RELATIONSHIP BETWEEN DIFFUSION CONSTANTS AND MOLECULAR WEIGHT

by

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It has recently been shown[1] that the relationship

$$D = \frac{a}{M^{1/3}} \qquad (1)$$

which was derived from the STOKES-EINSTEIN equation, where D is the diffusion constant, M the molecular weight and a is an empirical constant, is applicable to substances of compact form and molecular weights ranging from those of the globular proteins to those of tannic acid ($M = 1700$) and Gramicidin S ($M = 1140$). This equation, however, is not applicable to substances of molecular weights lower than 1500. Below this value of $M = 1500$, a shows an ever-increasing value and at $M = 19$ becomes roughly twice that which it has above $M = 1500$.

In an attempt to extend formula (1) to cover these cases an excellent fit over the entire range of the data from molecules of the size of water to African horsesickness virus was obtained by the following empirical equation

$$D = \frac{a}{M^{1/3}} + \frac{b}{M^{2/3}} + \frac{c}{M} \qquad (2)$$

where b and c are constants.

The first term in equation (2) resembles the relationship of PEDERSEN AND SYNGE[2] .

$$D = \frac{k}{(MV)^{1/3}} \qquad (3)$$

and in its derivation (eq. 2) $V^{1/3}$ was assumed to be constant as a first approximation. a in equation (2) equals $\frac{k}{V^{1/3}}$ in equation (3).

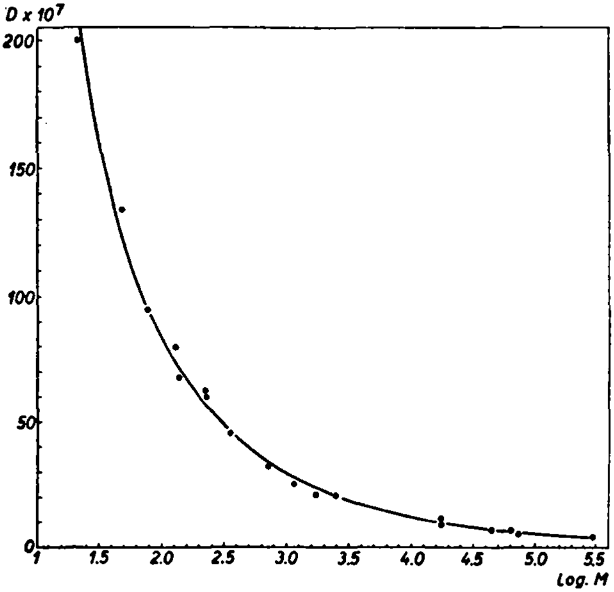

Fig. 1. Curve showing the relationship between log mol. weight and diffusion constant.

The equation was fitted by an empirical process. After a was estimated, the first component calculated was subtracted from the observed data and then b was estimated from the residues obtained, and so on. The goodness of fit can be judged from Fig. 1 where, in order to show the whole range, the diffusion constants are plotted against the logarithm of M.

Table I below and Fig. 2 show the contribution of each component of formula (2) to the estimated value of D. It will be observed that while the contributions of the $M^{1/3}$ and M factors are very important, below M 1500 they are almost negligible for molecular weights above 1500.

Since the dimensions of the second and third components are those of surface and volume respectively, it is suggested that these components measure the effects of the medium on the diffusing particle.

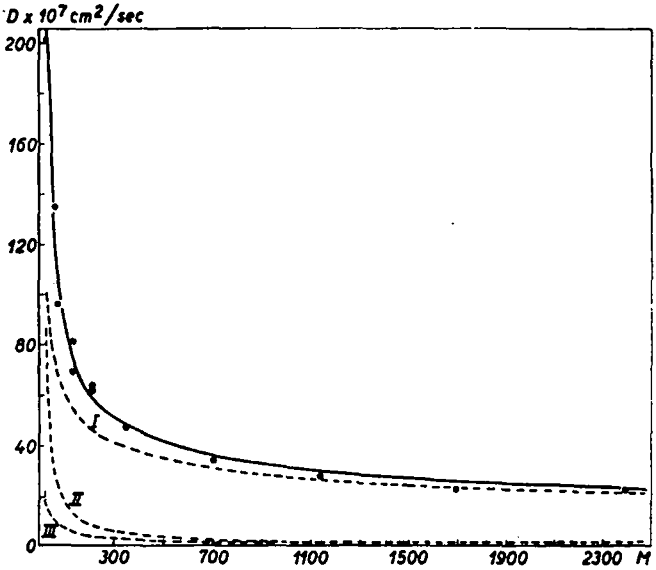

Fig. 2. Contribution of each component in equation (2) to the diffusion constant

$$\text{I} = \frac{a}{M^{1/3}}; \quad \text{II} = \frac{c}{M}; \quad \text{III} = \frac{b}{M^{2/3}}$$

