The Diamagnetic Susceptibility of Benzoate, Salicylate, Propionate, Butyrate and Succinate Ions

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Magnetic susceptibilities of simple ions were evaluated by a number of workers. The importance of such a study was clearly brought out by the work of Hoare and Brindley(1), Varadachari(2) and Subramaniam(3). In the present investigation a few alkali and alkaline earth compounds containing benzoate, salicylate, propionate, butyrate and succinate radicals have been studied in the solid state and the susceptibilities of the anions calculated assuming the previously accepted values for the cations.

Experimental

The substances used were mostly either Merck's G. R. or B. D. H., A. R. and a few whose purity was not definite were recrystallized befor use. The salts were all found to be free from ferromagnetic impurities. Great care was taken to prevent the solids from absorbing atmospheric moisture and where this tendency existed the salts were analyzed for the moisture content by gravimetric methods and kept in vacuum desiccator before use.

Measurements of the susceptibilities of the acids

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1) F. E. Hoare and G. W. Brindley, *Proc. Roy. Soc.*, **147A**, 88 (1934).

2) P. S. Varadachari, *Proc. Ind. Acad. Sci.*, **2A**, 16 (1935).

3) K. C. Subramaniam, ibid., **4A**, 404 (1936).

and their salts were made with a Curie balance. The retorsion method[4] was employed. A correction for the displaced air was applied for every bulb. For every salt and acid more than half a dozen bulbs containing different masses of the salts were examined at three field currents, viz. 4, 5 and 6 amp. Benzene (B. D. H., A. R. grade) was used as the standard and its specific susceptibility was taken as 0.702*. The susceptibilities of the salts were calculated from the usual formula.

$$\frac{\theta_S}{\theta_B}=\frac{m_S\chi_S-K_a v_S}{m_B\chi_B-K_a v_B}$$

Here θ_S, θ_B and m_S, m_B represent the deflections for and the masses of, the substance and benzene respectively; v_S and v_B represent the volume of the air displaced by the substance and benzene respectively. K_a refers to the paramagnetic susceptibility of air at the room temperature. Its value at N. T. P. is 0.029×10^{-6} (I. C. T. 6, 354, 1929) and its value at the room temperature (30°C) was found from the relation K_a/T^2 is constant where K_a is the susceptibility of air at absolute temperature T°K.

Results

The susceptibilities obtained for the acids and their salts are recorded in Table I. For the evaluation of ionic susceptibilities of the anions under investigation, Flordal and Frivold's[5] values derived from salts in dissolved

TABLE I. SUSCEPTIBILITY VALUES FOR THE ACIDS AND THEIR SALTS

No.	Substance	Mol. wt.	χ_S	χ_M	χ_{Ma}*	χ_{Ma} (others)
1	Benzoic acid, C_6H_5COOH	122.20	0.5832	71.27	71.27	67.78[6] 70.29[7] 70.28[8] 70.62[9]
2	$NaC_7H_5O_2$	144.11	0.5350	77.10	77.10	77.60[10]
3	$KC_7H_5O_2$	160.25	0.5332	85.45	85.45	82.62[10]
4	$Ca(C_7H_5O_2)_2\cdot3H_2O$	336.15	0.5575	187.40	148.52	151.00[10]
5	$Sr(C_7H_5O_2)_2$	311.63	0.4912	153.07	153.07	166.70[10]
6	$Ba(C_7H_5O_2)_2\cdot2H_2O$	415.16	0.4589	190.52	164.60	177.30[10]
7	Salicylic acid, HOC_6H_4COOH	137.12	0.5367	73.59	73.59	72.23[9]
8	$NaC_7H_5O_3$	160.11	0.5138	82.26	82.26	85.70[10]
9	$KC_7H_5O_3$	176.21	0.5146	90.68	90.68	93.70[10]
10	$Ca(C_7H_5O_3)_2$	314.33	0.5050	158.74	158.74	162.00[10]
11	$Sr(C_7H_5O_3)_2$	361.88	0.4700	170.08	170.08	176.10[10]
12	$Ba(C_7H_5O_3)_2$	411.60	0.4305	177.19	177.19	188.00[10]
13	Propionic acid, CH_3CH_2COOH	74.04	0.5898	43.67	43.67	43.60[11]
14	$NaC_3H_5O_2$	96.07	0.5308	50.99	50.99	48.90[10]
15	$KC_3H_5O_2$	112.18	0.5347	59.98	59.98	57.20[10]
16	$Ca(C_3H_5O_2)_2$	186.24	0.5475	101.97	101.97	100.40[10]
17	$Sr(C_3H_5O_2)_2$	234.00	0.4423	103.50	103.50	107.90[10]
18	$Ba(C_3H_5O_2)_2$	283.52	0.4118	116.75	116.75	123.50[10]
19	Butyric acid, $CH_3CH_2CH_2COOH$	88.10	0.6146	54.15	54.15	55.70[12]
20	$NaC_4H_7O_2$	110.09	0.5391	59.35	59.35	61.60[10]
21	$KC_4H_7O_2$	126.10	0.5220	65.82	65.82	70.00[10]
22	$Ca(C_4H_7O_2)_2$	214.29	0.4988	106.89	106.89	119.50[10]
23	$Sr(C_4H_7O_2)_2$	261.81	0.4400	115.20	115.20	129.60[10]
24	$Ba(C_4H_7O_2)_2$	311.59	0.4018	125.20	125.20	145.60[10]
25	Succinic acid, $COOH(CH_2)_2COOH$	118.09	0.4804	56.73	56.73	57.10[13]
26	$Na_2C_4H_4O_4$	162.16	0.4159	67.44	67.44	76.82[10]
27	$K_2C_4H_4O_4$	194.31	0.4480	87.05	87.05	89.22[10]
28	$CaC_4H_4O_4$	156.20	0.4245	66.31	66.31	54.84[10]
29	$SrC_4H_4O_4$	203.75	0.3584	73.02	73.02	71.50[10]
30	$BaC_4H_4O_4$	253.43	0.3345	84.77	84.77	97.60[10]

