

IONIC SUSCEPTIBILITY OF BARIUM

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RECENTLY several systematic investigations have been carried out to determine the ionic susceptibilities of several elements in their different valency states, from the molecular susceptibilities of their compounds. Hollens and Spencer¹ measured the susceptibilities of several compounds of cadmium and deduced therefrom the ionic susceptibility of cadmium. Bhatnagar and co-workers have carried out an extensive investigation on the determination of the ionic susceptibilities of various elements and they find that, generally, the experimentally deduced values are in fair agreement with those calculated theoretically by Slater's and Angus's methods. Bhatnagar and Bahl² studied salts of trivalent bismuth and deduced the ionic susceptibility of Bi^{+3} . Bhatnagar and Khanna³ determined the ionic susceptibility of rubidium and Bhatnagar, Nevgi and Sharma⁴ that of tin in di- and tetra-valent states. Trew⁵ studied thallium compounds in different valency states to determine the ionic susceptibility of thallium. Nevgi⁶ also studied thallium salts and found that his mean value for the thallium ion is less than that obtained by Trew. Bhatnagar, Nevgi and Ohiri⁷ studied salts of mercury in mono- and di-valent states and deduced the ionic susceptibility of mercury which is in good agreement with the calculated values. Rao and Sriraman⁸ have studied a number of salts both in solid and dissolved states and have determined the susceptibilities of ions like formate, acetate, nitrate, selenite and nitrite. They have pointed out the desirability of investigating compounds both in the solid and dissolved states, as they found slight changes in the ionic susceptibility values determined by the two methods.

The ionic susceptibility of barium calculated either by Slater's (-33.3×10^{-6}) or by Angus's (-31.51×10^{-6}) method is different from the experimental value given in the *International Critical Tables* (-38.2×10^{-6}). Hence the susceptibilities of a number of inorganic and organic salts of barium were measured and using the known values of the susceptibility of the various ions the susceptibility of barium ion was deduced therefrom.

Experimental

All substances used in this investigation were of extra pure quality. Some of them were Kahlbaum products while a few were obtained from Dr. Theodor Schuchardt. A few substances were prepared in the laboratory from extra pure chemicals. They were analysed quantitatively and only those substances which were found to be absolutely pure were employed for the purpose of investigation.

Barium carbonate was prepared by passing purified CO_2 through baryta water. Barium chromate, oxalate, tartarate and succinate were prepared by precipitation from a solution of Merck's extra pure barium chloride by the addition of the solution of ammonium salt of the corresponding acids. The formate, acetate, phthalate and salicylate were prepared by adding an excess of the corresponding acids to pure barium carbonate and crystallising them from solutions thus obtained. The crystals obtained were recrystallised thrice. The crystals of barium acetate were heated in a steam oven to get the anhydrous sample.

The Magnetic Balance employed and the procedure followed were the same as described by Prasad and Dharmatti.^{1,2}

The results obtained are given in Tables I and II. In all cases the values obtained are the mean of three independent readings. Various values for the anions given by different workers have been utilised to deduce the ionic susceptibility of barium.

Discussion of Results

(a) *Salts of Inorganic Acids.*—The ionic susceptibilities of barium were calculated by the Slater's, Angus's and modified methods of Slater and Angus in the same manner as in the case of selenium (*cf.* Prasad and Dharmatti, *loc. cit.*). These values are given in Table III.