As a certain amount of slipping must take place when small molecules move amongst solvent molecules of similar size, the term related to the volume, or M, will most likely come into consideration.

TABLE I

Substance	M	$D_{obs} \cdot 10^7$	$\frac{a}{M^{1/3}}$	$\frac{b}{M^{2/3}}$	$\frac{c}{M}$	$D_{calc} \cdot 10^7$	Ref.
Exelsine	294,000	4.26	4.12	0.037	0.006	4.16	3
Seram albumin	70,100	6.17	6.65	0.097	0.024	6.77	3
Haemoglobin	63,000	6.90	6.89	0.104	0.027	7.02	3
Ovalbumin	43,800	7.76	7.77	0.133	0.039	7.94	3
Lactalbumin	17,500	10.57	10.55	0.245	0.100	10.90	3
Myoglobin	17,200	11.25	10.61	0.248	0.100	10.96	3
Tyrocidine	2,473	21.30	20.26	0.902	0.687	21.85	2
Tannic acid	1,700	22.00	22.96	1.158	1.000	25.12	1
Gramicidin S	1,140	26.00	26.23	1.512	1.491	29.23	2
Transvaalin	700	32.90	30.86	2.093	2.429	35.38	4
Sucrose	346	46.00	39.03	3.348	4.913	47.29	5
Citric acid	208	61.10	46.24	4.700	8.173	59.11	1
Tryptophane	208	62.00	46.24	4.700	8.173	59.11	5
Pentaerythrite	136	68.00	53.28	6.239	12.500	72.02	6
Proline	125	80.20	54.80	6.600	13.600	75.00	5
Glycine	75	95.00	64.97	9.278	22.667	96.92	5
Formic acid	46	134.00	76.46	12.852	36.957	126.28	5
Deuterium oxide	19	200.00	100.94	22.394	85.000	208.33	6

The surface effect or $M^{2/3}$ will most probably be related to the extent that a molecule is solvated.

The numerical values of the coefficients of the emperical equation were found to be $a = 2.74 \cdot 10^{-5}$, $b = 1.65 \cdot 10^{-5}$ and $c = 17.00 \cdot 10^{-5}$. It is, however, possible in practice to change these values somewhat without sensibly affecting the goodness of fit.

It would be very interesting to deduce this relationship from theoretical considerations.

SUMMARY

The diffusion constants of electrically neutral organic compounds of compact structure can be presented by an empirical equation of the form

$$D = \frac{a}{M^{1/3}} + \frac{b}{M^{2/3}} + \frac{c}{M}$$

a, b and c are constants and M is the molecular weight.

From this equation it is suggested that the diffusion constant is a function of the radius of the molecule, its area and its volume.

RÉSUMÉ

Les constantes de diffusion de composés organiques électriquement neutres et de structure compacte peuvent être représentées par une équation empirique de la forme

$$D = \frac{a}{M^{1/3}} + \frac{b}{M^{2/3}} + \frac{c}{M}$$

où a, b et c sont des constantes et M le poids moléculaire.

Cette équation suggère que la constante de diffusion est fonction du rayon, de la surface et du volume de la molécule.

ZUSAMMENFASSUNG

Die Diffusionskonstanten organischer, elektrisch neutraler Verbindungen mit kompakter Struktur können durch eine empirische Gleichung von der Form

$$D = \frac{a}{M^{1/3}} + \frac{b}{M^{2/3}} + \frac{c}{M}$$

ausgedrückt werden, wo a, b und c Konstanten und M das Molekulargewicht bedeuten.

Aus dieser Gleichung geht hervor, dass die Diffusionskonstante eine Funktion des Radius, der Oberfläche und des Volumens der Molekel ist.

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