MAGNETIC SUSCEPTIBILITY OF THE CH_2 GROUP IN A HOMOLOGOUS SERIES OF ALIPHATIC ORGANIC ACIDS AND THEIR ALKALI AND ALKALINE EARTH SALTS

BY MATA PRASAD, F.A.SC., S. S. DHARMATTI, D. D. KHANOLKAR AND S. P. WALVEKAR

(Chemical Laboratories, Institute of Science, Bombay)

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THE literature reveals that the values for χ_{CH_2} deduced from several homologous series vary from 11·87 to 11·36 (*cf.* Table I) (All values of the susceptibilities in this paper have been expressed in the units of -1×10^{-6}c.g.s.). This leads one to conclude that the value of χ_{CH_2} may not be a fixed quantity but may vary with the homologous series. Actually, Angus and Hill[2] have observed that the substitution of a methyl group in an acid lowers the value of χ_{CH_2} by 1·0. It is, however, not possible to ascertain how far these differences are significant.

In this paper, the authors have examined the data obtained by them on the susceptibilities of some aliphatic acids and their alkali and alkaline earth salts with a view to find the susceptibility of the $> CH_2$ group.

TABLE I

Investigator	χ_{CH_2}	Series investigated
Pascal ..	12·35 Uncorrected 11·86 Corrected	Alcohols, aldehydes, ketones, acids and amines
Bhatnagar, Mitra and Tuli[1]	11·36	Aliphatic alcohols, acids, esters and aromatic hydro-carbons
Angus and Hill[2] ..	11·68	Alcohols, acids, esters, aromatic hydro-carbons and esters
Bhatnagar and Mitra[3] ..	11·68	Alcohols, acids, hydro-carbons, aliphatic and aromatic aldehydes, ketones, esters, halogen derivatives, nitrogenous compounds and acetylinic compounds
Cabrera and Fahlenbrach[4]	11·48	Alcohols
Woodbridge[5] ..	11·67	Acetic acid and alkyl acetates
Gray and Cruickshank[6] ..	11·87	Organic nitrates, nitrites and nitro-compounds
Farquharson and Sastri[7] ..	11·64	Normal aliphatic acids

Experimental

All the compounds used in this investigation were chemically pure. Their magnetic susceptibilities were measured on a modified form of Gouy's balance by the method adopted by Prasad, Dharmatti and Gokhale[8] using KCl (A.R. quality) as standard substance. The results obtained are a mean of six independent readings.

Results

The observed magnetic susceptibilities of the compounds are given in Table II in which the following notations have been used:—

χ_a = specific susceptibility.

χ_m = molecular susceptibility.

χ_{ma} = molecular susceptibility of anhydrous substance.

The values of χ_m and χ_{ma} have been given one below the other. Wherever hydrated substances have been studied, the molar susceptibility of the anhydrous salt has been calculated by subtracting the susceptibility of the molecules of water of crystallisation from the molecular susceptibility of the hydrate, assuming strict additivity.

Table II

Substance	χ_a	χ_m and χ_{ma}
Formic acid ..	0·434	20·00
Acetic acid ..	0·535	32·10
Propionic acid ..	0·578	42·80
Butyric acid ..	0·636	56·00
Palmitic acid ..	0·772	197·80
Stearic acid ..	0·771	219·40
Lithium formate, $1H_2O$ ..	0·494	34·57 21·61
,, acetate ..	0·533	35·20
,, propionate ..	0·573	45·90
,, butyrate ..	0·608	57·20
,, palmitate ..	0·730	191·40
,, stearate ..	0·721	209·10
Sodium formate ..	0·360	24·50
,, acetate, $3H_2O$ ..	0·574	78·10 39·22
,, propionate ..	0·509	48·90
,, butyrate ..	0·560	61·60
,, palmitate ..	0·706	196·40
,, stearate ..	0·729	223·10

TABLE II—(*Contd.*)

