Microviscosity of aqueous dextran solutions investigated by square-wave polarography

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The polarographic method of measuring microviscosity in aqueous solutions of polymers was applied to dextran solutions (MW 20 000 to 150 000). The diffusing species — Tl^+ ions, have already been shown to be an excellent microviscosity probe in the investigation of polyethyleneglycol solutions. At low concentrations of dextrans, the microviscosity is much lower than the macroviscosity measured conventionally. The polarographically measured microviscosities, when compared to the macroviscosity, were used to determine several characteristics of the state of dextran molecules of different molecular weight, and their variation with concentration of the polymer. Values of characteristic concentrations, marking dramatic changes of the structure of the solution as well as coil parameters of dextran were thus determined. The experimental critical concentration, limiting the zone of microviscosity, was found to be close to the theoretical value. This, and other parameters not previously available by experiment, contribute to the better understanding of the structure of polymer solutions and permit comparisons between different polymers.

INTRODUCTION

Present treatment of rheological phenomena shows clearly that the response of the medium depends both on the kind of viscogenic factor and on the diffusing species. The situation is comparatively simple if the viscogenic molecules are small and of compact, spherical shape (e.g. glycerine in water). The size of particle being hampered in its movement by the medium, is of secondary importance in such systems.

Viscosity measured by the motion of macro-objects (e.g. movement of Hoppler-balls, flow in capillaries) has an unequivocal meaning in discussion of the diffusion of small objects, like ions and molecules. Usually the diffusion of small species is proportional to the square root of macroviscosity.

The situation is changed if the viscogenic compound is a macromolecule, especially a long-chain one since macroviscosity is no longer identical with microviscosity and diffusion of small species is not hampered to the degree which would be suggested by the macroviscosity. For example, in the case of aqueous solution of gelatin as the viscogenic agent, the influence of the medium on the diffusion of small species is remarkably small and even the formation of a gel does not cause much, in spite of the macroviscosity being practically infinite in comparison to water[1].

These phenomena make it necessary to distinguish between macro- and microviscosity. Nishijima and Oster[2] investigated the diffusion of saccharose in solutions of polyvinylpyrrolidone of different molecular weights by microinterferometry. Th dependence of microscopic viscosity (calculated from the diffusion coefficient of saccharose) on the concentration of polyvinylpyrrolidone permitted the determination at so called critical concentration. At concentrations higher than critical concentration, the microviscosity increases considerably and small diffusing species

begin to 'see' the molecules of polymer. The critical concentration is connected with the commencement of the overlapping of the polymer coils. The critical concentration C_c^T (T for theoretical) depends on the parameter of the coil expansion:

$$C_c^T = 1.56 p^{-1} [\eta]^{-1} \tag{1}$$

where $[\eta]$ is the intrinsic viscosity and p equals 1 at maximal packing, or $\sqrt{3}$ at total expansion. The measurement of diffusion coefficient of small species may yield precise information about the microscopic viscosity of the solution but the method mentioned above is rather a difficult one, and in looking for a simpler experimental approach, we used the polarographic technique. The basis of this method is that small species diffuse to the electrode (DME) where they react, giving rise to an electric current which may be measured with a high degree of precision.

The intensity of polarographic diffusion current changes linearly with the reciprocal of square root of viscosity. The relation is true only in monomer solutions[3]. Deviations from this equation have been found in this laboratory[4,5] if the solution contains polymers and the effect was used for the determination of molecular weight of polyethyleneglycols and dextrans[7], using DC polarography. Later the square-wave polarography was applied[8] yielding more sensitive and precise results for the microviscosity of dextran solutions.

EXPERIMENTAL*

Measurements were made using a square-wave polarograph OH-104 (Radelkis, Budapest, Hungary), the capillary of

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* Polarography is seldom used as the experimental method in polymer chemistry, but in spite of this we have refrained from a general description, limiting the information to that quoted in electrochemical papers

Table 1 Characteristic parameters of dextrans

Dextran	$\bar{M}$	$[\eta]$ (dl/g)	ϵ_0	V ($\times 10^{19}$ cm³)
20 000	19 900	0.13	6.09	0.27
40 000	33 000	0.18	9.28	0.42
70 000	79 000	0.27	14.7	0.94
110 000	119 000	0.29	18.9	1.26
150 000	145 000	0.36	23.6	1.46

which had a mercury flow rate of 0.25 mg/s and a dropping time controlled to 4s by a mechanical drop dislodger. The rectangular signal was applied in the 3rd second of the drop life. A three electrode measuring system was used, the dropping mercury electrode being the working electrode, a low resistance calomel electrode the reference and the mercury pool, the auxiliary electrode. The total resistance of the polarographic cell was lower than 85Ω (i.e. well below 135Ω maximum advised by the manufacturers). The square-wave amplitude was usually 40 mV and the supporting electrolyte was 1M KC1.

