, *Trans. Faraday Soc.*, 1927, **23**, 445; Brönsted and Delbanco, *Ber.* 18 *Skand. Naturforskermøde*, 1929, 220), acidity in different media (Brönsted, *Chem. Rev.*, 1928, **5**, 296), heat of dilution of strong electrolytes (Bjerrum, *loc. cit.*), etc. In general, only a qualitative agreement with experiment is found, even when corrections are applied for " non-electrical " molecular forces and the partial solvation of the ions (Bjerrum and Larsson, *loc. cit.*). The reason for the discrepancies lies probably in the incorrectness of the assumption that the solvent directly surrounding the ion is continuous and has the same dielectric constant as the pure solvent in bulk. Thus Webb (*J. Amer. Chem. Soc.*, 1926, **48**, 2589) has shown that a better agreement is obtained by taking into account the clustering of the water dipoles round the ion.

Even in the absence of a free charge, a molecule may be surrounded by an electrical field due to the imperfectly symmetrical distribution of electricity in its interior, describable in the simplest case as a dipole moment. In aqueous solutions, such fields are probably small compared with those due to ions, but in solvents of low dielectric constant, where free ions cannot exist, the dipole fields may be of importance. By assuming a simple model for the dipole molecule, we can again calculate the energy of its electrical field in different media, and as before tentatively identify the difference of those energies with the free energies of transfer of the molecule between different media. The simplest model is that of a rigid sphere of dielectric constant unity, with a dipole situated at its centre, the distance of separation of the charges of the dipole being small compared with the radius of the sphere. Falkenhagen

(*Physikal. Z.*, 1922, **23**, 87) has shown that it is possible to calculate the second virial coefficients and viscosities of a number of dipole gases on the basis of this simple model. Independently of any particular model, we can, however, predict that for any given rigid molecule, the energy of the electric field will depend only on, and vary continuously with, the dielectric constant of the surrounding medium. (This will be true not only for dipole molecules, but for molecules possessing higher types of electrical symmetry—quadrupoles, octupoles, etc.)

As in the case of ions, it is questionable whether we can consider the dielectric constant in the immediate neighbourhood of the molecule as being equal to the macroscopic dielectric constant of the solution, especially since dipole forces are more "short-range" in character than those of ionic origin. It is possible, however, that the assumption may be more justified in this case, since the field about the dipole is unsymmetrical, and the clustering effects will be opposite on the two sides. Further, we are in this case not confined to ionising solvents, which in general contain the highly polar hydroxyl groups, but can use solvents possessing more symmetrical molecules, which will not be so prone to orientation round the solute molecule.

If the gas laws are assumed to hold, the reversible work of transferring a molecule from one medium to another is related to the partition coefficient by the equation

$$A = \kappa T \log_e c_2/c_1$$

If the substance in question is incompletely miscible with both media, we can write

$$A = \kappa T \log_e s_2/s_1 \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

where s_1 and s_2 are the solubilities in the two solvents, the gas laws again being assumed. The determination of the solubility of dipole molecules in solvents of different dielectric constants thus provides a means of testing the above considerations concerning the electrical energy of the two dipole fields.

As solutes we have chosen ammonia, hydrogen chloride, and hydrogen sulphide, each of which has a well-defined dipole moment, is readily determined by chemical means, and is not too soluble in inert solvents. The solvents used were all hydrocarbons or their chloro- or bromo-derivatives, thus obviating the possibility of ionisation or solvation for the solutes concerned. In using the solubilities as a measure of the change of free energy in passing from one solvent to another, we are assuming that the gas laws are valid for each solution. Wynne-Jones (J., 1930, 1064) has shown that this is the case for solutions of hydrogen chloride in benzene and nitrobenzene. Bell and Feild (*J. Amer. Chem. Soc.*, 1911, **33**, 940) have determined the partition coefficients of ammonia between water and chloroform, and a combination of their data with those of Perman (J., 1903, **83**, 1168) for the partial vapour pressure of aqueous solutions shows that there is proportionality between the concentration of ammonia in the chloroform and its vapour pressure. The same is also found to be the case for the partition coefficients of ammonia between water and carbon tetrachloride or bromoform, given in the International Critical Tables. It is thus reasonable to suppose that there are no large divergences in any of the solutions studied here.

EXPERIMENTAL.

