Influence of Turbulence on Electrokinetic Phenomena; Experimental Determination of the Thickness of the Diffuse Part of the Double Layer

A laminar flow of liquid through a capillary is accompanied by a streaming current given by

$$I_{lam.} = D\zeta\, v_{ax} = 2\, D\zeta\, \bar{v} \tag{1}$$

where

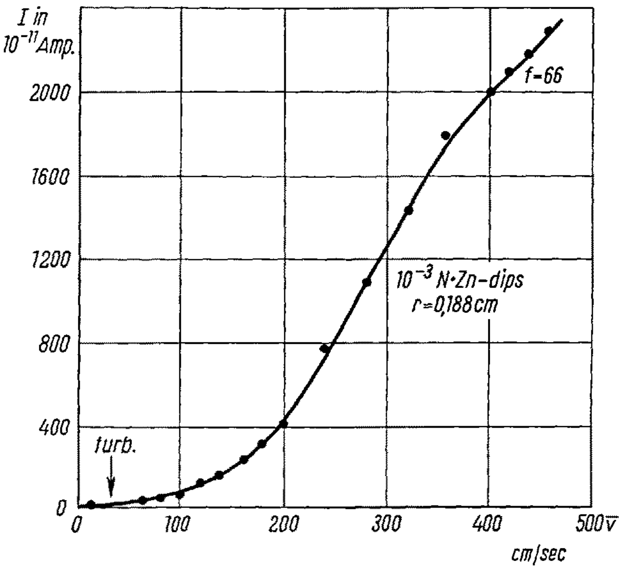
$$\bar{v} = \frac{Q}{\pi r^2} = \frac{r^2}{8\eta}\,\frac{p}{l} \tag{2}$$

is the bulk velocity of the liquid; D is the dielectric constant of the liquid, η its viscosity, ζ the electrokinetic potential, Q the volume of liquid passing per second through a cross section.

The electric charges in the liquid lie in a diffuse layer close to the wall; consequently, in the case of laminar flow, they obtain only very small speeds.

In the case of turbulent flow, however, parts of the liquid near the wall may be carried to the central part of the capillary, and obtain the speed $\bar{v}$; therefore we can expect, as was pointed out to us by Dr. A. KLINKENBERG of the Hague, a big effect of turbulence upon streaming potentials and streaming currents.

Our first experiments were carried out with thrice distilled water; here we measured streaming potentials and streaming currents; in these experiments, turbulence set in at $p = 26{\cdot}5$ cm of water pressure; we measured up to $p = 120$ cm; the results were negative: no influence of turbulence was detected.



Influence of turbulence on streaming current

We then studied benzene, which we had made a little conductant by means of Zn-di-i-propylsalicylate (Zn-dips); the solutions were $10^{-5}N$, $10^{-4}N$, and $10^{-3}N$; the conductivities were $0{\cdot}5$, $1{\cdot}2$ and $2{\cdot}6 \times 10^{-12}$ ohm^{-1} cm^{-1}; the radii of the capillaries were 0·188, 0·116 and 0·044 cm; turbulence set in at $p_t = 6$ cm, 13 cm, and 80 cm of water pressure respectively. There was a big effect of turbulence upon the streaming current I; at low pressure (laminar flow), I is proportional to $\bar{v}$, the charges in the liquid move with speeds of the layers of liquid near the wall; at $p \cong 3p_t$ I begins to increase more strongly; at much higher pressures I is again proportional to $\bar{v}$, but the value of $I/\bar{v}$ is much higher than for laminar flow (*cf.* the fig.). This part of the curve we interprete by supposing that here all the charges in the liquid move with the bulk velocity $\bar{v}$ of the turbulent flow:

$$I_{turb.} = 2\pi r \times q\,\bar{v} = 2\pi r \times \frac{D\zeta}{4\pi\delta}\bar{v} = 2\,D\,\bar{v}\,\zeta\,\frac{r}{4\delta} \tag{3}$$

Here q is the charge in the liquid opposite 1 cm^2 of the wall.