* χ_{Ma}=Anhydrous molar susceptibility.

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* All susceptibility values given in this paper indicate the diamagnetic susceptibilities in 10^{-6} c. g. s. unit.

[4] S. R. Rao, ibid., 1, 123 (1934).

[5] V. M. Flordal and D. E. Frivold, *Ann. Physik*, **23**, 425 (1935).

[6] F. M. Gray and W. M. Birse, *J. Chem. Soc.*, **105**, 2715 (1914).

[7] K. Kido, *Sci. Rep. Tohoku, Imp. Univ.*, **24**, 701 (1936).

[8] C. M. French, *Trans. Faraday. Soc.*, **50**, 1321 (1954).

[9] K. Venkateswarlu and S. Sriraman., ibid., **53**, 438 (1957).

[10] Mata Prasad et al., (a) *Proc. Ind. Acad. Sci.*, **16A**, 307 (1942); (b) ibid., **20A**, 224 (1944); (c) *J. Chem. Phys.*, **17**, 819 (1949); (d) ibid., **18**, 936 (1950); (e) ibid., **18**, 941 (1950); (f) ibid., **20**, 129 (1952).

[11] P. Pascal, (a) *Compt. rend.*, **149**, 342 (1909); (b) ibid., **158**, 158 (1914); (c) ibid., **159**, 429 (1914); (d) ibid., **173**, 144 (1921).

[12] K. Kido, *Sci. Rep. Tohoku. Imp. Univ.*, **21**, 869 (1932); ibid., **22**, 835 (1933).

[13] B. K. Singh, *Proc. Ind. Acad. Sci.*, **22A**, 163 (1945).

TABLE II. SUSCEPTIBILITIES OF THE CATIONS

Ion	Na^+	K^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
χ_{ion}	6.90	15.00	8.80	18.30	29.30

state for Na^+, K^+, Ca^{2+}, Sr^{2+} and Ba^{2+} are used and these are given in Table II for ready reference.

The susceptibilities of the anions are evaluated using Pascal's law. Also the acid values were taken to represent the value of the corresponding ion on the assumption that H^+ does not contribute anything[14]. The mean values obtained for the anions under study are given in Table III.

TABLE III. IONIC SUSCEPTIBILITIES

Ion	Mean value from salts	χ_{ion} from acid	Mean
Benzoate $C_7H_5O_2^-$	69.11	71.27	70.19
Salicylate $C_7H_5O_3^-$	75.17	73.59	74.38
Propionate $C_3H_5O_2^-$	44.39	43.67	44.03
Butyrate $C_4H_7O_2^-$	49.74	54.15	51.95
Succinate $C_4H_4O_4^{2-}$	55.68	56.73	56.21