Dextrans ('Polfa' Kutno, Poland) symbols 20 000, 40 000, 70 000, 110 000, 150 000 were investigated in water.

The viscosity-average molecular-weight was determined from measurements of intrinsic viscosity with an Ubbelohde viscometer (*Table 1*). Constants K and α were taken from the paper of Kiciak[9]. Macroviscosity was determined by a Höppler viscometer.

Tl⁺ ions were used as microprobes and typical experimental solutions contained 5×10^{-4} M Tl⁺, 1M KCl and a range of concentrations of the particular dextran. All measurements were performed at $25.0 \pm 0.1°C$, and calculations were carried out on an ODRA 1305 computer.

RESULTS AND DISCUSSION

Previous experience gained during the investigation of viscosity effects of polyethyleneglycols in square-wave polarography of thallium enabled us to reduce the number of measuring points in the present research. Only those values were measured which contribute to the interpretation of microviscosity in the range needed by the polymer chemist. The electrochemistry of the system does not differ qualitatively from the PEG's system although there were quantitative differences. To accord with the previous[2] concept of microviscosity, the polarographic results were expressed in the same units.

In square-wave polarography, the peak current intensity (i_p) is given by the Barker equation[11]:

$$i_p = KD^{1/2} \tag{2}$$

where K is constant and D the diffusion coefficient of the diffusing species. If the change of solution viscosity, η, is the only factor causing a difference in diffusion coefficient, then, according to Stokes–Einstein equation

$$D = K'\eta^{-1} \tag{3}$$

Combination of equations (2) and (3) produces the so called Stokes–Einstein–Barker equation

$$i_p = K''\eta^{-1/2} \tag{4}$$

where K'' is constant.

If η is a macroscopic viscosity (measured with a viscometer) then the equation is true only for solutions of monomers but a universal validity is achieved only by insertion of the microviscosity η'.

If i_p^0 and i_p^{pol} are the peak current intensities in the pure supporting electrolyte and in the solution containing viscogenic compound and if η_0' and η' are microviscosities of these solutions, than the relative microviscosity η_r' may be expressed as

$$\eta_r = \frac{\eta_1'}{\eta_0'} = \left(\frac{i_p^0}{i_p^{pol}} \right) \tag{5}$$

Reported measurements are usually performed at concentrations higher than $10^{-2}\%$, at which the adsorption of viscogenic substance at the electrode becomes constant and correction for the damping of current is straight forward. Thus if the peak current above the concentration of adsorption stabilization is denoted i_p^A and

$$\eta_r' = \left[\frac{i_p^0 - (i_p^0 - i_p^A)}{i_p^{pol}} \right]^2 = \left(\frac{i_p^A}{i_p^{pol}} \right)^2 \tag{6}$$

For a more detailed investigation of η_r' as a function of concentration of viscogenic substance, diagrams of $(\eta_r' - 1)/c = f(c)$ for dextran solution were obtained. (*Figure 1, a* and *b* for two ranges of concentration).

The experimental critical concentration C_c^E, limiting the zone of microviscosity, was determined by linear approximation of inflection point of the function $(\eta_r' - 1)/c = f(c)$. The results are summarized in *Table 2* and the graphical construction for C_c^E is shown on *Figure 1b*.

For comparison with equation 1, values of critical concentration C_c^T in dextran solution were calculated theoretically (*Table 2*).

Solution viscosity η (macroviscosity) has been shown to be adequately represented by the following equation[11] for most common polymer systems:

$$\frac{\eta_0}{\eta} = 1 - 2.5\phi + 11\phi^5 - 11.5\phi^7 \tag{7}$$

where η_0 is the solvent viscosity and ϕ is the volume fraction of polymer solution.

The volume of dextran fraction in the solution (ϕ) was found by solving the equation (7). ϕ is defined by:

$$\phi = CN_0 V\epsilon M^{-1} \tag{8}$$

where C is the polymer concentration (g/cm³), N_0 is Avogadro's number, M is the viscosity-average molecular weight, V is the volume (cm³/molecule) of an unsolvated polymer molecule and ϵ is the effective volume factor to allow for swelling of the polymer by the liquid medium.