Preparation of Gases.—The hydrogen chloride was prepared by dropping pure concentrated hydrochloric acid into pure concentrated sulphuric acid, the hydrogen sulphide by dropping a saturated solution of sodium sulphide into 6*N*-hydrochloric acid, and the ammonia was obtained from a cylinder. Each gas was dried by calcium chloride, and the air was thoroughly removed from the generating flasks and connecting tubes by a rapid current of gas before they were connected to the solubility apparatus.

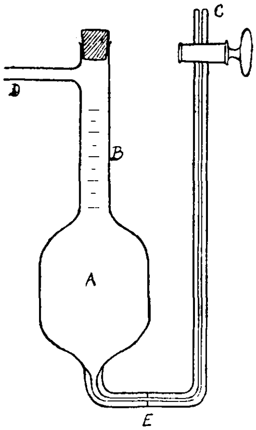
Preparation of Solvents.—The solvents used were all " zur Analyse " products from Merck or Kahlbaum, with the exception of tetrachloroethane, tetrachloroethylene, and trichloroethylene, which were obtained by fractionating commercial products. Before use, all solvents were dried over calcium chloride and redistilled, the middle portion being used. The following table gives the (uncorrected) boiling-point ranges of the final products.

Solvent.	B. p.	Solvent.	B. p.
Hexane	67·1—67·6°	Chloroform	60·6—61·6°
*cyclo*Hexane	81·30—81·40	Bromobenzene	155·0—155·3
Carbon tetrachloride...	76·20	Chlorobenzene	130·8—131·2
Benzene	79·60—79·65	Benzyl chloride ...	177·0—177·5
Toluene	110·0—111·0	Benzotrichloride ...	216·5—217·5
Tetrachloroethylene ...	119·0—120·0	*s*-Tetrabromoethane	107—109/11 mm.
Trichloroethylene	85·9—86·0	*s*-Tetrachloroethane	144·0—144·8
Pentachloroethane ...	158—160	Ethyl bromide	37·0—37·5
Bromoform..............	148—149	Ethylene chloride...	83·2—84·2
Ethylene bromide ...	129—131		

Method of Solubility Determination.—The principle of the method employed was to saturate the solvent with the gas in question, and then to remove all the gas from a known amount of solution by a current of air, the amount of gas in the emerging air current being determined by chemical means. The solvent was contained in the apparatus shown in Fig. 1. The volume of the bulb *A* was *ca*. 50 c.c., and the tube *B* was graduated in 0·1 c.c. In taking readings of volume, the liquid surface in the capillary was always adjusted to the mark *E*, by applying a slight pressure at *C*, and the apparatus was calibrated by weighing with water adjusted to the same mark. The apparatus was contained in a thermostat at 20° ± 0·01°, the level of the thermostat water coming a little below the tube *D*.

The saturating gas entered through *C* and bubbled at first rapidly, and later more slowly, through the liquid. In the case of volatile solvents, the gas was first approximately saturated with the solvent vapour by passing through a small bubbler also contained in the thermostat, in order to prevent undue evaporation and consequent fall of temperature. Saturation was continued for about 3 hours, and the total amount of gas passed was 8—10 times the amount corresponding to complete saturation. (Experiments with longer periods of saturation showed that this was sufficient.) The gas current was then stopped, the tube *D* closed by a rubber cap, and the volume of the solution read off at *B*. The barometric pressure was also read. *D* was then connected to the apparatus for absorbing the gas, and a slow current of dry, carbon dioxide-free air was led in through *C*. After a time the air-stream was quickened, and was continued in all for 8—10 hours. Calculation showed that the volume of air thus passed should be sufficient to remove 99·9% of the gas even from the most concentrated solutions, and a further period of aeration employed as a test in a few cases gave a negligible amount of gas.

FIG. 1.



Absorption and Estimation of Gases.—Hydrogen chloride was absorbed in water and titrated with *N*-sodium hydroxide. Two U-tubes were used, the first containing *ca.* 50 c.c. of water and the second *ca.* 10 c.c. There was rarely sufficient hydrogen chloride in the second tube to change the colour of methyl-red, and never any appreciable quantity. Ammonia was absorbed in a similar manner, but in a known volume of *N*-hydrochloric acid, which was afterwards titrated with *N*-sodium hydroxide. Here again the amount absorbed by the second tube was negligible. Hydrogen sulphide was absorbed in a known volume of *N*-sodium hydroxide containing excess of neutral 30% hydrogen peroxide above that required for oxidation to sulphate. On account of the heat evolved during absorption, the first U-tube was replaced by a flask, which was immersed in cold water. After absorption, the excess hydrogen peroxide was destroyed by heating to 60—70° until gas evolution had ceased, and after cooling, the excess alkali was titrated with *N*-hydrochloric acid. The amount of hydrogen sulphide absorbed by the second tube never amounted to more than 1% of the whole.

