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AN EMPIRICAL RELATION BETWEEN BOND DISTANCE AND THE PERCENTAGE OF IONIC CHARACTER

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ABSTRACT

We demonstrate for the MY series of halogen bonds (M=metal; Y=halogen) the empirical relation

$$R^{-1} = a\,\Delta x + b$$

R is the reciprocal of bond distance and ΔX is the percentage of ionic character of Hannay-Smyth

$$\Delta x = 16\,|\chi_M - \chi_Y| + 3.5\,(\chi_M - \chi_Y)^2$$

where χ_M and χ_Y are Pauling's electronegativities of the atoms M and Y. The parameters a and b are shown to be given by

$$10^3\,a = 12.2078\,\chi_M/(n+1) + 0.8359$$

$$b = 0.1046\,\chi_M\,(1+0.75/nm) + 0.1024$$

where n is the valence quantum number and m is the number of valence electrons of the atom M.

It has been shown by Yeranos [1-3] for the series of halogen bonds MY (M=metal; Y=halogen), a general formula $Y=K\omega+c$ which is simultaneously applicable to stretching force constants, f, the dissociation energy, De, as well as the reciprocal of the mean square amplitudes, σ_r. Here ω is given by the expression.

$$\omega = \Delta x + \theta_f$$

where Δx is the percentage of ionic character of Hannay-Smyth[4]

$$\Delta x = 16|\chi_M - \chi_Y| + 3.5\,|\chi_M - \chi_Y|^2$$

and θ_f is non-zero only for fluorides and with different values for each type of molecular parameter, and χ_M and χ_Y are Pauling's electronegativities of the atoms M and Y. Recently a similar relation between the reciprocal of the bond distance and the percentage of ionic character has been shown for the halides[5]. In this paper we report an empirical formula relating these parameters.

In figures 1 to 5 we see for a number of series of

INSERT FIGURES 1 to 5

halogen bonds a relation between the reciprocal of bond distance and the percentage of ionic character of the form

$$R^{-1} = a\,\Delta x + b$$

where a and b are constants for each M. The bond distances are

given in table 1, and are from references 5 to 23. The figure

INSERT TABLE 1

shows almost perfect linear correlations, without the θ_f correction. By considering this observation, we extrapolate a number of bond distances, which are given in parenthesis in Table 1.

A number of observations which might be helpful in the understanding of the correlations can be made:

(i) The slope of the curves decreases as the valence quantum number, n, of the atoms M increases, provided we compare metals M from the same column of the periodic table.

(ii) As one moves from the left to the right of the periodic table, keeping n constant, the slope of the curves increases.

The observations (i) and (ii) are valid for other molecular parameters, reinforcing the universality of ω for the description of the halide molecular parameters. In Table 2, we give the empirical values of $\underline{a}$ for the present molecules. By considering

INSERT TABLE 2

(i) and (ii) and the dependence of $\underline{a}$ on χ_M, we propose the following empirical form for a

$$a=\alpha\ \chi_M/(n+1) + \beta$$

where α and β are constants. In figure 6, we show the relation

INSERT FIGURE 6

between $\underline{a}$ and $\chi_M/(n+1)$. We see an almost linear correlation between $\underline{a}$ and $\chi_M/(n+1)$ with $\alpha = 12.2078 \times 10^{-3}$ and $\beta = 0.8359 \times 10^{-3}$.

In table 3, we give the observed values of $\underline{b}$ for the

INSERT TABLE 3

present molecules. If $\Delta x = 0$ we have $R^{-1} = b$; the molecules F_2, $C\ell_2$, Br_2 and I_2 show $\Delta x = 0$. So the reciprocals of the bond distances of these molecules were assigned to $\underline{b}$ and included in table 3. The parameter $\underline{b}$ is almost proportional to χ_M, showing a slight dependence on n and m, where m is the number of valence electrons. From this consideration, we propose the following empirical form for $\underline{b}$

$$b = \gamma \chi_M \left(1 + \frac{\delta}{nm} \right) + \varepsilon$$

where γ, δ and ε are constants. In figure 7, we show the relation between $\underline{b}$ and $\chi_M(1+0.75/nm)$, which is almost linear with $\gamma = 0.1046$ and $\varepsilon = 0.1024$.

INSERT FIGURE 7

From the above considerations we have for the prediction of the reciprocal of bond distance

$$R^{-1} = 12.2078\ \chi_M/(n+1) + 0.8359\ 10^{-3}\ \Delta x$$

$$+ 0.1046\ \chi_M\ (1+0.75/nm) + 0.1024$$

By using this formula we evaluate the bond distances of the present molecules, and compare with the experimental values in table 4. The

INSERT TABLE 4

greatest error of the above formula in the prediction of the bond distance is 12.8% for CI_4. The mean relative error is 3.7%. We apply the above empirical formula to predict bond distances for a number of molecules, provided they exist, and show the results in table 5. It is easy to observe three series of molecules with

INSERT TABLE 5

unspected behaviour for R. In the series OY_2, SeY_2 and NY_3 we observe that the present empirical relation predicts a decrease in bond distance from $OC\ell_2$ to OBr_2, from $SeBr_2$ to SeI_2 and from NBr_3 to NI_3. But, the bond distance must increase from F to I, because the atomic radii of the halogens increase from F to I. We observe that $\chi_M - \chi_Y$ changes sign from $OC\ell_2$ to OBr_2, from $SeBr_2$ to SeI_2 and from NBr_3 to NI_3, and so we associate the failure of the present empirical relation to this observation. That is, our relation can not be applied if $\chi_M - \chi_Y$ changes sign.