TABLE I
Barium Salts of Inorganic Acids

Substance	$-xa \times 10^6$	$-xm \times 10^6$	Values of other radicals $-x \times 10^6$	$-xBa^{+2} \times 10^6$	Mean $-xBa^{+2} \times 10^6$	
1. BaCl ₂ ·2H ₂ O ..	0.4070	99.42	H ₂ O	27.3 29.3 32.7 33.3 33.8 33.5 27.3 27.3 29.1	29.89	
			xCl'			12.96 (Hocart)
						23.1 (Kido)
						22.1 (Ikenmeyer)
						20.4 (Pascal)
						20.1 (Bhatnagar)
						19.85 (Sugden)
						20.0 (Weiss)
						23.1 (Pauling)
						24.1 (Abonnene)
						23.1 (Leiferer)
2. BaBr ₂ ·2H ₂ O ..	0.3925	130.8	H ₂ O	37.08 35.48 35.28 43.88 39.88 42.08 42.88 36.68 36.68	38.88	
			xBr'			12.96 (Hocart)
						33.9 (Kido)
						34.7 (Ikenmeyer)
						34.8 (Pascal)
						30.5 (Reichender)
						32.5 (Farquharson)
						31.4 (Sugden)
						31.0 (Abonnene)
						34.1 (Weiss)
			3. Ba(NO ₃) ₂ ..			0.2513
	14.2 (Pascal)					
	20.1 (Kido)					
	18.0 (Sugden)					
	18.4 (Raychaudhari and Sengupta)					
	18.2 (Pauling)					
4. BaCO ₃ ..	0.2847	56.20	xCO ₃ '	34.0 28.1 26.0	29.37	
						22.2 (Pascal)
						28.1 (Kido)
						30.2 (Pauling)

TABLE I—(Contd.)

Substance	$-x\sigma \times 10^6$	$-x\pi \times 10^6$	Values of other radicals $-x \times 10^6$	$-x\text{Ba}^{+2} \times 10^6$	Mean $-x\text{Ba}^{+2} \times 10^6$
5. BaSO_4	0.3062	71.44	$x\text{SO}_4''$ = 33.6 (Pascal) = 39.0 (Kido) = 37.0 (Trew) = 41.6 (Pauling)	37.84 32.44 34.44 29.84	33.64
6. BaSeO_4	0.2113	59.29	$x\text{SeO}_4''$ = 23.89 (S)* = 23.821 (A) = 22.74 (MS) = 22.672 (MA)	35.40 35.469 36.55 36.618	36.01
7. $\text{Ba}(\text{ClO}_3)_2, \text{H}_2\text{O}$	0.3584	115.5	H_2O = 12.96 $x\text{ClO}_3'$ = 25.8 (Trew) = 30.2 (Kido) = 26.0 (Sugden)	50.94 42.14 50.54	47.87
8. BaCrO_4	0.0501	12.7	$x\text{CrO}_4''$ = -21.86 (Bhatnagar, Prakash and Hamid's data) = -35.2 (Trew) = -33.0 (Trew)	34.56 47.9 45.7	42.72
9. BaSeO_3	0.2563	67.81	$x\text{SeO}_3''$ = 44.9 (Rao) = 47.5 (Kido)	22.91 20.31	21.61

* Value for SeO_4'' has been computed by using the values for Se^{+6} calculated by Slater's method (S), Angus' method (A) and modified methods of Slater and Angus (Ms and MA) (cf. Prasad and Dharmatti, *Proc. Ind. Acad. Sci.*, 1940, 12, 185).