Substance	χ_a	χ_m and χ_{ma}
Potassium formate* ..	0·370	31·10
,, acetate* ..	0·454	44·60
,, propionate* ..	0·510	57·20
,, butyrate* ..	0·555	70·00
,, palmitate ..	0·700	205·90
,, stearate ..	0·720	232·30
Magnesium formate, $2H_2O$ ..	0·464	69·74 43·82
,, acetate, $4H_2O$ ..	0·567	116·20 64·36
,, propionate, $1H_2O$ ..	0·527	99·30 86·34
,, butyrate ..	0·558	110·60
,, palmitate ..	0·705	376·80
,, stearate ..	0·718	423·90
Zinc formate, $2H_2O$ ..	0·400	76·63 50·71
,, acetate, $2H_2O$ ..	0·460	100·90 74·98
,, propionate ..	0·470	99·40
,, butyrate ..	0·499	119·50
,, palmitate ..	0·673	387·00
,, stearate ..	0·692	436·60
Cadmium formate, $2H_2O$ ..	0·336	80·90 54·98
,, acetate ..	0·363	83·66
,, propionate ..	0·437	109·30
,, butyrate, H_2O ..	0·473	144·00 131·04
,, palmitate ..	0·645	401·60
,, stearate ..	0·650	440·60
Calcium formate ..	0·348	45·30
,, acetate ..	0·433	68·40
,, propionate ..	0·539	100·40
,, butyrate ..	0·558	119·45
,, palmitate ..	0·707	389·10
,, stearate ..	0·721	436·70
Strontium formate ..	0·339	60·30
,, acetate, ½ H_2O ..	0·318	87·70 81·22
,, propionate ..	0·462	107·90
,, butyrate, H_2O ..	0·510	142·60 129·64
,, palmitate ..	0·675	403·30
,, stearate ..	0·677	444·00
Barium formate ..	0·325	73·70
,, acetate ..	0·390	99·49
,, propionate, $1H_2O$ ..	0·453	136·50 123·54
,, butyrate ..	0·468	145·60
,, palmitate ..	0·645	417·40
,, stearate ..	0·654	459·95

* These salts being hygroscopic, their susceptibilities have been measured in solution.

Discussion of Results

Evaluation of χ_{CH_2}.—Pascal's method consists in subtracting the molecular susceptibility of a compound from that of its next higher homologue and then averaging all the values thus obtained for the series concerned. It is obvious that in such a case the accuracy of χ_{CH_2} would depend on the purity of first and the last members of the series.

Farquharson and Sastri[7] plotted χ_m of compounds belonging to a homologous series against n the number of CH_2 groups in the molecule, subtracted the intercept of the straight line on the χ_m axis from the molecular susceptibility of each member of the series, and therefrom calculated the average value of χ_{CH_2}. The same method has been adopted by Angus and Hill.[2] This method has an advantage over that of Pascal's as it utilises the observed molar susceptibility of each member of the homologous series.

The present authors, however, consider that the value of χ_{CH_2} should be calculated from the slope of the $\chi_m - n$ straight lines as it will be free from small errors involved in the actual measurements of the molecular susceptibilities of individual compounds which are smoothened out in drawing the straight lines. The authors have, therefore, plotted the graphs of the molecular susceptibilities of (*i*) the aliphatic fatty acids and (*ii*) the Ca, Sr, Ba, Mg, Zn, Cd, Li, Na and K salts of these acids against the number of CH_2 groups in the molecules. These are shown in Fig. 1.

The values of χ_{CH_2} calculated from each straight line are given in Table III. It will be seen from the table that (*i*) the value of χ_{CH_2} obtained from the series of acid agrees quite well with those reported by Bhatnagar and Mitra and Angus and Hill (*cf.* Table I), and (*ii*) the values of χ_{CH_2} obtained from different series may be different.

Table III

Series	χ_{CH_2}
Acids ..	11·83
Lithium salts ..	11·06
Sodium salts ..	11·50
Potassium salts ..	11·78
Magnesium salts ..	11·17
Zinc salts ..	11·30
Cadmium salts ..	11·36
Calcium salts ..	11·56
Strontium salts ..	11·42
Barium salts ..	11·47

In a recent publication, Mll. K. Kadomtzeff[9] has determined the susceptibilities of some plumbanes and has calculated the values of χ_{Pb} from these

compounds. The paper does not give the actual molar susceptibilities of these compounds but merely records the values of χ_{Pb}. Presuming *that values of χ_{Pb} were calculated by deducting the corrected data of Pascal for the susceptibilities of C and H from the observed molar susceptibilities of the plumbanes, the present authors have calculated the molar susceptibilities of these compounds and have plotted them against the number of CH_2 groups. The plotted points definitely lie on a straight line. The value of χ_{CH_2} calculated from the slope of the straight line is 10·8 which is again different from the values obtained from the homologous series of the acids and the alkali and alkaline earth salts. This observation lends further support to the conclusion that the value of χ_{CH_2} is specific for a given homologous series.

