

DEPENDENCE OF VISCOSITY ON THE CONCENTRATION OF POLYMER SOLUTIONS. USE OF THE LYONS-TOBOLSKY EQUATION

O. QUADRAT

*Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6*

Received September 4th, 1975

The suitability of the Lyons-Tobolsky equation for the description of the dependence of viscosity on concentration in solutions of polystyrene and cellulose nitrate was examined, and the effect of molecular weight, temperature and thermodynamic quality of the solvent on the parameters of the equation, k_L and b , was investigated. They were determined from experimental data by numerical computing using the optimization method. It was found that although the parameters had not yet assumed any physical meaning and the equation was a purely empirical one, it can be used to describe the dependence of relative viscosity on concentration within a broad concentration range for both polymeric systems with an accuracy better than several per cent.

One of the basic unexplained problems of the rheology of concentrated polymer solutions is mathematical formulation of the course of viscosity as a function of polymer concentration. So far no theoretical expression has been derived which would explicitly describe this dependence. In the best case the existing theoretical papers¹⁻⁵ only indicate what parameters are concentration-dependent, without however demonstrating the shape of these functions. In practice, a number of empirical or semiempirical equations⁶⁻¹⁶ are recommended in order to describe the dependence of viscosity on the polymer concentration. Of these, equations of the exponential type⁹⁻¹⁶ are confined to the range of medium concentrations and fail at lower concentrations, while others can be used at very moderate concentrations only⁶⁻⁸. The only relationship suggested for expressing the concentration dependence of viscosity within the broadest possible concentration range, *i.e.* from an infinitely dilute solution to the polymer melt, is the Lyons-Tobolsky equation¹⁷

$$\ln(\eta_{sp}/[\eta]c) = k_L[\eta]c/(1 - bc); \quad (1)$$

η_{sp} is specific viscosity, $[\eta]$ is intrinsic viscosity, c is polymer concentration in g/dl of solution, k_L is a parameter identical with the Huggins interaction constant k_H , and b is the empirical parameter of the equation. The validity of the equation was verified in the original paper¹⁷ on one sample of poly(propylene oxide) ($M = 2 \cdot 10^3$)

in two solvents of different thermodynamic quality, and later¹⁸ on three samples of polydimethylsiloxane in the pentamer. On the basis of the free volume theory, Rodriguez¹⁸ assigned a certain physical meaning to the parameter b by using the relationship

$$b = f_1[\eta] k_H, \quad (2)$$

where f_1 is the fractional free volume of pure solvent. However, some experimental data yielded a negative b , which is absolutely inconsistent with the above expression. We therefore regarded it as useful to extend the experiments and (a) to find out whether the equation is generally valid in various polymer-solvent systems, (b) to elucidate the relation between the parameter b and molecular quantities, thermodynamic quality of the solvent, or temperature, (c) to check the physical meaning of the parameter b .

EXPERIMENTAL

Polymers

Polystyrene was prepared by block polymerization initiated with di-*tert*-butyl hyponitrite. Each of the two polydisperse samples having molecular weights M_n $2.23 \cdot 10^6$ and $4.28 \cdot 10^5$ were divided into five fractions. The fractionation was carried out by gradual precipitation of the polymer from benzene solutions with methanol (starting concentration 0.5–1% according to molecular weight); the fractions were reprecipitated and dried *in vacuo* over phosphorus pentoxide at 60°C. The molecular weight of the fractions was determined from the intrinsic viscosity of benzene solutions using Meyerhoff's equation¹⁹, $[\eta] = 1.23 \cdot 10^{-4} M_n^{0.72}$.

The cellulose nitrate was obtained from the Research Institute of Synthetic Resins and Lacquers in Pardubice. Ethyl alcohol used for moistening the samples was removed by evaporation *in vacuo*. Prior to weighing the samples were dried over phosphorus pentoxide to constant weight. The nitrogen content was determined volumetrically by the Dumas micromethod modified by Večeřa²⁰; it varied between 11.88 and 12.13%, *i.e.* the degree of nitration was roughly that of dinitrate. The molecular weight was estimated from a relationship suggested by Moore and Edge²¹, $[\eta] = 2.24 \cdot 10^{-4} M_n^{0.81}$ using the intrinsic viscosity of cyclohexanone solutions (although the above authors employed osmotically determined molecular weights in calibrating their equation, this was the only feasible procedure for the estimation of molecular weight, because no other calibration for cellulose nitrate with c. 12% nitrogen is known).

Solvents and Solutions

Butyl acetate, cyclohexanone and decalin (a mixture of *cis* and *trans* isomers), reagent grade, were simply redistilled.