TABLE II
Barium Salts of Organic Acids

Substance	$-x\alpha \times 10^6$	$-xm \times 10^6$	Values of other radicals $-x \times 10^6$	$-x\text{Ba}^{+2} \times 10^6$	Mean $-x\text{Ba}^{+2} \times 10^6$
1. $(\text{HCOO})_2\text{Ba}$..	0.3250	73.7	$(\text{HCOO})^-$ = 16.9 (Pascal's corrected data) = 20.2 (Kido) = 17.3 (Rao)	39.9 33.3 39.1	37.43
2. $(\text{CH}_3\text{COO})_2\text{Ba}$..	0.3896	99.49	$(\text{CH}_3\text{COO})^-$ = 28.9 (Pascal) = 32.0 (Kido) = 30.0 (Trew) = 30.0 (Hollens and Spencer) = 29.8 (Rao)	41.69 35.49 39.49 39.49 39.89	39.21
3. BaC_2O_4 ..	0.2870	64.77	$\text{C}_2\text{O}_4^{--}$ = 27.94 (Pascal's corrected data) = 28.5 (Hollens and Spencer) = 28.44 (<i>Int. Crit. Tables</i>)	36.83 36.27 36.33	36.48
4. $(\text{CH}_3\text{COO})_2\text{Ba}$..	0.3851	97.59	$(\text{CH}_3\text{COO})_2^{--}$ = 51.66 (Pascal's corrected data) = 53.14 (<i>Int. Crit. Tables</i>)	45.93 44.45	45.19
5. $(\text{CHOHCOO})_2\text{Ba}$..	0.4103	117.1	$(\text{CHOHCOO})_2^{--}$ = 62.36 (<i>Int. Crit. Tables</i>) = 63.8 (Trew) = 60.88 (Pascal's corrected data)	54.74 53.3 56.22	54.75
6. $(\text{C}_6\text{H}_4\text{COOHCOO})_2\text{Ba}$, H_2O	0.4621	224.3	H_2O $(\text{C}_6\text{H}_4\text{COOHCOO})^-$ = 12.96 = 83.11 (Pascal's corrected data) = 85.89 (<i>Int. Crit. Tables</i>)	45.12 39.56	42.34
7. $(\text{C}_6\text{H}_4\text{OHCOO})_2\text{Ba}$, H_2O	0.4681	201.0	H_2O $(\text{C}_6\text{H}_4\text{OHCOO})^-$ = 12.96 = 71.44 (Pascal's corrected data) = 74.68 (<i>Int. Crit. Tables</i>)	45.16 38.68	41.92

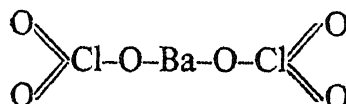
TABLE III

Calculated Ionic Susceptibilities of Divalent Barium

Slater's method ($-x \times 10^6$)	Angus's method ($-x \times 10^6$)	Modified method of Slater ($-x \times 10^6$)	Modified method of Angus ($-x \times 10^6$)
33.3	31.51	37.90	34.16

It will be noticed from Table I that except in the case of chlorate, chromate and selenite, the mean ionic susceptibility of barium deduced from all other salts is in good agreement with the calculated values. These discrepancies have been examined critically in the following:—

(1) The value for the chlorate ion was calculated in the manner similar to the one followed by Gray and Farquharson,⁹ representing the barium chlorate as:



Slater's value for double bond oxygen, and (i) Gray and Farquharson's value for Cl^{+5} (-5.71×10^{-6}) and (ii) Slater's value for Cl^{+5} (-4.49×10^{-6}) were used. The ionic susceptibilities of barium deduced by subtracting these values for the chlorate ion from the experimental molecular susceptibility of barium chlorate are shown in Table IV.

TABLE IV

$-xm \times 10^6$ of $\text{Ba}(\text{ClO}_3)_2$, H_2O	Values of other radicals ($-x \times 10^6$)	$-x\text{Ba}^{+2} \times 10^6$
115.5	(i) $x\text{H}_2\text{O} = 12.96$ (i) $x\text{ClO}_3 = 36.62$ (ii) " = 35.4	29.30 31.74

The ionic susceptibility of barium thus obtained agrees fairly well with the calculated values. The agreement is very good with the value (-31.51×10^{-6}) calculated by Angus's method when Slater's value for Cl^{+5} is used.