ACKNOWLEDGMENT

One of the authors (K.W.) conveys his thanks to FUNDAÇÃO DE AMPARO A PESQUISA DO ESTADO DE SÃO PAULO for awarding a research scholarship which enabled him to pursue this investigation.

TABLE 1. Halogen Bond Distances in Angstrons [a].

Molecules	F	Cℓ	Br	I
HY	0.9171	1.2746	1.4138	1.6041
LiY	1.5639	2.0207	2.170	2.392
NaY	1.9259	2.3606	2.502	2.7114
KY	2.1714	2.6666	2.8208	3.0478
RbY	2.2655	2.7867	2.9445	3.1768
CsY	2.3453	2.9062	3.0722	3.3152
MgY_2	1.77	2.18	2.34	(2.52)
SrY_2	2.20	2.67	2.82	3.03
BaY_2	2.32	2.82	2.99	3.20
BY	1.2625	1.7157	1.877	(2.115)
AℓY	1.6544	2.1230	2.2950	(2.526)
GaY	1.7744	2.2017	2.3525	2.5747
InY	1.9854	2.4011	2.5432	2.7539
TℓY	2.0844	2.4847	2.6180	2.8135
CY_4	1.320	1.768	1.94	2.14
SiY_4	1.545	2.01	2.15	2.43
GeY_4	1.67	2.09	2.314	2.49
SnY_4	(1.86)	2.315	2.44	2.64
PY_3	1.52	2.043	2.20	2.46
AsY_3	1.712	2.161	2.33	2.55
SbY_3	(1.91)	2.352	2.51	2.67
SOY_2	1.585	(1.99)	2.27	(2.52)

a. The values in parentheses were obtained from linear extrapolation through the figures 1 to 5.

TABLE 2. Values of a in (10^3 Å)$^{-1}$

Column / Row	IA	IIA	IIIA	IVA	VA	VIA
1	14.891					
2	5.194	(7.225)	9.705	10.350	(13.207)	(14.834)
3	3.474	4.254	5.772	6.797	7.974	8.398
4	2.997	(3.277)	4.959	5.988	6.048	(7.062)
5	2.870	2.897	3.940	4.699	4.545	(4.926)
6	2.815	2.734	3.737	(4.899)	(4.359)	

TABLE 3. Values of b in Å^{-1}

Column / Row	IA	IIA	IJIA	IVA	VA	VIA	VIIA
1	0.502						
2	0.227	(0.297)	0.364	0.447	(0.460)	(0.530)	0.705
3	0.237	0.278	0.277	0.320	0.340	0.385	0.503
4	0.205	(0.217)	0.311	0.331	0.343	(0.394)	0.437
5	0.196	0.221	0.300	0.318	0.323	(0.328)	0.376
6	0.182	0.205	0.316	(0.354)	(0.322)		

TABLE 4. Bond Distances in Å and Percentage Errors.

Molecule	F			Cℓ			Br			I		
	Re exp	Re calc	Δ %	Re exp	Re exp	Δ %	Re exp	Re calc	Δ %	Re exp	Re calc	Δ %
LiY	1.564	1.596	2.0	2.021	2.034	0.6	2.170	2.163	0.3	2.392	2.378	0.6
NaY	1.926	1.913	0.7	2.361	2.387	1.1	2.502	2.524	0.9	2.711	2.746	1.3
KY	2.171	2.238	3.1	2.667	2.741	2.8	2.821	2.883	2.2	3.048	3.112	2.1
RbY	2.266	2.409	6.3	2.787	2.918	4.7	2.945	3.059	3.9	3.177	3.286	3.4
CsY	2.345	2.583	10.1	2.906	3.098	6.6	3.072	3.240	5.5	3.315	3.465	4.5
MgY_2	1.770	1.714	3.2	2.180	2.186	0.3	2.340	2.325	0.7	(2.520)	2.553	1.3
SrY_2	2.200	2.313	5.1	2.670	2.822	5.7	2.820	2.964	5.1	3.030	3.192	5.4
BaY_2	2.320	2.506	8.0	2.820	3.021	7.1	2.990	3.163	5.8	3.200	3.389	5.9
BY	1.263	1.340	6.1	1.716	1.831	6.7	1.877	1.984	5.7	(2.115)	2.246	6.2
AℓY	1.654	1.624	1.8	2.123	2.102	1.0	2.295	2.244	2.2	(2.526)	2.478	1.9
GaY	1.774	1.747	1.6	2.202	2.220	0.8	2.353	2.356	0.1	2.575	2.576	0.0
InY	1.985	1.886	5.0	2.401	2.348	2.2	2.543	2.477	2.6	2.754	2.684	2.6
TeY	2.084	1.927	7.5	2.485	2.366	4.8	2.618	2.486	5.0	2.814	2.673	5.0
CY_4	1.320	1.368	3.7	1.768	1.930	9.2	1.940	2.109	8.7	2.140	2.414	12.8
SiY_4	1.545	1.576	2.0	2.010	2.066	2.8	2.150	2.212	2.9	2.430	2.454	1.0
GeY_4	1.670	1.720	3.0	2.090	2.199	5.2	2.314	2.337	1.0	2.490	2.560	2.8
SnY_4	(1.862)	1.853	6.5	2.315	2.315	0.0	2.440	2.445	0.2	2.640	2.650	0.4
PY_3	1.520	1.538	1.2	2.043	2.033	0.5	2.200	2.180	0.9	2.460	2.422	1.5
AsY_3	1.712	1.690	1.3	2.161	2.165	0.2	2.330	2.301	1.2	2.550	2.520	1.2
SbY_3	(1.915)	1.827	4.6	2.352	2.283	2.9	2.510	2.410	4.0	2.670	2.612	2.2
SY_2	1.585	1.513	4.5	1.990	2.012	1.1	2.270	2.159	4.9	(2.525)	2.397	5.1