Dilute and moderately concentrated low-viscosity solutions were prepared by shaking a weighed amount of the polymer with the solvent in volumetric flasks; when the polymer had dissolved, the solutions were made up to the required volume. More concentrated and viscous solutions were obtained by stirring the polymer with the solvent by means of steel balls sealed in glass, c. 15 mm in diameter, in conical flasks by rotating them on an inclined plane. Extremely viscous

solutions were prepared at an elevated temperature, 50–60°C. No degradation of the polymer occurred under any of the conditions used.

Viscometry

Diluting capillary viscometers with a capillary 0.6–1.2 mm dia of the Ubbelohde type were used in the measurements. Owing to the low shear stress (1–2 Pa), the viscosity measured even for polystyrene samples of the highest molecular weight was identical with the value at zero shear stress or zero velocity gradient, *i.e.* the non-Newtonian drop in viscosity was negligibly small. At shorter flow times (below 100 s) a correction for the loss of kinetic energy was necessary. Heller's plot²² was used in the extrapolation of intrinsic viscosity and in the determination of the Huggins constant.

RESULTS AND DISCUSSION

Determination of the Parameters of the Equation

Intrinsic viscosity and the Huggins constant can be determined by measuring dilute solutions employing the usual procedure. Lyons and Tobolsky calculated the parameter b from the melt viscosity after replacing the concentration c with the polymer density. Such procedure of course calls for an experimental temperature higher than that of the glass transition of the polymer. If this is not the case (which at an experimental temperature near 20°C holds for the majority of polymers), Rodriguez¹⁸ has suggested a rearrangement of Eq. (1):

$$[\eta]/\ln(\eta_{sp}/[\eta]c) = 1/k_L c - b/k_L \quad (3)$$

with the constant b determined from an intercept on the y -axis of the linear plot $[\eta]/\ln(\eta_{sp}/[\eta]c)$ vs $1/c$. He demonstrated the procedure on the results obtained by Kataoka and Ueda²³ with three samples of polydimethylsiloxane. In all three cases the plot was linear only for values from the higher concentration range. We found that if all measured values were included in this plot (Rodriguez did not take into account data from the lower concentration range), the dependence became curved at lower concentrations. The curvature is most probably due to a high sensitivity of the $[\eta]/\ln(\eta_{sp}/[\eta]c)$ values to small errors. Similar difficulties emerged in the treatment of our data. The plot $[\eta]/\ln(\eta_{sp}/[\eta]c)$ vs $1/c$, though linear within the whole range of the concentrations used (Fig. 1a), was nevertheless directed to the beginning, so that any estimate of the parameter b was completely ruled out.

The plot $[\eta]c/\ln(\eta_{sp}/[\eta]c)$ vs c according to the relationship

$$[\eta]c/\ln(\eta_{sp}/[\eta]c) = -bc/k_L + 1/k_L, \quad (4)$$

seemed more promising; the plot should also be linear, having the slope $-b/k_L$ and the intercept $1/k$. It appeared, however that the plot was very sensitive to the accuracy of intrinsic viscosity determination (Fig. 1*b*).

Owing to the difficulties encountered in the graphic methods, we tried to calculate the constants by employing the numerical optimization method. The minimal sum of square deviations of the measured relative viscosity values and values calculated for defined intrinsic viscosity (measured in the viscometry of dilute solutions) and for various combinations of the constants k_L and b within the concentration range used was regarded as the criterion of the optimal solution. A desk programmable WANG 600 computer was used for this purpose. The results of the calculation were very good; for all polystyrene and cellulose nitrate solutions under investigation, the procedure allowed to find the parameters k_L and b by means of which the Lyons–Tobolsky equation very adequately describes the experimental dependences; the difference between calculated and experimental relative viscosity values is several per cent at utmost, and frequently ten times smaller. The optimal constant k_L obtained by calculations is not quite identical with the Huggins constant k_H determined from the Heller plot in the range of dilute solutions. Deviations, though small, can nevertheless increase errors of the calculated relative viscosity in the Lyons–Tobolsky equation up to ten times.

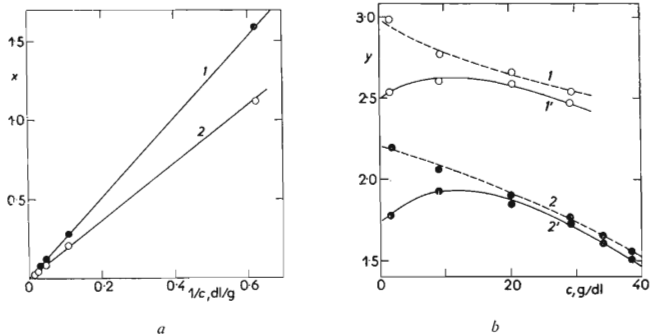


FIG. 1

Determination of the Parameter b of the Lyons–Tobolsky Equation from the Intercept on the y -Axis (*a*) of Eq. (3) ($x = [\eta]/\ln([\eta]_{sp}/[\eta]c)$) and from the Slope (*b*) of Eq. (4) ($y = x \cdot c$) for Polystyrene Solution in Cyclohexanone

$M \cdot 10^{-3}$: ● 19, ○ 43.2; the broken line (*b*) plotted through the points corresponds to $[\eta]$ higher by 1% than for points lying on the full line.