(2) The value for the chromate ion if calculated from the molecular susceptibility of silver chromate observed by Bhatnagar, Prakash and Hamid¹⁰ by subtracting from it the value for two silver ions ($\chi_{\text{Ag}}^{+1} = -31.0 \times 10^{-6}$;

cf. *International Critical Tables*) comes out to be $+21.86 \times 10^{-6}$. The value for the ionic susceptibility of barium obtained by using this value for chromate ion is in good agreement with the theoretically calculated values. The use of the other two values for chromate ion given by Trew, gives very high values for the ionic susceptibility of barium and hence the mean of all the values is also considerably high. One of the values (-33.0×10^{-6}) given by Trew does need modification. This value has been obtained by subtracting the ionic value for potassium (-18.5×10^{-6} ; cf. *International Critical Tables*) from the observed molecular susceptibility of K_2CrO_4 . This value for potassium ion is higher than the value calculated by Slater's method (-14.43×10^{-6}), and is even higher than the experimentally obtained values of Pascal and Pauling (-14.5×10^{-6}), Stoner (-13.4×10^{-6}), Joos (-14.5×10^{-6}), Ikenmeyer (-16.9×10^{-6}), Abonnene (-16.3×10^{-6}) and Brindley (-13.5×10^{-6}), most of which are nearly the same as the Slater's calculated value. If a mean of all the experimental values (-14.83×10^{-6}) is used for potassium ion, the ionic susceptibility for chromate ion comes out to be $+25.7 \times 10^{-6}$, which is nearly the same as the one obtained by Bhatnagar, Prakash and Hamid.

The susceptibilities of barium ion obtained by using these values of chromate ions are shown in Table V.

TABLE V

Substance	$-x_m \times 10^6$	$-x \times 10^6$ for cations	$-xCrO_4^{2-} \times 10^6$	$-xBa^{+2} \times 10^6$	Mean $-xBa^{+2} \times 10^6$
K_2CrO_4 ..	4.00	14.85	- 25.70	38.40	36.48
Ag_2CrO_4 ..	40.14	31.00	- 21.86	34.56	

The mean value thus obtained is in fair agreement with the values calculated by Slater's and Angus's methods.

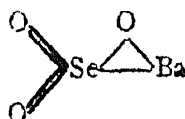
(3) The discrepancy in the case of selenite may be due to the very high values of selenite ion given by Kido¹¹ and Rao.⁸ Prasad and Dharmatti¹² who studied silver selenite and selenious acid have found that susceptibilities of these substances calculated from Kido's and Rao's data are higher than the experimental values. The values for the selenite ion were, therefore, calculated from the susceptibilities of silver selenite and selenious acids and from those of sodium, ammonium and zinc selenite which have been investigated in this laboratory and they were used in deducing the ionic susceptibility of barium. The results obtained are shown in Table VI.

TABLE VI

Substance	$-xm \times 10^6$	$-x \times 10^6$ for cations	$-x\text{SeO}_3'' \times 10^6$	Mean $-x\text{SeO}_3'' \times 10^6$	$-xBa^{+2} \times 10^6$
H_2SeO_3 ..	45.45	H = 3.05 (<i>Int. Crit. Tables</i>) = 2.93 (Pascal's corrected data)	39.35 39.59	39.47	28.34
Ag_2SeO_3 ..	102.2	Ag = 31.0 (<i>Int. Crit. Tables</i>)	40.2	40.20	27.61
$(\text{NH}_4)_2\text{SeO}_3$..	68.74	NH_4 = 12.0 (Stoner) = 12.4 (Kido) = 20.0 (Sugden)	44.74 43.94 28.74	39.14	28.67
Na_2SeO_3	58.45	Na = 5.4 (Abonneve) = 7.0 (Kido) = 7.6 = 9.2 (<i>Int. Crit. Tables</i>) = 5.2 (Brindley) = 8.0 (Weiss) = 10.4 (Ikenmeyer) = 6.1 (Hoare and Brindley) = 6.9 (Flordal and Frivold)	47.65 44.45 43.25 40.05 48.05 42.45 37.65 46.25 44.65	43.83	23.98
ZnSeO_3 ..	54.23	Zn = 13.5	40.73		27.08

$$\text{Mean } -xBa^{+2} \times 10^6 = 27.14$$

Thus the mean value obtained for barium ion is lower than the value calculated by Angus's method but it is in better agreement with the theoretical value than the value given in Table I. The low value of the ionic susceptibility is probably due to the tight-binding of barium in barium selenite as can be seen from its constitution.