The factor

$$f = \frac{r}{4\delta} \tag{4}$$

is the ratio between the slopes of the laminar and the turbulent part of the $I-\bar{v}$-curves. To give only one example, for our $10^{-3}N$ solution of Zn-dips in benzene, measured in the capillary with $r = 0{\cdot}188$ cm, we found $f = 66$, giving $\delta = 7 \times 10^{-4}$ cm.

r / c	0·188 cm	0·116 cm	0·044 cm	$\varkappa^{-1}$
$10^{-5}\,N$	$f = 12{\cdot}6$	$f = 6$	–	
	$\delta = 37\mu$	$\delta = 48\mu$	–	23μ
$10^{-4}\,N$	$f = 35$	$f = 20{\cdot}6$	–	
	$\delta = 13\mu$	$\delta = 14\mu$	–	15μ
$10^{-3}\,N$	$f = 66$	–	–	
	$\delta = 7\mu$	–	–	11μ

In the table we give the experimental values of f, the values of δ calculated from these, and the values of $\varkappa^{-1}$ ($\varkappa^2 = 4\pi\varepsilon^2 \Sigma n_k z^2{}_k/D\,k\,t$) although we realize that we are outside the region where the DEBYE-HÜCKEL theory is valid.

A. J. RUTGERS, M. DE SMET,
and G. DE MOYER

Laboratorium voor Physische Chemie, Ryksuniversiteit, Gent (Belgium), June 29, 1956.

Zusammenfassung

Durch Messungen in 10^{-5}, 10^{-4} und $10^{-3}N$ benzolischen Lösungen von Zn-di-i-propylsalizylat haben wir einen beträchtlichen Einfluss von Turbulenz auf Strömungsströme feststellen können. Dieser Einfluss kann ausgedrückt werden durch einen Faktor f, der in einem unserer Experimente einen Wert von $f = 66$ erreichte; aus den Werten von f kann die Dicke der diffusen Doppelschicht in der Flüssigkeit berechnet werden.

β-Brazan from Isocoumaranone

It has been shown by CHATTERJEA[1], and also independently in a preliminary way by GEISSMAN and ARMEN[2], that the product obtained by the self-condensation of *iso*coumaranone is 3-*o*-hydroxyphenylacetyl-

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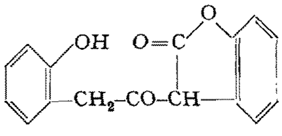
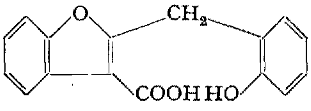
[1] J. N. CHATTERJEA, J. Indian chem. Soc. *33*, 175 (1956).

[2] T. A. GEISSMAN and A. ARMEN, J. Amer. chem. Soc. *77*, 1623 (1955).

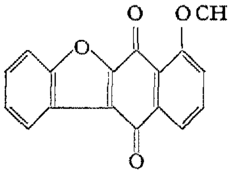
coumaranone-2 (I). On boiling this compound with hydrochloric acid in acetic acid, the furan ring is opened up and reconstituted to give an isomeric phenolic acid (m. p. 194–95°; methyl ester, m. p. 131°) whose structure is found to be (II). The methyl ether (m. p. 157·5°) of this acid on cyclisation by way of the acid chloride,



I



II



III

afforded 7-methoxy-11-hydroxy-β-brazan (not isolated) which furnished the corresponding quinone (III, m. p. 242°) on oxidation with chromic acid in acetic acid. On energetic treatment with hydriodic acid, this quinone gave a small quantity of β-brazan[3] (m. p. 208°) identical with an authentic specimen.

J. N. CHATTERJEA

Chemical Laboratory, Science College, Patna-5, India, June 9, 1956.

Résumé

L'autocondensation de l'isocoumaranone donne le composé (I), qui par l'acide hydrochlorique est isomerisé en l'acide (II). Celui-ci est transformé en β-brazan par cinq réactions consécutives.

[3] J. N. CHATTERJEA, J. Indian chem. Soc. *31*, 101 (1954).

The Application of Hudson's Lactone Rule to γ- and δ-Hydroxyamino Acids and the Question of the Configuration of δ-Hydroxy-L-lysine from Collagen

Configurational assignments for L-*threo*- and L-*erythro*-γ-hydroxyornithine (IIa; Va) and for their corresponding *cis*- and *trans*-disubstituted γ-lactones (IIIa; IVa) have been made on the basis of their conversions to hydroxyprolines[1].

In a greatly simplified presentation of the complicated experimental results (complete retention of configuration at C [2]) IIa leads to allohydroxy-L-proline (Ia) and Va to hydroxy-L-proline (VI)[1].