TABLE 5. Evaluated Bond Distances in Å

Molecule	F	Cℓ	Br	I
BeY_2	1.38	1.84	1.97	2.21
CaY_2	2.11	2.61	2.75	2.98
OY_2	1.49	1.67	1.53	1.34
SeY_2	1.65	2.12	2.25	1.96
TeY_2	1.82	2.26	2.39	2.59
NY_3	1.43	2.06	2.10	1.83
BiY_3	1.93	2.37	2.49	2.68
PbY_4	1.89	2.32	2.44	2.62

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FIGURE CAPTIONS

Figure 1. Reciprocal of bond distance (R^{-1})vs percentage of ionic character (Δx) of Group IA diatomic halides. R is in Angstroms and Δx in %.

Figure 2. Reciprocal of bond distance (R^{-1}) vs percentage of ionic character (Δx) of Group IIA triatomic halides. R is in Angstroms and Δx in %.

Figure 3. Reciprocal of bond distance (R^{-1}) vs percentage of ionic character (Δx) of Group IIIA diatomic halides. R is in Angstroms and Δx in %.

Figure 4. Reciprocal of bond distance (R^{-1}) vs percentage of ionic character (Δx) of froup IVA tetrahedral halides. R is in Angstroms and Δx in %.

Figure 5. Reciprocal of bond distance (R^{-1}) vs percentage of ionic character (Δx) of Group VA pyramidal halides. R is in Angstroms and Δx in %.

Figure 6. a (10^{-3}) vs $\chi_M/(n+1)$. a is in A^{o-1} and χ_M is the Pauling's electronegativity.

Figure 7. b vs χ_M (1+0.75/nm). b is in A^{o-1}.