The results for barium salts of inorganic acids have been summarised in Table VII in which these salts have been arranged in the order of increasing number of electrons. Column 3 gives their observed susceptibilities, and column 4 gives the mean values for the ionic susceptibility of barium as modified according to the discussion in the foregoing pages. The last column gives the mean of all the values, which is fairly in good agreement with the values calculated by Angus's method.

TABLE VII

Substance	No. of electrons N_m	$-\chi_m \times 10^6$	$-\chi_{Ba^{+2}} \times 10^6$	Mean $-\chi_{Ba^{+2}} \times 10^6$
1. BaCO ₃	86	56.20	29.37	32.30
2. BaSO ₄	104	71.44	33.64	
3. BaCl ₂ ·2H ₂ O	110	99.42	29.89	
4. BaCrO ₄	112	12.70	36.48	
5. BaSeO ₃	114	67.81	27.14	
6. Ba(NO ₃) ₂	118	65.69	30.03	
7. BaSeO ₄	122	59.29	36.01	
8. BaBr ₂ ·2H ₂ O	146	130.80	38.88	
9. Ba(ClO ₃) ₂ ·H ₂ O	148	115.50	29.30	

Ikenmeyer¹³ has studied the halides of alkali and alkaline earth metals in solution and finds that the molecular susceptibility is a linear function of the sum of the nuclear charges of the atoms constituting the molecules,

$$-\chi_m = C_1 N_m + C_2$$

where N_m is the sum of the electrons in the compound, $C_1 = 0.803 \times 10^{-6}$ and C_2 is another constant specific for a given series of salts. Trew (*loc. cit.*) found that this relation generally holds in the case of thallos salts, though there are some marked deviations. He finds $C_1 = 0.7 \times 10^{-6}$ and $C_2 = -17 \times 10^{-6}$. An application of this relation to the case of barium salts of inorganic acids showed that the various points on $-\chi_m$ and N_m graph do not lie on a straight line; only points corresponding to (i) barium halides and (ii) barium carbonate, sulphate and chlorate lie on two separate straight lines; the values for C_1 and C_2 for the two straight lines being 0.87×10^{-6} and $+3.7 \times 10^{-6}$ in the first case and 1.0×10^{-6} and -32.5×10^{-6} in the second. The two values of C_1 are in fair agreements with each other and with the value found by Ikenmeyer.

Ikenmeyer also found that the susceptibility of an ion is given by the relation

$$-\chi_{ion} = C_1 Z + C_2'$$

where Z is the number of electrons in the ion and C_2' is another constant (-5.1×10^{-6}) in the case of the alkaline-earth ions. If the value of the ionic susceptibility of barium obtained experimentally from the inorganic salts and the two values of C_1 are used in the above equation, the values of C_2' come out to be -14.68×10^{-6} and -21.7×10^{-6} respectively. These are far different from the one obtained by Ikenmeyer.

The radius of barium ion was calculated from its mean ionic susceptibility (-32.30×10^{-6}) by the method adopted by Trew (*ibid.*) and was

found to be 1.61 Å. The value observed by Wassastjerna for the ionic radius of barium is 1.40 Å.

(b) *Barium Salts of Organic Acids.*—Barium salts of organic acids have been arranged in the order of increasing number of electrons, in Table VIII, which gives the molecular susceptibilities (column 4) and the ionic susceptibilities of barium (column 5), obtained from these salts (*cf.* Table II).