In the case of ammonia, there is a possibility that for some halogenated solvents a chemical reaction may take place with sufficient velocity to interfere with the determination of solubility. For several solvents it was, in fact, found that, on standing, a solid substance separated, presumably either the hydrochloride of the organic base formed or ammonium chloride. For such solvents, therefore, determinations were not carried out with ammonia. For the solvents for which results are given, there was no evidence of chemical reaction; in a few cases where such reaction seemed probable, the density and b. p. of the solvent remaining after removal of ammonia were determined and found to be identical with those of the original liquid.

Calculation of Results.—The solubility of the gas referred to 760 mm. and 20° was calculated from the equation

$$c = 760(m - a)/v(P - p + p'),$$

in which c = solubility (in equivs./litre); m = equivs. of gas absorbed; a = correction for gas contained between the liquid surface in *B*, and *D* (Fig. 1); v = volume of solution (litres); P = atmospheric pressure in mm.; p = vapour pressure correction, mm.; p' = correction for hydrostatic pressure of solution, taken as the pressure due to a column of pure solvent having one half the height between *E* and the liquid surface in *B*.

The corrections a and p' were both very small. The vapour pressure p was in most cases taken to be that of the pure solvent, the values being taken from "International Critical Tables." (In the case of benzyl chloride, tetrabromoethane, tetrachloroethylene, and trichloroethylene, the values were extrapolated from data at higher temperatures.) In a few cases where both the solubility and the vapour pressure are high, a correction has been made for the vapour-pressure lowering caused by the solute. This has been done for ammonia in ethylene chloride, carbon tetrachloride, and chloroform; and for hydrogen chloride and hydrogen sulphide in carbon tetrachloride, chloroform, ethylene chloride, and ethyl bromide. This correction, which was in all cases small, was calculated on the assumption that the partial pressure of the solvent is proportional to its mole-fraction.

In the tables of values given, the volume solubility is expressed as s, the partition coefficient between the liquid and the vapour, *i.e.*, $s = c/0{\cdot}0417$, since $s/c = 22{\cdot}4 \times 293/273$. We have also given the mole-fraction solubilities x, calculated on the assumption that the densities of the solutions obey the ideal mixture law. (Since the density is never far different from that of the pure solvent, no appreciable error will be introduced by deviations from this law.)

In the column D_0, we have given the dielectric constants of the pure solvents at 20°, the values being taken from International Critical Tables, with the exception of those for the normal paraffins, which are from the work of Dornte and Smyth (*J. Amer. Chem. Soc.*, 1930, **52**, 3546). We have also calculated the dielectric constants of the saturated solutions (D), assuming the Clausius–Mosotti mixture law in the form

$$\frac{D-1}{D-2} \cdot \frac{x_1M_1 + x_2M_2}{\rho} = x_1\frac{D_1-1}{D_1+2} \cdot \frac{M_1}{\rho_1} + x_2\frac{D_2-1}{D_2+2} \cdot \frac{M_2}{\rho_2}$$

where the D's represent the dielectric constants, ρ's the densities, M's the molecular weights, and x's the mole-fractions of the two components corresponding to the subscripts, and ρ is the density of the mixture. It will be seen that the values obtained differ but little from those for the pure solvents.

The values for the solvents octane, dodecane, and cetane are taken from hitherto-unpublished measurements by Professor Brönsted and Miss Volqvartz in this laboratory, each being the mean of several determinations. Most of the other values correspond to one determination only, but repetitions in a few cases gave values agreeing to within 1%, which may be taken as the probable accuracy of the results.

Ammonia.

