[Jour. Indian Chem. Soc., Vol. 30, No. 1, 1953]

MOLECULAR POLARISATION IN SOLIDS

By K. D. Pathak and B. V. Bhide

Dielectric constants of salts of alkalies and alkaline earths with straight chain aliphatic acids have been determined. Molecular polarisation calculated according to the Clausius-Mosotti equation has been found to be additive in sodium, potassium and barium salts of monobasic acids and in sodium salts of dibasic acids. Calcium salts show marked deviations. In all the series of salts molecular volume has been found to be additive.

A survey of the theories of dielectrics shows that there is no generalised theory of the dielectric properties of salts or solids in general. The previous work done on the subject has been in most cases related to the role of water in hydrates (Cheng, *Phil. Mag.*, 1940, 30, 505), or changes in allotropic forms. The rest of the work is mainly concerned with the determination of dielectric constants of salts and interpreting them qualitatively in terms of the ionic and non-polar bonds. In the absence of a generalised theory, it was thought desirable to study the effect of organic radicals on the dielectric properties of inorganic ions. Such a scheme is easily available if one considers the inorganic salts of straight chain aliphatic acids. The aliphatic part of the acid is mostly non-polar and the effect of the addition of this component on the inorganic cation can be easily studied.

Experimental

Some of the acids required for the preparation of these salts were available in the laboratory. The remaining had to be prepared. Formic, acetic and butyric acids were redistilled before use. For the preparation of the salts of heptylic acid, first heptaldehyde was obtained by fractional distillation of castor oil which was further oxidised to heptylic acid by potassium permanganate. Lauric acid was obtained from Pisa seeds (*Actinodaphne hookeri*) and further distilled under reduced pressure. Stearic acid was obtained from Coccum butter (*Purpura*). It was obtained in the purest form after three crystallisations from ethyl alcohol, m. p. 71.5°.

The salts were prepared by standard methods. They were purified by crystallisation from water or alcohol, wherever possible. The salts were dried to a constant weight and were further analysed by standard methods to test their purity. In every case the purity was found to be over 99.5%.

Measurement of Dielectric Constants and Densities.—The dielectric constants were measured by the resonance method at 100 meter wave-length. The mixture method was used for determining the dielectric constants of solids. The liquids used for this method were xylene and nitrobenzene; for density measurements benzene was used.

Xylene was dried over sodium and then distilled twice over phosphorus pentoxide. Merck's pure thiophene-free benzene, distilled over phosphorus pentoxide, was further dried over sodium; nitrobenzene was dried over calcium chloride and then distilled under reduced pressure.

All the density measurements were carried out at 30°. All the weights were corrected for buoyancy of air.

Table I gives the dielectric constant ϵ, density d, molecular polarisation P, and the molecular volume of salts. P is calculated according to Clausius-Mosotti equation

$$P = \frac{\epsilon-1}{\epsilon+2} \cdot \frac{M}{d}.$$

TABLE I

	Salt.	Formula.	ϵ.	d (g./c.c.).	P.	Mol. vol (M/d).
1.	Sodium formate	CHO_2Na	4.85	1.925	19.86	35.33
2.	Sodium acetate	$C_2H_3O_2Na$	4.44	1.518	28.87	54.03
3.	Sodium butyrate	$C_4H_7O_2Na$	3.825	1.324	40.29	83.08
4.	Sodium heptylate	$C_7H_{13}O_2Na$	3.61	1.204	58.73	126.3
5.	Sodium laurate	$C_{12}H_{23}O_2Na$	3.24	1.102	86.12	201.5
6.	Sodium stearate	$C_{18}H_{35}O_2Na$	3.125	1.07	118.4	286.0
1.	Sodium oxalate	$C_2O_4Na_2$	6.1	2.888	36.88	46.39
2.	Sodium malonate	$C_3H_2O_4Na_2$	5.6	2.08	43.07	71.15
3.	Sodium succinate	$C_4H_4O_4Na_2$	5.01	1.88	51.6	86.16
4.	Sodium adipate	$C_6H_8O_4Na_2$	4.14	1.66	58.3	114.5
5.	Sodium azealate	$C_9H_{14}O_4Na_2$	4.16	1.45	82.08	160.0
1.	Potassium formate	CHO_2K	7.46	1.954	29.36	42.99
2.	Potassium acetate	$C_2H_3O_2K$	4.61	1.534	34.89	63.89
3.	Potassium butyrate	$C_4H_7O_2K$	3.9	1.315	47.1	95.88
4.	Potassium laurate	$C_{12}H_{23}O_2K$	2.81	1.136	78.84	209.50
5.	Potassium stearate	$C_{18}H_{35}O_2K$	2.65	1.12	102.1	287.00
1.	Barium formate	$Ba(HCO_2)_2$	7.9	3.179	49.85	71.53
2.	Barium acetate	$Ba(C_2H_3O_2)_2$	5.62	2.47	62.67	103.4
3.	Barium butyrate	$Ba(C_4H_7O_2)_2$	4.55	1.875	89.89	166.2
4.	Barium heptylate	$Ba(C_7H_{13}O_2)_2$	3.62	1.568	117.6	252.2
5.	Barium laurate	$Ba(C_{12}H_{23}O_2)_2$	3.1	1.345	163.9	398.1
6.	Barium stearate	$Ba(C_{18}H_{35}O_2)_2$	2.815	1.244	213.2	265.4
1.	Calcium formate	$Ca(HCO_2)_2$	6.825	1.959	43.81	66.36
2.	Calcium acetate	$Ca(C_2H_3O_2)_2$	6.3	1.509	66.88	104.7
3.	Calcium butyrate	$Ca(C_4H_7O_2)_2$	4.9	1.271	95.23	168.4
4.	Calcium heptylate	$Ca(C_7H_{13}O_2)_2$	4.29	1.2	129.9	248.3
5.	Calcium stearate	$Ca(C_{18}H_{35}O_2)_2$	2.82	1.065	214.9	569.0