TABLE VIII

Substance	N	No. of carbon atoms	$-xm \times 10^6$	$-x\text{Ba}^{+2} \times 10^6$	Mean $-x\text{Ba}^{+2} \times 10^6$
1. BaC_2O_4	100	2	64.77	36.48	42.47
2. $(\text{HCOO})_2\text{Ba}$	102	2	73.70	37.43	
3. $(\text{CH}_2\text{COO})_2\text{Ba}$	116	4	97.59	45.19	
4. $(\text{CH}_3\text{COO})_2\text{Ba}$	118	4	99.49	39.21	
5. $(\text{CHOHCOO})_2\text{Ba}$	132	4	117.1	54.75	
6. $(\text{C}_6\text{H}_4\text{OHCOO})_2\text{Ba}$	208	14	201.0	41.92	
7. $(\text{C}_6\text{H}_4\text{COOHCOO})_2\text{Ba}$, H_2O	236	17	224.3	42.34	

The susceptibility of barium formate and acetate [$(\text{CH}_3\text{COO})_2\text{Ba}$, H_2O] have also been determined by Rao and Sriraman⁸ and the values for their molecular susceptibilities are, respectively, -66.6×10^{-6} and -100.1×10^{-6} . It will be seen from the above table, that the values found by the authors are higher than those found by Rao and Sriraman.

A study of the above table shows that the mean ionic susceptibility of barium (-42.47×10^{-6}) obtained from these salts is considerably higher than the values calculated by Slater's and Angus's methods and that obtained from barium salts of inorganic acids. Similar observations have been made by Trew (*loc. cit.*) in the case of the thallium salts. The increase in the ionic susceptibility can be attributed either to the bond effects in the compound or to the increase in the size of the ionic radius. As the increase due to the bond effects has been taken into account in calculating the values for the anions according to Pascal's data, it seems that the increase in the ionic susceptibility is mostly due to the second cause. This may be evidenced by the fact that the increase in the ionic susceptibility is roughly followed by an increase in the number of carbon atoms. The last-named observation was also made by Trew.

Nevgi (*loc. cit.*) holds that the high value obtained by Trew, for the ionic susceptibility of thallium, is due to the use of merely Pascal's data which will not be applicable to heteropolar salts as the data is based upon the investigation of homopolar compounds. In the case of barium formate,

acetate and oxalate, all the possible values for the anions have been used and it is found that even in these cases the ionic susceptibilities are higher than the calculated values. In the case of the oxalate, the susceptibility of the oxalate ion was determined from the susceptibilities of heteropolar oxalates and this value was employed in deducing the ionic susceptibility of barium. These calculations are shown in Table X.

TABLE X

Substance	$-xm \times 10^6$	Value of other ions ($-x \times 10^6$)	$-x(C_2O_4)^{-2} \times 10^6$	$-xBa^{+2} \times 10^6$	Mean $-xBa^{+2} \times 10^6$
CdC_2O_4 ..	53.13	24.85	28.28	36.49	33.33
$Tl_2C_2O_4$..	109.4	37.4	34.6	30.17	

The mean value for the ionic susceptibility of barium given above is almost the same as the one calculated by the Slater's method. However, the data for the deduction of the value for the oxalate ion is too meagre to arrive at a definite conclusion.

It might also be suggested that the high values for the barium ion obtained in the case of the salts of organic acids may also be due to the change in the electronic configuration of $-O-$ bond. Consequently Pascal's value (-4.61×10^{-6}) used for organic compounds for this bond may not be applicable in the case of ionic salts. Further work in connection with this point is in progress.

From the mean ionic susceptibility of barium obtained from organic salts, the ionic radius of barium has been calculated and is found to be 1.849 \AA , which is higher than (1) the one obtained from the barium value deduced from the salts of inorganic acids (1.61 \AA) and (2) the one found by Wassastjerna (1.40 \AA) by the X-ray method.

Summary

The susceptibilities of a number of barium salts of inorganic and organic acids have been determined by Guoy's Balance and using all possible available values for the anions, the ionic susceptibility of barium has been calculated. In the case of salts of inorganic acids the mean ionic susceptibility of barium agrees well with the values theoretically calculated by Slater's and Angus's methods. The mean value deduced from the salts of organic acids is found to be higher than the calculated value and that found from inorganic salts. The probable reasons have been discussed in detail. It has been suggested that the values of several anions need revision.

The ionic radius of barium has also been calculated and has been compared with the value observed by Wassastjerna.

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