Properties of the Parameter b

The parameter b decreases with increasing molecular weight of the polymer or with increasing intrinsic viscosity (Fig. 2); it assumes both positive and negative values in the systems under investigation within a range of $+0.03$ to -0.15 dl/g. Eq. (2) fails to elucidate such dependence. Since the fractional free volume of pure solvent is constant, and the Huggins constant decreases only slightly with increasing molecular weight while intrinsic viscosity rapidly increases, the parameter b should increase with increasing molecular weight, in accordance with the above equation. A question arises as to the cause of the experimentally observed course.

If the dependence $\ln(\eta_{sp}/[\eta])$ vs c is plotted for several samples having different molecular weight, it can be seen (Fig. 3) that for low molecular weights the dependence is concave from the beginning, at a molecular weight of $c \cdot 3 \cdot 10^5$ it is linear and at higher molecular weights it becomes convex. The respective parameters b are as follows: positive for the concave curvature, negative for the convex curvature, and $b = 0$ for the linear dependence.

Allen and Fox³ described the dependence of viscosity on molecular weight and concentration by using the equation

$$\eta = (N/6) X_c (X/X_c)^a \zeta, \quad (5)$$

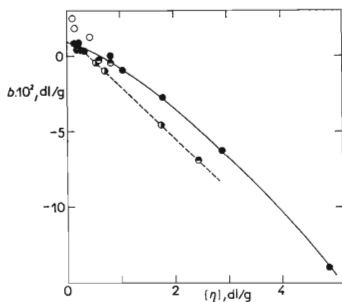


FIG. 2

Dependence of the Parameter b (dl/g) on Intrinsic Viscosity

● Polystyrene in cyclohexanone, ○ polystyrene in decalin, ● cellulose nitrate in cyclohexanone, ● cellulose nitrate in butyl acetate.

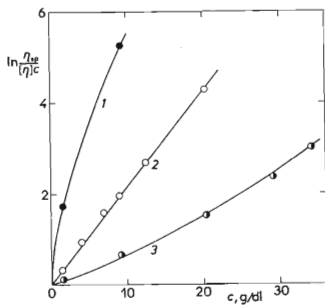


FIG. 3

Dependence of $\ln[\eta_{sp}]/[\eta]c$ on Concentration of Polystyrene Solutions in Cyclohexanone

M : 1 $19 \cdot 10^3$, 2 $3.1 \cdot 10^5$, 3 $2.6 \cdot 10^6$.

which they derived by extending the validity of expressions derived for the polymer melt. The parameter $X = (s_0^2/M) Zc$; $(s_0^2)^{1/2}$ is the radius of gyration of unperturbed polymer coil, M is molecular weight, Z is the number of frictional groups in the chain (in practice equal to the number of atoms on the backbone of the polymer chain), ζ is the frictional coefficient of one such group, c is concentration, and N is the Avogadro number. The exponent a should depend on the critical value of the parameter X denoted as X_c ; it should be 1.0 for $X \ll X_c$ and 3.4 for $X > X_c$. On the other hand, however, Eq. (5) neglects the effect of the viscosity of solvent, η_s , and loses its meaning at zero concentration. According to a theoretical solution suggested by Debye¹ and Rouse², it seems justified for a more exact expression of viscosity in the low concentration range, to replace the absolute viscosity with specific viscosity, $(\eta - \eta_s)/\eta_s$. Using the free volume theory, one obtained for frictional coefficient

$$\ln \zeta = \ln \zeta_0 + B/f; \quad (6)$$

ζ_0 is the characteristic frictional coefficient independent of concentration and molecular weight, B is a constant close to unity, and f is the fractional free volume of the system. It may be assumed for solution that the partial fractional free volumes of the polymer and of the solvent are additive:

$$f = f_1\varphi_1 + f_2\varphi_2, \quad (7)$$

where f_1 , f_2 respectively are fractional free volumes of the pure solvent and of the polymer, φ_1 is the volume fraction of the solvent, and φ_2 is the volume fraction of the polymer. The volume fraction of the polymer is given by the product of the specific volume of the polymer v_2 , and of concentration, $\varphi_2 = v_2c/100$, the number of frictional groups in the chain is given by $Z = M/M_0$ (M_0 is the molecular weight of one frictional group). By substituting expressions (6) and (7) into Eq. (5) and expressing intrinsic viscosity in terms of the Mark-Houwink equation $[\eta] = KM^{\bar{a}}$ (K and \bar{a} are constants of the equation, M is molecular weight), we obtain

$$\ln (\eta_{sp}/[\eta] c) = \bar{K} + (a - \bar{a}) \ln M + (a - 1) \ln c + 1/[f_1 - (f_1 - f_2) v_2c/100]. \quad (8)$$