The lactone of N-carbobenzyloxy-γ-allohydroxy-L-proline (VIIb)[2] has been used as a model to test the applicability and validity of HUDSON's lactone Rule[3] to the (bicyclic) lactone of a γ-hydroxyamino acid. The configuration of VIIa is fixed in an unequivocal manner, since C(2) has the natural $\mathrm{L_s}$-arrangement and since the lactone requires the *cis*-arrangement for the C(2), C(4) substituents involved. The absolute configuration at C(4) is then that of D-glyceraldehyde and leads to the designation $\mathrm{D_G}$. Table I shows that the rotational data and the application of HUDSON's Rule[4] agree with the $\mathrm{D_G}$-configuration of C(4) as required by chemical evidence.

The application of HUDSON's Rule to the *cis*- and *trans*-disubstituted γ-lactones (IIIb, IVb) of α,δ-dihexahydrobenzoyl-L-*threo*- and L-*erythro*-γ-hydroxyornithine (IIb; Vb) became possible when a suitable solvent for these lactones was found. The solvent used up to now has been pyridine in which both lactones show negative rotations (Table). Pyridine, especially for lactones with small rotatory power, should apparently be avoided when configurational assignments are at stake. Dimethyl sulfoxide, m.p. 18·5°[5], on slight warming, dissolved the lactones IIIb and IVb easily and was miscible with the standardized methanolic KOH solution. The results in the Table show again agreement of configurational assignments by chemical and rotational data.

The ring homolog of natural hydroxy-L-proline (VI) is 5-hydroxy-L-pipecolic acid (XII) occurring naturally in dates and other plants. Its configuration (XII) is exactly analogous to that of hydroxy-L-proline (VI)[6]. The conversion of XII, *via* $NaBH_4$ reduction of the N-carbobenzyloxy-5-keto-L-pipecolic acid to allohydroxy-derivatives (XIVa, XIVb) and lactonization to XIIIb and XIIIa established the configurations at C(2) and C(5) in the same unambiguous way as in the case of VIIb and VIIa. The Table shows again the applicability of HUDSON's Rule to this lactone XIIIb.

δ-Hydroxy-L-lysine, despite numerous investigations on its isolation and synthesis[7], is the last important amino acid of unknown configuration. Its lactone is not

[1] B. WITKOP and T. BEILER, J. Amer. chem. Soc. *78*, 2882 (1956).

[2] A. A. PATCHETT and B. WITKOP, J. Amer. chem. Soc. *78*, December 1956.

[3] C. S. HUDSON, J. Amer. chem. Soc. *32*, 338 (1910); *61*, 1525 (1939). – E. ANDERSON, J. Amer. chem. Soc. *34*, 51 (1912). – *cf.* F. BATES and Associates, *Polarimetry, Saccharimetry and the Sugars*, Circular of the National Bureau of Standards C440 (U. S. Government Printing Office, Washington 1942), p. 434.

[4] In its simplest form HUDSON's lactone Rule says: γ- or δ-(sugar) lactones in which the carbon carrying the hydroxyl group is related to D-glyceraldehyde are dextrorotatory, or $[\alpha]_D$ (lactone)-$[\alpha]_D$ (acid) is positive. The opening of the lactones with one equivalent of base, as recorded in the Table, leads to the alkali salts of the open acids which in the examples studied were all N-acyl- or N,N'-diacylamino acids. Only minor rotational changes were observed when the solutions, after completion of mutarotation by base, were brought to a pH of 1.

[5] T. B. DOUGLAS, J. Amer. chem. Soc. *68*, 1072 (1946). – The compound was obtained from: The Stepan Chemical Company, 20 North Wacker Drive, Chicago 6, Illinois.

[6] B. WITKOP and C. M. FOLTZ, J. Amer. chem. Soc. *78*, December (1956).

[7] J. C. SHEEHAN and W. A. BOLHOFER, J. Amer. chem. Soc. *72*, 2466, 2472 (1950). – O. TOUSTER, J. Amer. chem. Soc. *73*, 491 (1951). – G. VAN ZYL, E. E. VAN TAMELEN, and G. D. ZUIDEMA, J. Amer. chem. Soc. *73*, 1765 (1951). – W. S. FONES, J. Amer. chem. Soc. *75*, 4865 (1953). – J. R. WEISIGER, J. biol. Chem. *186*, 591 (1950). – S. BERGSTROM and S. LINDSTEDT, Arch. Biochem. *26*, 323 (1950).