Solvent.	D_0.	D.	s.	x.
Hexane	1·89	1·91	4·16	0·0223
Octane	1·95	1·96	2·56	0·0170
Dodecane	2·02	2·04	2·13	0·0197
Cetane	2·05	2·08	1·84	0·0219
Carbon tetrachloride	2·24	2·28	7·17	0·0281
Benzene	2·28	2·32	9·95	0·0474
Toluene	2·39	2·42	7·23	0·0313
Chloroform	5·05	5·88	69·8	0·193
Bromobenzene	5·40	5·50	8·08	0·0340
Chlorobenzene	5·88	6·11	11·35	0·0423
Benzyl chloride	6·40	6·69	12·20	0·0556
Ethylene chloride	10·50	11·20	26·6	0·0797

	Hydrogen Chloride.				*Hydrogen Sulphide.*			
Solvent.	D_0.	D.	s.	x.	D_0.	D.	s.	x.
Hexane	1·89	1·90	3·64	0·0197	1·89	1·90	6·30	0·0341
Octane	1·95	1·96	4·50	0·0296	1·95	1·96	6·80	0·0440
Dodecane	2·02	2·05	3·42	0·0314	2·02	2·07	5·71	0·0513
Cetane	2·05	2·07	2·28	0·0270	2·05	2·08	5·05	0·0578
*cyclo*Hexane	2·05	2·05	3·42	0·0154	2·05	2·07	7·50	0·0338
Carbon tetrachloride	2·24	2·22	4·54	0·0181	2·24	2·29	10·79	0·0419
Benzene	2·28	2·31	11·05	0·0425	2·28	2·35	15·68	0·0563
Toluene	2·39	2·39	11·90	0·0507	2·39	2·41	16·90	0·0672
Tetrachloroethylene	2·46	2·52	3·88	0·0163	2·46	2·55	8·90	0·0372
Trichloroethylene	3·42	3·44	5·79	0·0206	3·42	3·41	13·16	0·0482
Pentachloroethane	3·70	3·75	3·86	0·0214	3·70	3·81	10·63	0·0514
Bromoform	4·51	4·62	4·78	0·0306	4·51	4·70	16·76	0·0581
Ethyl bromide	4·86	4·96	10·3	0·0348	4·86	5·09	17·80	0·0608
Chloroform	5·05	5·08	13·80	0·0444	5·05	5·24	32·8	0·103
Bromobenzene	5·40	5·43	7·13	0·0305	5·40	5·60	12·92	0·0376
Chlorobenzene	5·94	5·88	7·63	0·0315	5·88	5·97	13·80	0·0388
Benzyl chloride	6·40	6·58	9·75	0·0448	—	—	—	—
Benzotrichloride	6·40	6·37	4·77	0·0275	—	—	—	—
s-Tetrabromoethane	7·10	7·33	3·93	0·0236	7·10	7·40	9·49	0·0446
s-Tetrachloroethane	8·20	8·30	6·20	0·0265	8·20	8·48	16·66	0·0702
Ethyl bromide	9·45	9·63	35·15	0·1019	9·45	9·62	43·3	0·126
Ethylene chloride	10·50	10·40	14·74	0·0457	10·50	10·50	23·0	0·0719

Discussion of Results.

It is clear from the tables that in no case is there a rigid connexion between the partition coefficients and the dielectric constants of the solutions. There is, however, in each case a tendency to increasing solubility with increasing dielectric constant.

There are two factors, which may account for the absence of a greater regularity. (*a*) The solute molecule may be deformed in the different media. (*b*) The presence of the solute molecule may displace the solvent molecules in its neighbourhood from their normal spacing and orientation distribution. This effect may be regarded as being due partly to the molecular fields, and partly to purely spatial considerations, arising from the fact that the solute and solvent molecules have not in general the same size.

It is not probable that a change of medium produces any great deformation of dipole molecules, since it has been shown by Hassel and Uhl (*Z. physikal. Chem.*, 1930, *B*, **8**, 187) that the dipole moment is but little dependent on the solvent used, even when the latter is of a polar character. The probable cause for the failure of the simple theory is therefore (*b*) above. In other words, in this case, as in the case of ions, it is not permissible to consider the solvent as a homogeneous medium. The solubilities will depend on individual properties of the solvent molecule (size, shape, polar characteristics, etc.) and it is at present impossible to give any further theoretical treatment.

It is, however, of interest to calculate the magnitude of the partition coefficients derived from the simple theory, taking the model mentioned on p. 1371. To obtain an idea of the order of magnitude of the effects to be expected, it is sufficient to calculate the electrical energy of the external field in a vacuum, and hence obtain a maximum value for the partition coefficient, *i.e.*, the partition coefficient between a solvent of infinitely great dielectric constant, in which this electrical energy becomes zero, and the gas phase.