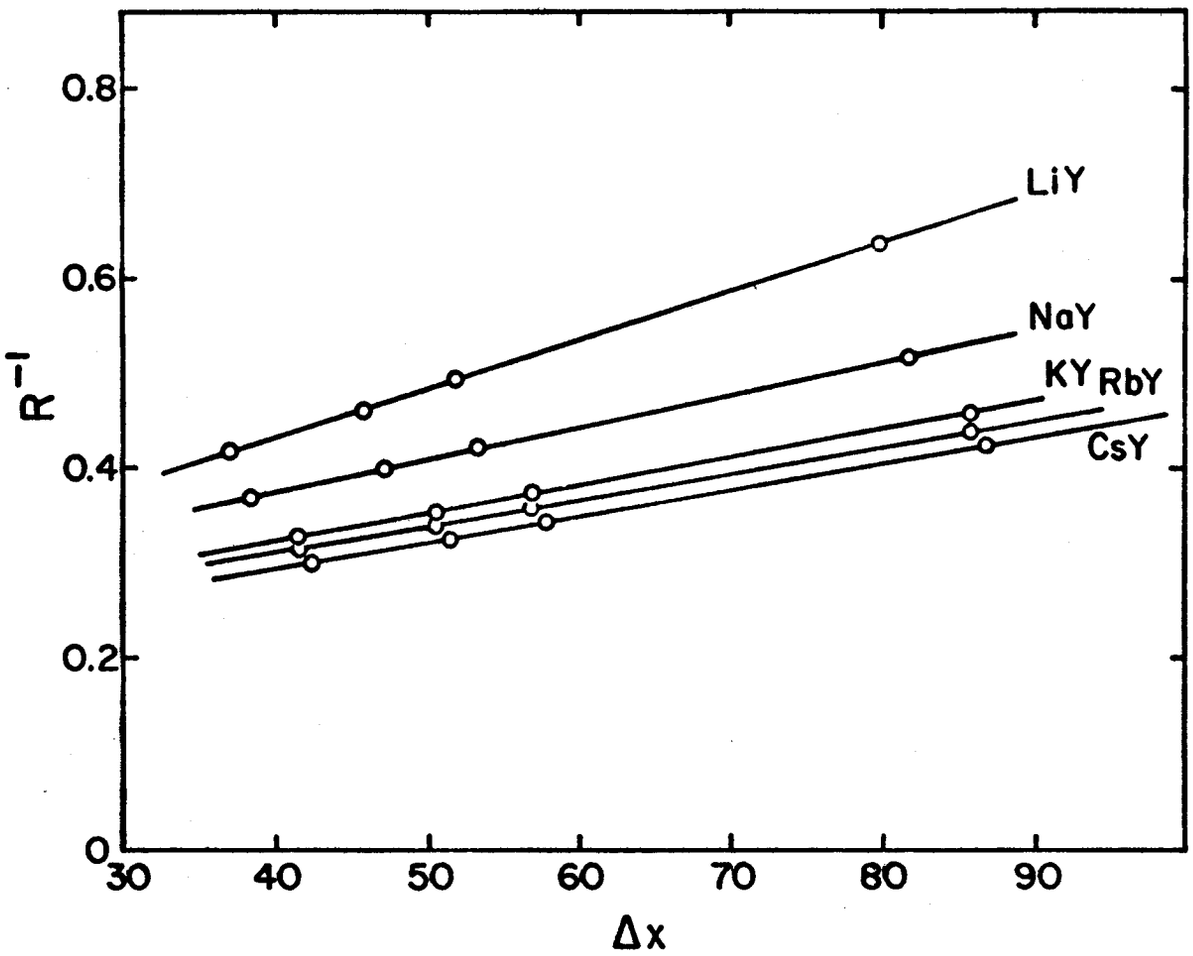


FIGURE 1.