Introducing values of ϕ into equation (8) for particular molecular weights, the effective volume of molecules $V\epsilon$ was calculated. The dependence of $V\epsilon$ on concentration is shown in *Figure 2*. The value of C_A was found from the diagram by measuring the point of intersection of the extrapolated maximum and minimum slopes of the $V\epsilon = f(C)$ function. These values for particular dextrans are very close to those found polarographically (C_c^E) c.f. *Table 2*. There are good reasons for the coincidence of C_A and C_c^E if our understanding of the phenomena is correct. In dilute solu-

tions, molecules of dextran are separated and Tl^+ ions are not influenced seriously in their diffusion, in spite of macroviscosity reaching many centipoises. Increasing concentration causes an increase of polymer—polymer interaction resulting in the reduction of the size of the coils and eventually, at C_A, although the coils are touching they still preserve their identity. For $C > C_A$ coils are gradually starting to penetrate mutually.

The critical polymer concentration C_e^E may be defined as a condition at which the diffusing ion remains at every point of solution in the zone of strong interaction of the coils. We assume that the difference between C_A and C_e^E will increase with the size of ions forced to diffuse across the polymer solution.

For the purpose of defining the zone of polymer-ion interaction the value of $V_T/V\epsilon$ was used where V_T is the volume of solution per molecule.

$$V_T = \frac{100\bar{M}}{N_0 C} \quad (9)$$

The volume of solution was 100 cm³, C the concentration of polymer and N_0 Avogadro's number.

At $C = C_e^E$ the value of $V_T/V\epsilon$ depends on the molecular weight of dextran (*Figure 3*) and this indicates an increase of the interaction range with the degree of expansion.

The effective volume factor ϵ at the concentration C_c was determined after the calculation of coil-volume V for the amorphic dextran[11,12]

$$V = \frac{\bar{M}}{dN_0} \quad (10)$$

where d is the density of the amorphous polymer. Values of ϵ are shown in *Table 2*.

For comparison, the swelling factor ϵ_0 at infinite dilution was obtained (*Table 1*) from the intrinsic viscosity by using

$$\epsilon_0 = \frac{[\eta] d}{2.5} \quad (11)$$

The lower part of the *Figure 1* shows that with the increase of concentration all curves of microviscosity converge, which means that, starting with concentration denoted as C_B, the microviscosities of different dextran solutions are identical, independent of their molecular weight. The value of C_B and other parameters of the coils at that concentration are collected in *Table 2*. The increase of polymer concentration above C_c^E causes increasing mutual penetration of coils which eventually lose their identity. The effect occurs at $C = C_B$.
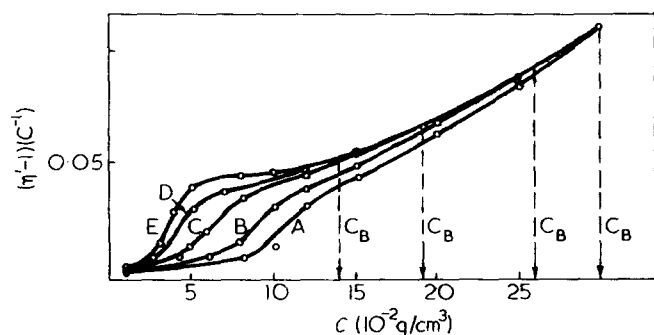