Discussion

The general method adopted for the evaluation of the ionic susceptibilities is on the basis that the molar susceptibility of a heteropolar salt is the sum of the constituent ions. The data available on the subject show that in the case of several ions, the values given by different authors differ sometimes by large amounts. Bhatnagar and co-workers[15] and Mata Prasad and co-workers[10] have followed a statistical method in which they subtracted all the known values of the susceptibilities of anions from the molar susceptibilities of a number of salts of a cation and took the arithmetical mean of the values thus obtained as the correct value for the cation. Kido[12], Joos[16] and Ikenmeyer[17] have observed that a linear relation exists between the susceptibilities of ions of chemically related elements belonging to the same group of the periodic table and their atomic numbers. This method of evaluation of the ionic susceptibilities has been questioned by Trew[18] and Selwood[19] on the ground that it is open to theoretical objection. Mata Prasad and co-workers[10] have followed Kido's[12] suggestion. Their results show that the susceptibility values of the anions deduced from the salts of Li, Na, K etc., are distinctly different from those deduced from the salts of Ca, Sr and Ba. This difference is large in some cases and small in others. If the linear relation is assumed then the assignment of ionic value could be done by measuring the molar susceptibilities of only two salts containing the cations of the same column of the periodic table.

When two ions combine there is every likelihood of a deformation taking place in both the ions. It is quite possible that the degree of deformations in ions may be different for the different groups of cations. To what extent this will affect the susceptibility of the anions is a question which is worth considering. On the basis of Pascal's additive law[11] the χ of anions can be calculated assuming the values of alkali and alkaline earth metallic ions. In Table IV this calculation has been made with the values obtained by Mata Prasad and co-workers[10], Rao and Sriraman[20] and Venkateswarlu and Sriraman[9] for formate, acetate and oxalate ions.

The anion values given in Table IV show definitely that they do not change abruptly as we pass from one group of metallic ions to another. All the values are of the same order subject to the error in the measurements of the susceptibility of the salts.

It is interesting to compare these values for a few typical ions with the values (Table V) obtained by Prasad and others by graphical method on the basis of linearity. For four ions the values from alkali salts are larger than from alkaline earth salts, for the last two ions the change is the other way about and for the oxalate ion no change is observed. If the values of the various ions are calculated from their own measurements on the basis of additivity, such marked variations are not found. Considering the graphical method adopted, Trew[18] has definitely pointed out that the graphs do not show linearity and the points do not lie on a single straight line. Our results in the present investigation also confirm this point. The linearity may be approximately true in a very few cases as Kido[12] found but it is certainly not applicable in all cases. The large amount of literatures available on the subject and the convincing facts brought out by Trew[18] show that the additivity method

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[14] K. Reichender, *Ann. Physik*, **1**, 169 (1929).

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[16] V. G. Joos, *Z. Physik*, **19**, 347 (1923).

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[18] V. C. G. Trew, *Trans. Faraday, Soc.*, **37**, 476 (1941).

[19] P. W. Selwood, "Magnetochemistry", Interscience Publishers Inc., New York (1952).

[20] S. R. Rao and S. Sriraman, *Phil. Mag.*, **24**, 1025 (1937).

TABLE IV

Substance	Prasad and co-workers		Rao and Sriraman	
	χ_{Ma}	χ_{Anion}	χ_{Ma}	χ_{Anion}
Sodium formate, NaHCOO	24.50	17.60	24.80	17.90
Calcium formate, $Ca(HCOO)_2$	45.30	18.30	39.50	15.35
Barium formate, $Ba(HCOO)_2$	73.70	22.20	66.60	18.65
Sodium acetate, $NaCH_3COO$	39.22	32.22	37.60	30.70
Barium acetate, $Ba(CH_3COO)_2$	99.49	35.10	88.04	29.37
			Venkateswarlu and Sriraman	
Sodium oxalate, $Na_2C_2O_4$	51.20	37.40	47.74	33.94
Potassium oxalate, $K_2C_2O_4$	65.64	35.64	64.89	34.89
Calcium oxalate, CaC_2O_4	44.30	35.50	42.08	33.28
Strontium oxalate, SrC_2O_4	54.64	36.34	51.20	32.90
Barium oxalate, BaC_2O_4	64.80	35.50	63.10	33.80

TABLE V

Anion	χ_{anion}, graphical		χ_{anion} additive
	Li, K, Na	Ca, Sr, Ba	
Formate	20.50	15.00	17.30[20]
Acetate	34.00	25.00	29.80[20]
Oxalate	34.40	34.00	33.86[9]
Succinate	58.80	36.00	55.67[21]
Salicylate	81.00	74.50	74.62[21]
Malonate	45.00	53.00	—
Stearate	206.00	212.00	—

of evaluating the ionic value is more reliable subject to the accuracy of the measurements and the small error involved in the assumption of the cation values.

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[21] S. Sriraman and S. Thiruvengadathan, This paper.