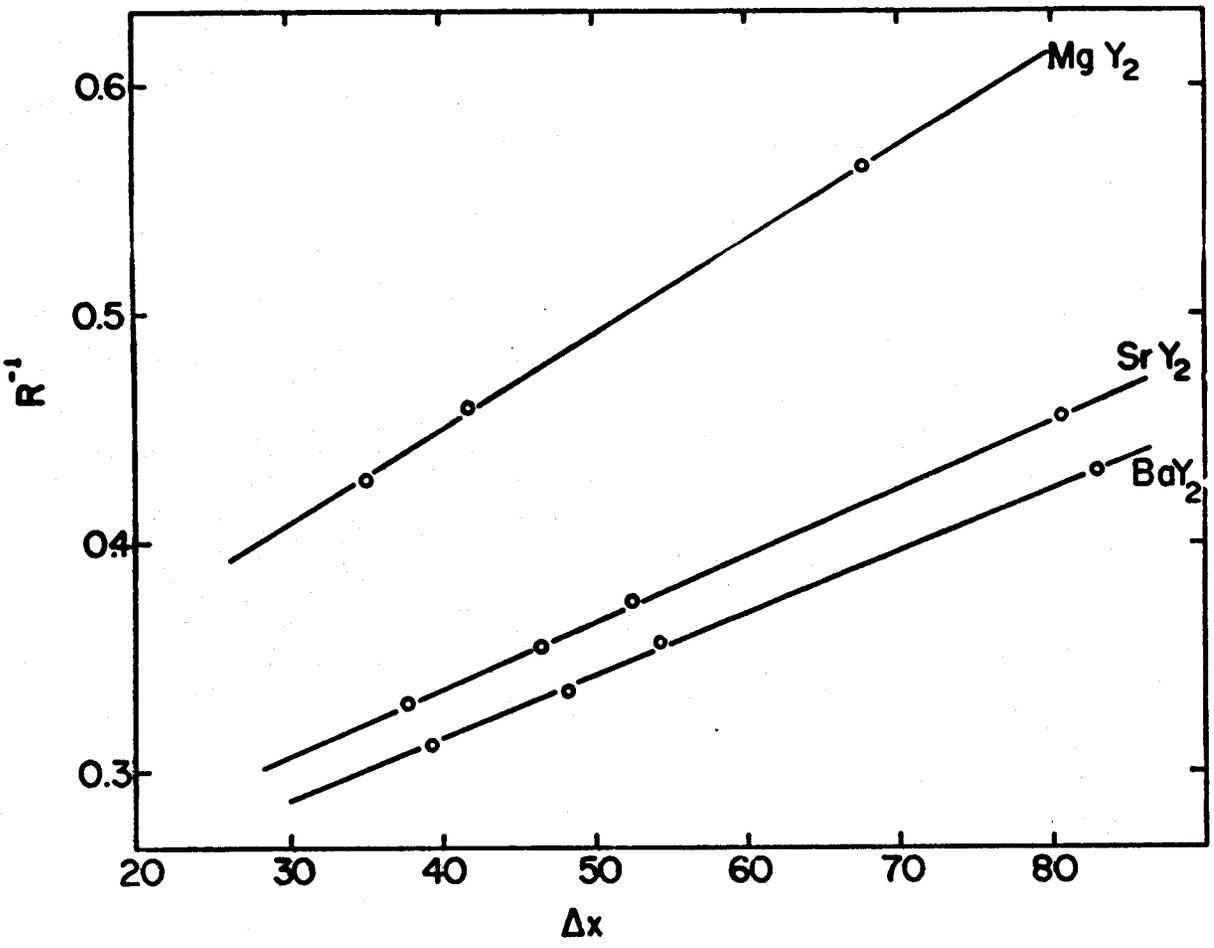


FIGURE 2

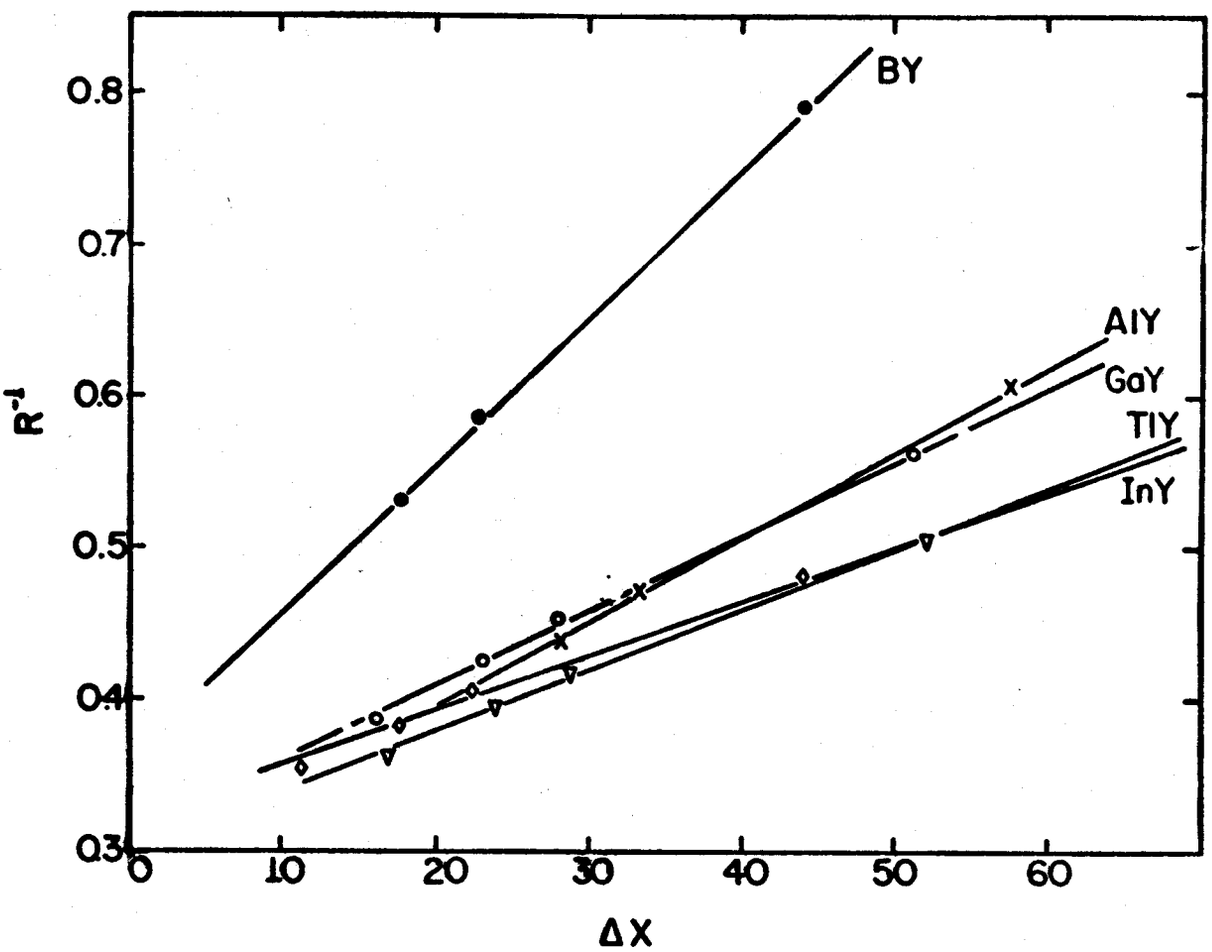