According to electrostatic theory, the electrical energy in a vacuum of a volume element ds where the field strength is E, is

$$dF = (E^2/8\pi)ds.$$

In the present case, since there is circular symmetry about the axis of the dipole, we can write for the total electrical energy outside the sphere of radius β

$$F = \frac{1}{8\pi}\int_\beta^\infty\int_0^{\pi/2} E^2 \,.\, 4\pi r^2 \,.\, \sin\theta \,.\, dr \,.\, d\theta$$

where E is the field at a point having polar co-ordinates r, θ, referred to the centre of the sphere and the axis of the dipole. When the separation of the charges of the dipole is small compared with r, we have

$$E = \mu\sqrt{1 + 3\cos^2\theta}/r^3$$

where μ = dipole moment, and hence

$$F = \frac{\mu^2}{2}\int_\beta^\infty\int_0^{\pi/2}\frac{1}{r^4}\sin\theta(1 + 3\cos^2\theta) \,.\, dr \,.\, d\theta$$
$$= \mu^2/3\beta^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In the following table we have calculated according to equation (2) the electrical energies of a few simple dipole molecules in a vacuum, and the corresponding " maximum " distribution coefficients at 20° according to the equation

$$F = \kappa T \log_e s_{\mathrm{max.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

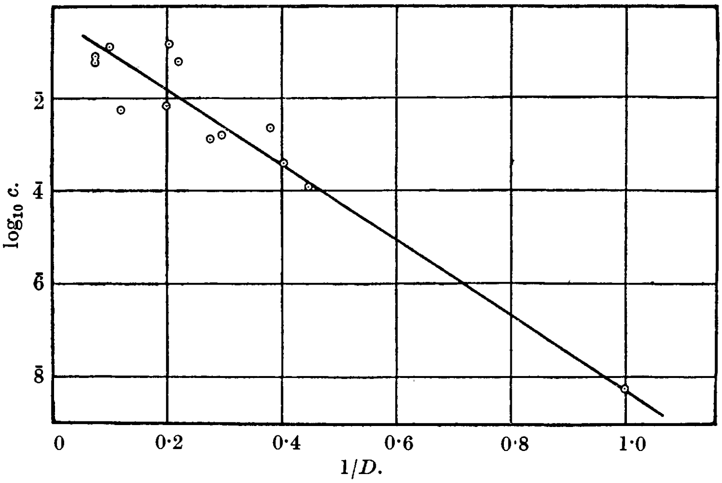
The values for the dipole moments and molecular radii are taken from the table given by Braune and Linke (*Z. physikal. Chem.*, 1930, *A*, **148**, 195).

Molecule.	$\mu \times 10^{18}$.	$\beta \times 10^8$.	$F \times 10^{13}$.	s_{max}:
HCl	1·03	1·47	1·12	16
HBr	0·788	1·56	0·54	3·9
HI	0·382	1·72	0·095	1·03
H_2O	1·87	1·14	7·82	2·9 × 10^8
H_2S	0·93	1·57	0·74	6·4
NH_3	1·44	1·20	4·23	3·9 × 10^4
SO_2	1·61	1·76	1·58	51
CH_3Cl	1·97	1·80	2·22	85

We can conclude from these figures that even for solvents of low dielectric constant, the electrical energy of dipole molecules can sometimes play a large part in determining their solubility (and related properties). In connexion with the small effect calculated for the hydrogen halides, it has previously been pointed out by Eucken and Meyer (*Z. physikal. Chem.*, 1930, **8**, 187; compare Braune and Linke, *loc. cit.*) that Falkenhagen's calculation (*loc. cit.*) of the intermolecular forces for dipole gases gives much too low results for these gases, probably owing to the fact that the dipole moment observed is the resultant of several electric displacements within the molecule. It also seems probable in the present calculation that the electrical energy is greater than that calculated on the basis of a simple dipole structure, and the same may be true for hydrogen sulphide.

FIG. 2.

Mercuric chloride.



In the solutions studied in the present work, the solute molecules are in all cases smaller than those of the solvent. There would seem more justification in assuming the solvent to be a continuous medium in the case where its molecules are small compared with those of the solute, and it would thus be of interest to study the solubility relations of much larger dipole molecules. (It will not, however, be of any use to take a large molecule containing a small polar group, since, for example, the distance of closest approach of the solvent molecules to the solute molecule is probably much the same for solutions of ethyl alcohol and cetyl alcohol.) We have collected data for the solubilities of the mercuric halides in inert solvents in the following tables (compare also Walden, "Elektrochemie nichtwässerige Lösungen, 1924, p. 433). The letters in the last column refer to the table of authors. In the case of the chloride in ethylene chloride and the iodide in carbon tetrachloride, there exist two discordant determinations: we have given both in the tables and the figures. The values given under "vacuum" corre-

FIG. 3.