Figure 1 Normalized microviscosity *vs* concentration of viscogenic substance M = 19 900 (A, +), M = 33 000 (B, x), M = 80 000 (C, □), M = 119 000 (D, O), M = 145 000 (E, △). For the explanation of C_c^E see the paragraph after equation (6); for C_B, the final part of the paper
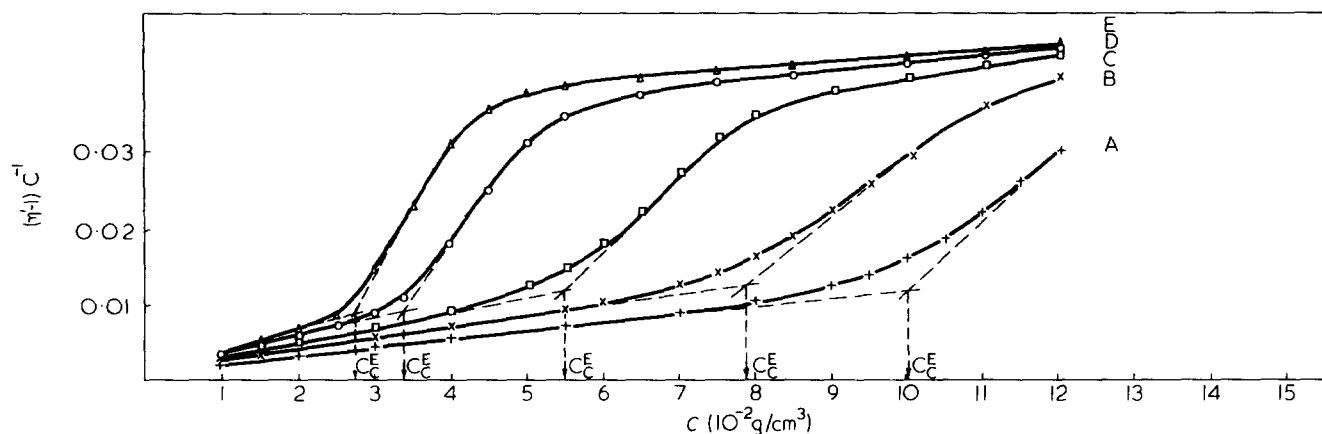

Table 2 Values of characteristic concentration in dextran solutions and coil parameters

Dextran	c_c^T $p = 1$	c_c^E $p = 3^{1/2}$	C_A (x 10⁻² g/cm)	C_B (x 10⁻² g/cm)		for $C = C_c^E$ ϵ	$V\epsilon$ (x 10¹⁹ cm³)	V_T (x 10¹⁹ cm³)	for $C = C_B$ ϵ	$V\epsilon$ (x 10¹⁹ cm³)	V_T (x 10¹⁹ cm³)
20 000	12.3	2.40	10.2	10.4	30	2.96	0.80	2.9	1.69	0.46	1.1
40 000	8.70	1.70	8.0	8.4	26	4.14	1.74	6.9	2.10	0.89	2.1
70 000	6.24	1.25	5.3	6.0	19	6.48	6.10	25.4	3.09	2.9	7.0
110 000	5.30	1.00	3.4	3.6	14	10.5	13.2	55.0	4.64	5.9	14.0
150 000	4.30	0.80	2.8	3.0	12	13.0	19.0	80.3	5.73	8.4	20.0

Figure 3 Volume ϕ of dextran fractions in the solutions and value of $V_T/V\epsilon$ as the function of molecular weight. (+) and (x) for volume; ($\square$) and (O) for $V_T/V\epsilon$

independent of molecular weight (*Figure 3*). For the system Tl^+ — dextran they are $V_T/V\epsilon = 2.4$, $\phi = 0.435$.

CONCLUSIONS

The polarographic investigation of microscopic viscosity is not limited to polyethyleneglycol[8] or dextran solutions but may be applied to all polymers which are polarographically inactive. Although aqueous solutions are preferred, there are no serious objections to the use of nonaqueous systems, if a proper supporting electrolyte may be found. The diffusing species is not limited to Tl^+ or Cd^{2+} and larger species may be chosen, among them organic compounds exhibiting polarographic activity.

Figure 2 Dependence of the effective volume of dextran coils on the concentration of solution. (a) $M = 19\,900$ (A), $M = 33\,000$ (B); (b) $M = 80\,000$ (C), $M = 119\,000$ (D), $M = 145\,000$ (E)

In that case ions are diffusing through a net, of microscopic viscosity independent from the molecular weight of polymer. This is evident from values V_T/V_c and ϕ, which at the concentration $C = C_B$ are identical for all dextrans and are
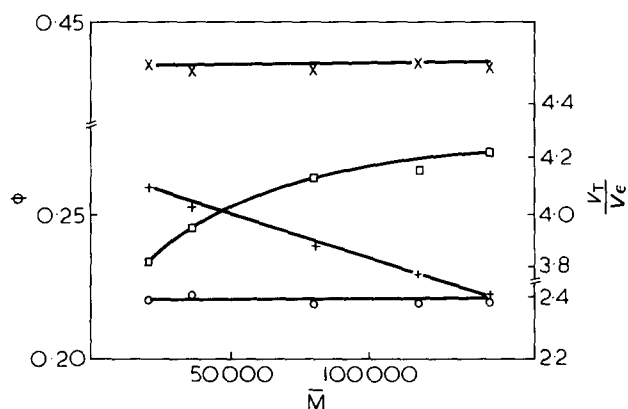
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