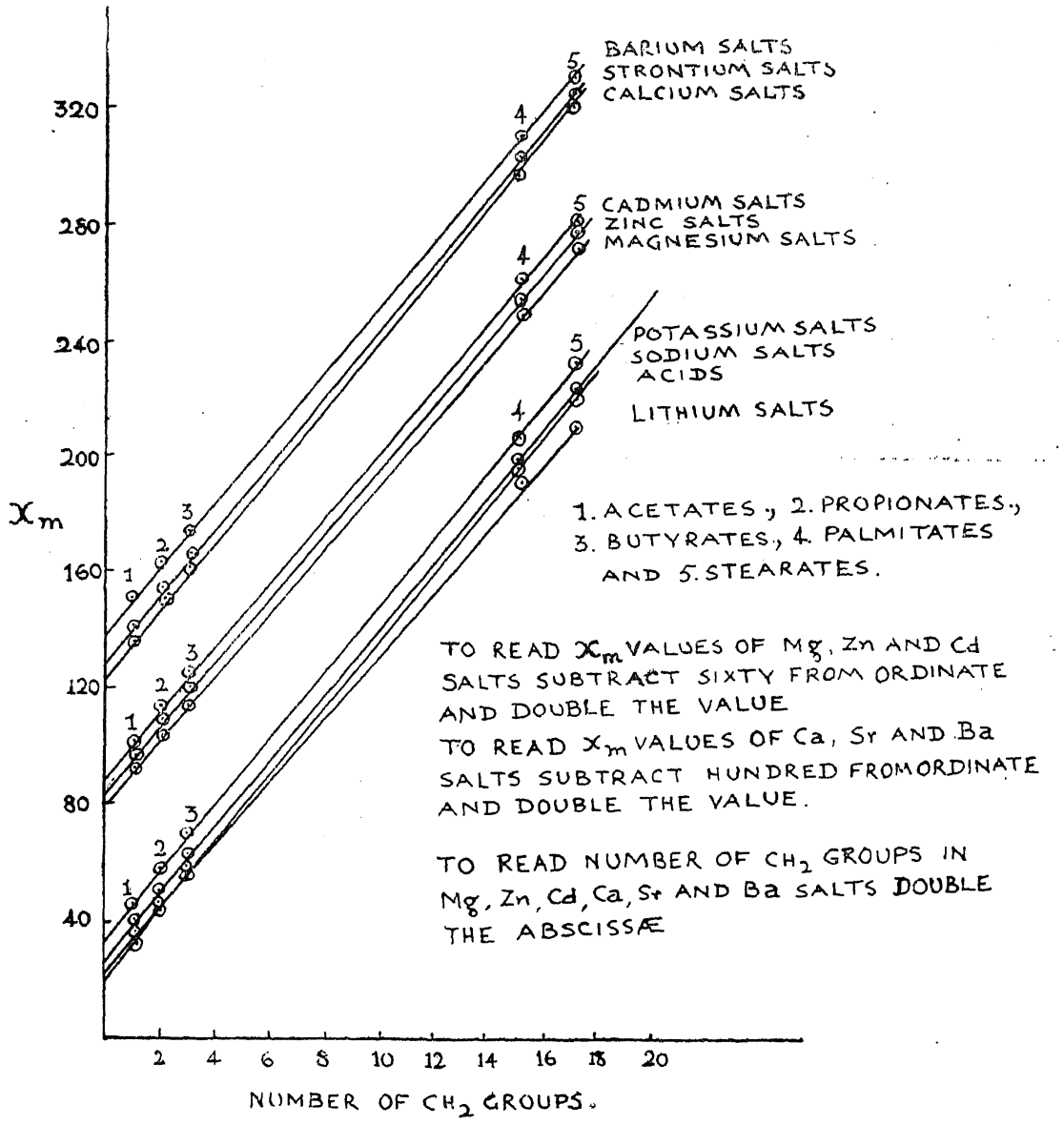

FIG. 1

* This presumption has been confirmed from Mll. Kadomtzeff in a private communication.

The values of the intercepts of the straight lines shown in Fig. 1 have been read and given in Column 2 of Table IV. They should represent the susceptibilities of formic acid and of the metal formates. Hence, these values have been compared with the observed values of formic acid and metal formates studied by the authors. The two values agree well with each other in most cases.

TABLE IV

End group in the homologous series	χ_m	
	(from the graph)	(Observed)
Formic acid ..	20·0	20·0
Lithium formate ..	22·0	21·61
Sodium formate ..	26·0	24·50
Potassium formate ..	32·0	31·10
Magnesium formate ..	42·0	43·82
Zinc formate ..	50·0	50·71
Cadmium formate ..	59·0	54·98
Calcium formate ..	44·0	45·30
Strontium formate ..	59·0	60·30
Barium formate ..	74·0	73·70

This confirms that (*i*) the relation between χ_m and n for a homologous series is definitely linear, (*ii*) the susceptibilities of the CH_2 group and the rest of the molecule of a particular homologous series is definitely additive, and (*iii*) probably the value of χ_{CH_2} is definite only for the $> CH_2$ group in the molecules of a given homologous series.

SUMMARY

The susceptibility of CH_2 group has been determined from the molecular susceptibilities of a homologous series of aliphatic acids and their alkali and alkaline earth salts. It has been found that the value of χ_{CH_2} is constant for a given homologous series but may be different for different series.

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