Mercuric bromide.

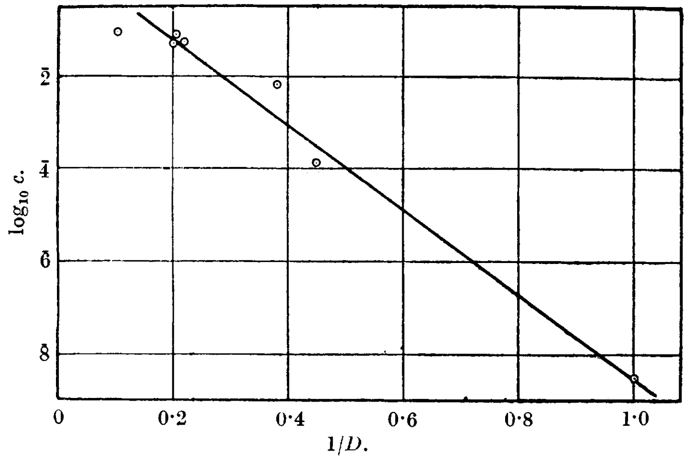
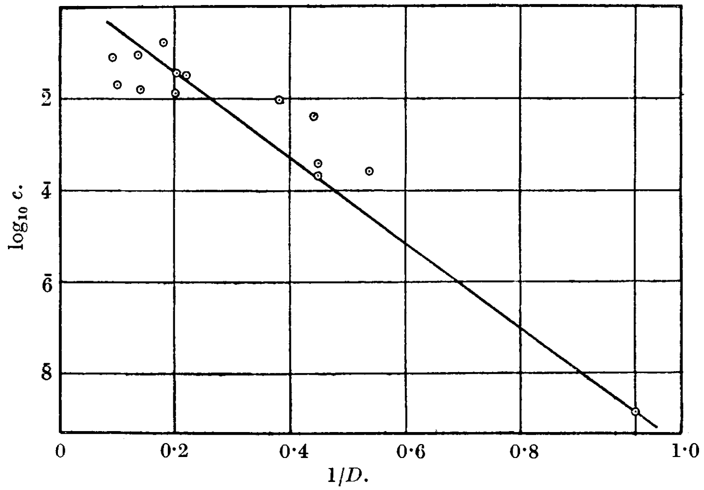


FIG. 4.

Mercuric iodide.



spond to the vapour pressure of the salts extrapolated by the equations given in the International Critical Tables for higher temperatures, and may, of course, be considerably in error.

In the following tables, c = solubility (in mols./litre) and D = dielectric constant of the pure solvent. In Figs. 2, 3, and 4, $\log_{10} c$ is plotted against $1/D$.

Mercuric chloride (25°).

Solvent.	c.	$\log_{10} c$.	D.	$1/D$.	Ref.
Ethylene chloride	0·0570	$\bar{2}$·756	10·5	0·095	(a)
,, ,,	0·0802	$\bar{2}$·904	,,	,,	(b)
s-Tetrachloroethane	0·00530	$\bar{3}$·724	8·20	0·122	(a)
Chloroform	0·00554	$\bar{3}$·774	5·05	0·199	(a)
Pentachloroethane	0·00128	$\bar{3}$·107	3·60	0·276	(a)
Trichloroethylene	0·00149	$\bar{3}$·173	3·42	0·291	(a)
Tetrachloroethylene	0·000402	$\bar{4}$·604	2·46	0·405	(a)
Carbon tetrachloride	0·00012	$\bar{4}$·079	2·24	0·448	(c)
Bromoform	0·0650	$\bar{2}$·813	4·51	0·222	(c)
Ethyl bromide	0·133	$\bar{1}$·124	9·45	0·106	(c)
Ethylene bromide	0·154	$\bar{1}$·188	4·86	0·206	(c)
Carbon disulphide	0·00239	$\bar{3}$·378	2·64	0·380	(d)
Vacuum	5×10^{-9}	$\bar{9}$·748	1·00	1·00	

Mercuric bromide (18—20°).