FIGURE 3

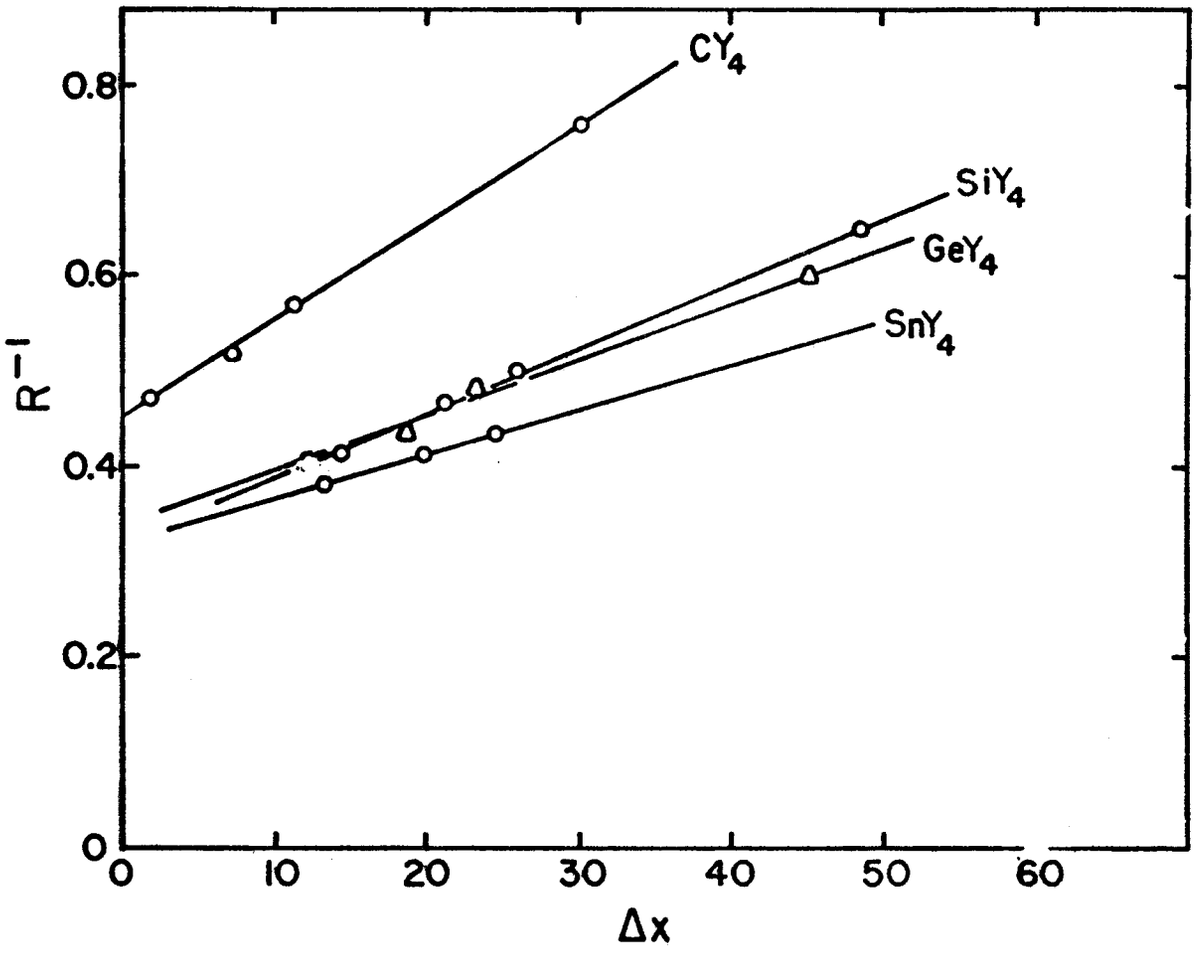
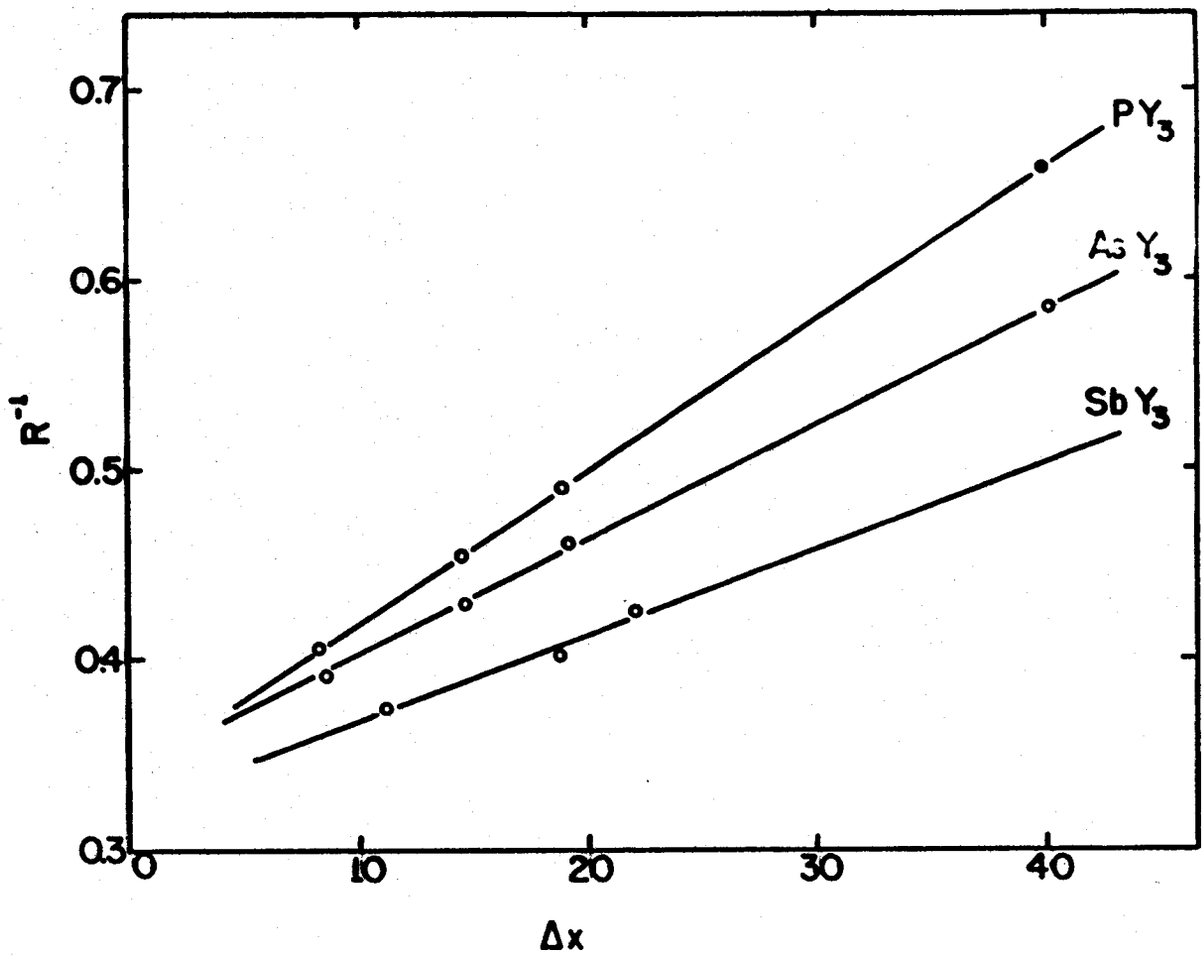