DISCUSSION

From the results the following deductions can be made.

Densities.—Fig. 1 shows the densities of the salts against the number of carbon atoms in the molecule. In every series of salts a smooth curve is obtained. The decrease in density with increase in carbon atoms is particularly prominent from formates to butyrates in the salts of monobasic acids where the increment in molecular weight represents a large proportion of the total. It is interesting to note that the curves of sodium and potassium salts of monobasic acids almost superimpose each other showing that the corresponding salts have nearly the same densities. No irregularity is observed in the values of the densities in these series of salts with odd and even number of carbon atoms.

Fig. 1

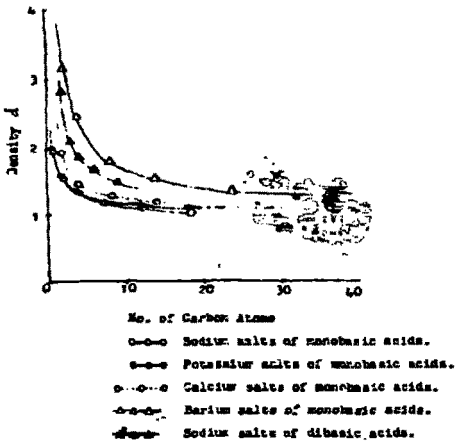
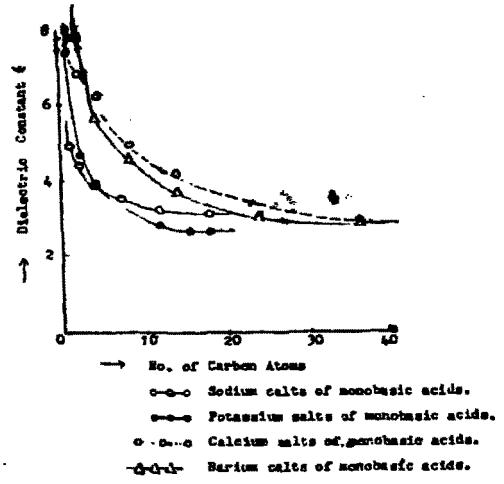


Fig. 2



Dielectric Constants.—Fig. 2 gives the curves of the dielectric constants against the number of carbon atoms in the molecule. Dielectric constants also follow the same order as that of the densities, and invariably decrease with the increase in the number of carbon atoms. All the curves are smooth and here also no irregularity is observed in salts containing odd and even number of carbon atoms.

Density-dielectric Constants.—As both the densities and dielectric constants follow the same order and decrease with the number of carbon atoms, it was thought desirable to draw the graphs of densities against the dielectric constants to test the relationship between them. Figure 3 gives such graphs of sodium, potassium, barium and calcium salts. Except in calcium salts which give a curve, the graphs are almost straight lines. Deviations are observed in sodium formate and barium acetate which may be due to these being the first few members. The graphs, straight lines as they are, give a clue to predict approximately the dielectric constant of a salt in series of sodium, potassium and barium salts, if the density is known or *vice versa*.