Solvent.	c.	$\log_{10} c$.	D.	$1/D$.	Ref.
Carbon disulphide	0·00665	$\bar{3}$·823	2·64	0·380	(d)
Chloroform	0·0522	$\bar{2}$·718	5·05	0·199	(c)
Bromoform	0·0545	$\bar{2}$·736	4·51	0·222	(c)
Carbon tetrachloride	0·00013	$\bar{4}$·114	2·24	0·448	(c)
Ethyl bromide	0·0920	$\bar{2}$·964	9·45	0·106	(c)
Ethylene dibromide	0·0810	$\bar{2}$·908	4·86	0·206	(c)
Vacuum	$3·16 \times 10^{-9}$	$\bar{9}$·500	1·00	1·00	

Mercuric iodide (18—20°).

Solvent.	c.	$\log_{10} c$.	D.	$1/D$.	Ref.
Carbon disulphide	0·00888	$\bar{3}$·948	2·64	0·380	(d)(e)
Benzene	0·00435	$\bar{3}$·638	2·28	0·438	(f)
Chloroform	0·0132	$\bar{2}$·121	5·05	0·199	(c)
Bromoform	0·0310	$\bar{2}$·491	4·51	0·222	(c)
Carbon tetrachloride	0·000211	$\bar{4}$·324	2·24	0·448	(c)
,, ,,	0·000375	$\bar{4}$·574	2·24	0·448	(g)
Ethyl bromide	0·0203	$\bar{2}$·308	9·45	0·106	(c)
Ethylene bromide	0·0360	$\bar{2}$·556	4·86	0·206	(c)
Ethyl iodide	0·0868	$\bar{2}$·939	7·4	0·135	(c)
Ethylene chloride	0·0830	$\bar{2}$·919	10·5	0·095	(c)
*iso*Butyl chloride	0·0154	$\bar{2}$·188	7·1	0·141	(c)
Hexane	0·00026	$\bar{4}$·418	1·87	0·536	(c)
Methylene iodide	0·165	$\bar{1}$·217	5·5	0·181	(h)
Vacuum	$1·31 \times 10^{-9}$	$\bar{9}$·117	1·00	1·00	

(a) Hoffmann, Kirmreuther, and Tal, *Ber.*, 1910, **43**, 188.
(b) Dukelski, *Z. anorg. Chem.*, 1907, **53**, 327.
(c) Sulc, *ibid.*, 1900, **25**, 401.
(d) Arctowski, *ibid.*, 1894, **6**, 267, 404.
(e) Linebarger, *Amer. Chem. J.*, 1894, **16**, 214.
(f) Beckmann and Stock, *Z. physikal. Chem.*, 1895, **17**, 130.
(g) Dawson, J., 1909, **95**, 874.
(h) Retgers, *Z. anorg. Chem.*, 1893, **3**, 253.

It is seen from Figs. 2, 3, and 4 that there is a fairly close parallelism between the solubility and the dielectric constant in each case. The dipole moments of the mercuric halides are not known, but they are probably high by analogy with silver perchlorate, which would account for the great change of solubility with dielectric constant. By assuming that the straight lines in Figs. 2, 3, and 4 can be extrapolated to $1/D = 0$ (*i.e.*, $D \longrightarrow \infty$), we can calculate the dipole moments from equations (2) and (3). This has been done, the values for molecular radii obtained by Braune and Linke (*loc. cit.*) being used. The values obtained for $\mu \times 10^{18}$ are: $HgCl_2 = 4{\cdot}0$, $HgBr_2 = 5{\cdot}7$, $HgI_2 = 6{\cdot}6$, which are of the order of magnitude we should expect, though they may be considerably in error owing to the uncertainty of the values for the vapour pressures at 20°, and the possibility that quadrupole forces play a part.

Summary.

(1) The connexion between the electrical energy of dipole fields and the solubility relations of dipole molecules is discussed.

(2) Values are given for the solubilities of hydrogen chloride, hydrogen sulphide, and ammonia in a number of solvents.

(3) It is concluded from the results that it is not permissible in these cases to treat the solvent as a continuous medium.

(4) More regular relations are found in previous data for the solubilities of the mercuric halides in various solvents, and a calculation on the basis of the theory here developed gives reasonable values for the dipole moments.

In conclusion, the author wishes to thank Professor J. N. Brønsted for the facilities placed at his disposal, and Professor N. Bjerrum for his kind criticism.

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[*Received, April 4th,* 1931.]