FIGURE 4



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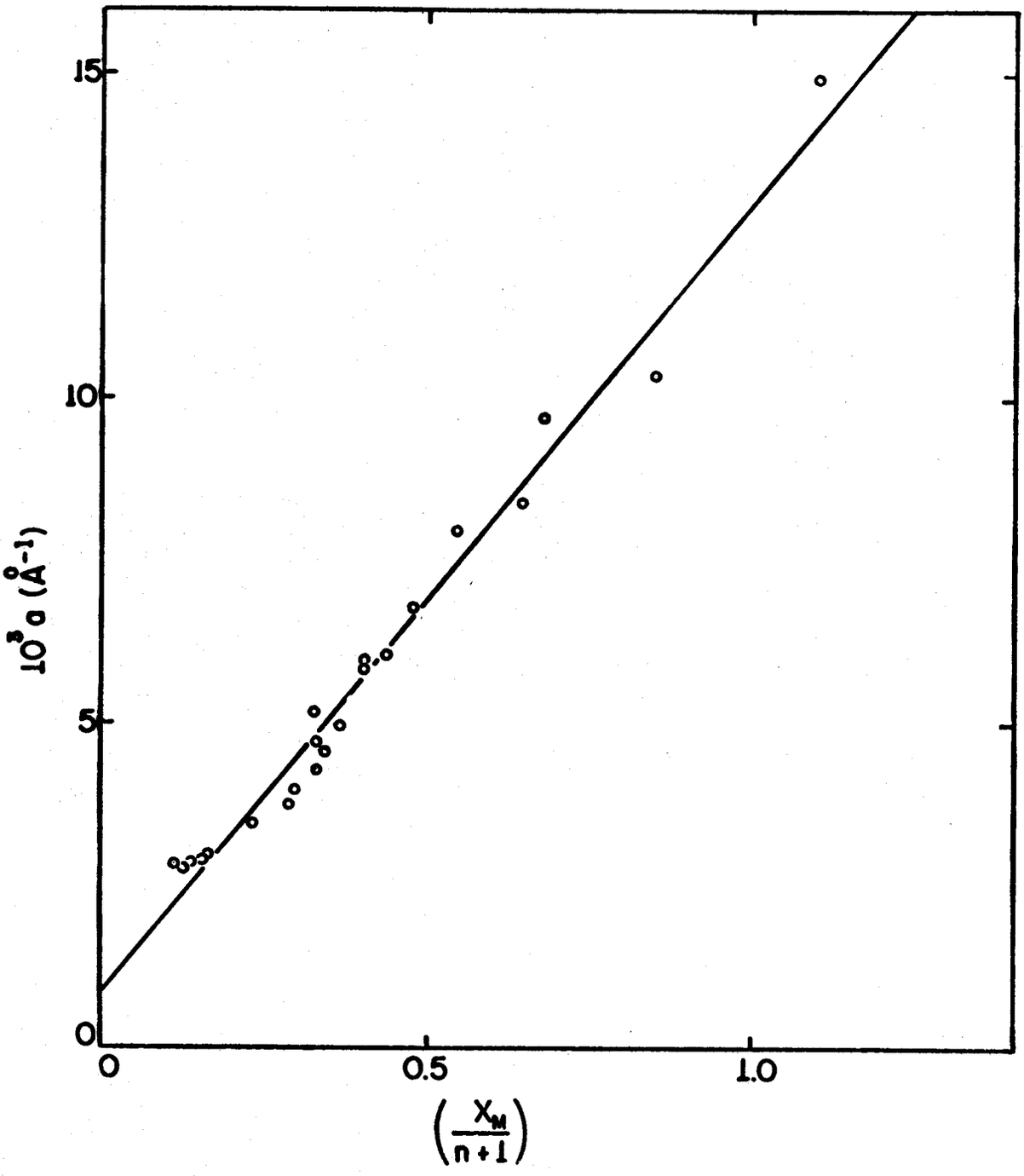