Molecular Polarisations.—Earlier work on molecular polarisation of inorganic salts by Sathe, Phalamkar and Bhide (this *Journal*, 1945, 22, 29) shows that in these salts molecular polarisation is not additive. The deviation from the additivity rule has been explained as due to a partial change in the nature of the

Fig. 3

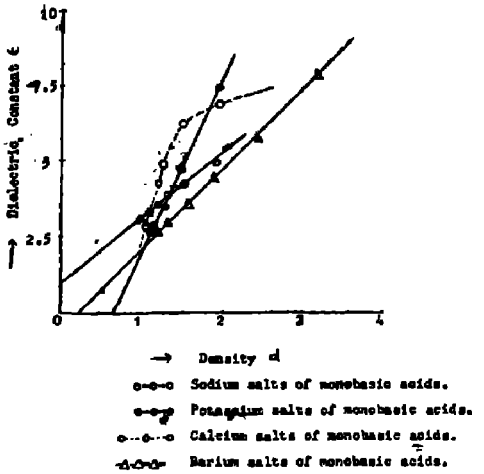
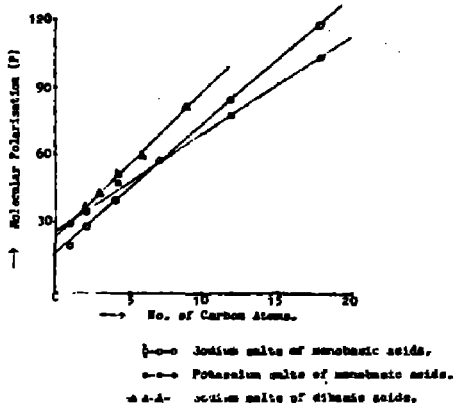


Fig. 4



bond from electrovalent to covalent. In the present work the salts of aliphatic carboxylic acids are under study. In such a series of acids the aliphatic part is mostly non-polar and it may be presumed that the increment in the molecular polarisation with the number of carbon atoms is entirely due to the increment in the molecular volume only. It is seen from Figs. 4 and 5 that in sodium, potassium and barium

Fig. 5

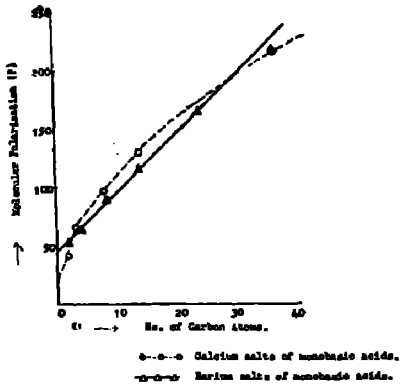
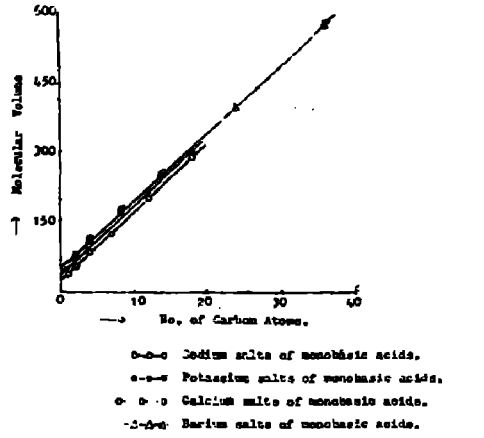


Fig. 6



salts, additivity relationship holds for molecular polarisation if the cation is kept the same; in other words in these salts the cation has no appreciable effect on the polarisation of the organic radical or the anion. In calcium salts the cation seems to have an appreciable effect on the polarisation of the anion.

Though the additivity relationship holds for molecular polarisation in these series of salts, the contribution of polarisation due to each carbon atom, when considered in separate series, does not seem to be identical, as is evident from the following equations (x denoting the number of carbon atoms) :

(1) $P = 5.178x + 17.73$ for Na salts of monobasic acids.
(2) $P = 6.296x + 24.23$ for „ „ of dibasic acids.
(3) $P = 4.178x + 27.91$ for K „ monobasic acids.
(4) $P = 4.712x + 46.32$ for Ba „ „ acids.

Thus, the contributions of polarisation due to each carbon atom 5.178, 6.296, 4.178 and 4.712 are different and it be only said that the contribution due to each carbon atom is constant to a particular series of salts of sodium, potassium and barium.

Molecular Volume.—It is well known that in an aliphatic series the molecular volume is an additive property. In this work also it has been found that the molecular volumes of the sodium, potassium, calcium and barium salts of monobasic acids are additive.

MAHARAJA PRATAPSINHA
CHEMICAL LABORATORY,
POONA 2.

Received May 3, 1952.