FIGURE 6

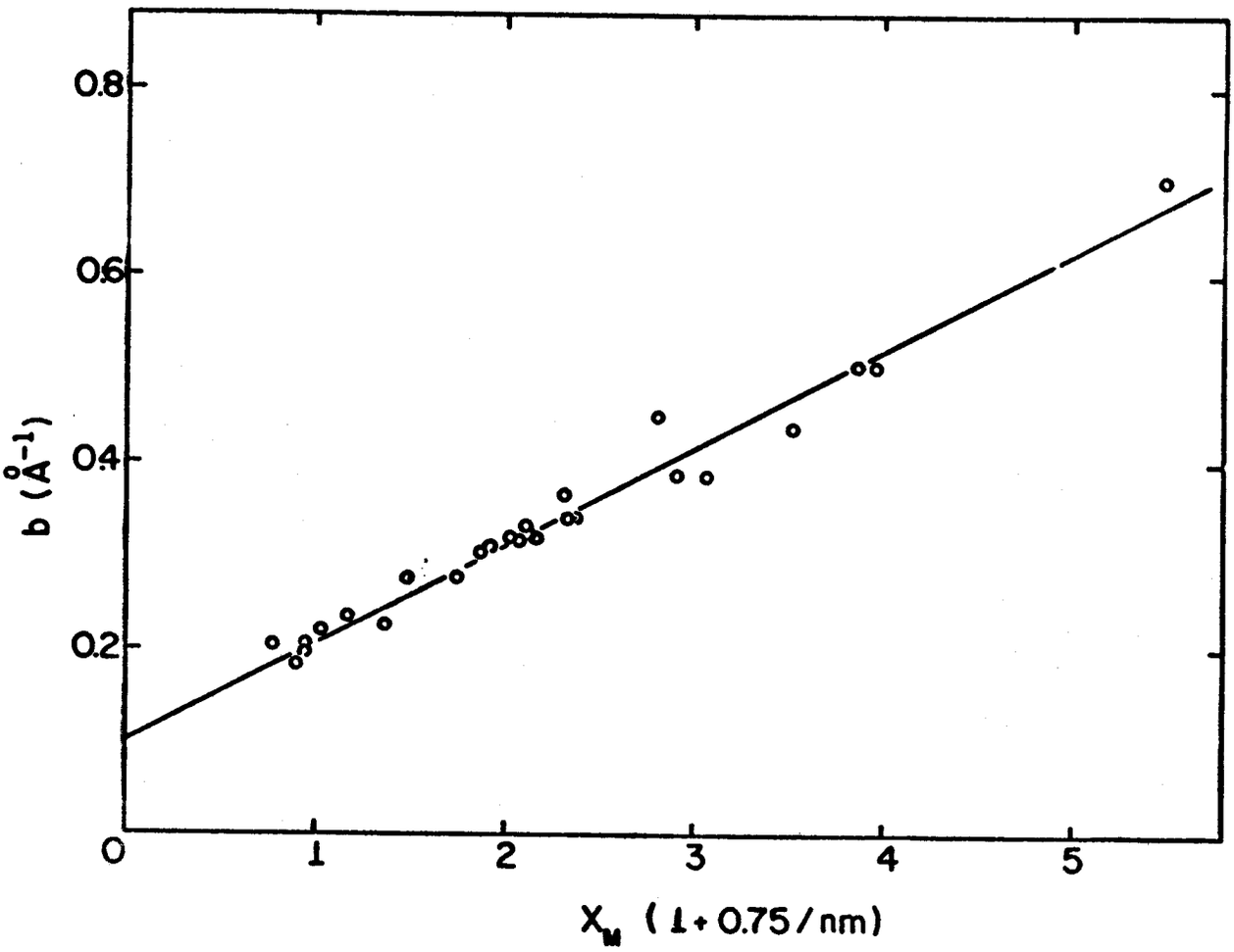

FIGURE 7