The first term, \bar{K} , involves all quantities independent of molecular weight and polymer concentration. The second term of the equation depends only on molecular weight. The constant a in the second and third term — as has been said above — is unity for low molecular weights below the critical value, and 3.4 above it. The dependence of $\eta_{sp}/[\eta] c$ on concentration above the critical molecular weight is represented by the third and fourth terms of the equation, while below the critical molecular weight it is represented only by the fourth term, as the third term is zero.

Let us now try to make a quantitative estimate of the concentration dependence of the fourth term in a solution in cyclohexanone. The fractional free volume can be expressed by^{24,25}

$$f = f_g + \alpha_f(T - T_g), \quad (9)$$

where α_f is the expansion free volume coefficient (approximately equal to the difference between the expansion coefficient of the liquid, α_1 , and the expansion coefficient of the compound in the glassy state, α_g), T is the temperature of measurement, T_g is the glass transition temperature, and f_g is the fractional free volume at T_g having a universal value 0.025. According to Pezzin²⁶, for cyclohexanone it holds $T_g = -120^\circ\text{C}$ and $\alpha_f = 8 \cdot 10^{-4} \text{ K}^{-1}$. If we take for polystyrene the tabulated values²⁷ $T_g = +100^\circ\text{C}$, $\alpha_1 = 5.5 \cdot 10^{-4} \text{ K}^{-1}$, $\alpha_g = 1.9 \cdot 10^{-4} \text{ K}^{-1}$, we obtain by computing f_1 0.141 and f_2 0.002. The fractional free volume of the polymer f_2 can be neglected against f_1 , so that the fourth term in Eq. (8) is simplified and becomes $1/[f_1(1 - v_2c/100)]$.

Fig. 4 shows the dependence of the third and fourth terms or of their sum on concentration. We can see that below the critical molecular weight (curve 1), where the third term is zero, the dependence of the fourth term on concentration is concave, similar to the experimental dependence $\eta_{sp}/[\eta] c$ vs c for lower molecular weights.

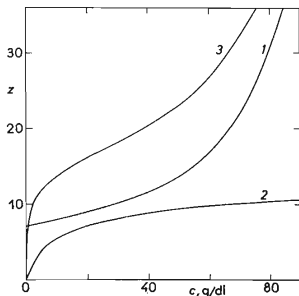


FIG. 4

Dependence of Terms in Eq. (8) on the Polymer Concentration

$1 z = 1/[f_1 - (f_1 - f_2) v_2c/100]$ for $X \leq X_c$, $2 z = (a - 1) \ln c$ for $X > X_c$, $3 z = (a - 1) \ln c + 1/[f_1 - (f_1 - f_2) v_2c/100]$ for $X > X_c$.

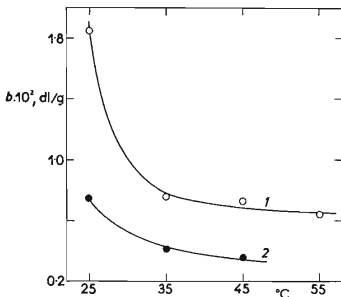


FIG. 5

Dependence of the Parameter b (dl/g) on Temperature for Polystyrene Solutions ($M = 3.0 \cdot 10^4$)

Solvent: 1 cyclohexanone, 2 decalin.

Above the critical M curve 3 has an inflexion point; at lower concentrations owing to the logarithmic course of the third term (curve 2), the dependence 3 is convex (the slope decreases), while at higher concentrations the effect of the fourth term of Eq. (8) prevails and the slope of the curve starts increasing. Such course seems to be similar to the experimental curve at higher molecular weights and explains the negative value of the parameter b ; b equal to zero corresponds to the critical molecular weight. To express a continuous decrease in the constant b , one would need a better knowledge of the dependence of the parameters B and f on molecular weight, which is not yet available.

A comparison of polymers having different static chain rigidity — that is, of polystyrene and cellulose nitrate — shows (Fig. 2) the low sensitivity of the parameter b to the polymer structure. Its differences between the individual polymers are not characteristic and can be compared with those between polymers of the same type having not too different molecular weights. With decreasing temperature and a worse thermodynamic quality of the solvent the parameter b increases (Fig. 5).

According to the results obtained in this work, the Lyons–Tobolsky equation can be evaluated as follows: a) the equation can be successfully used for polymer solutions to express the monotonic dependence of viscosity on concentration from infinite dilution within a broad concentration range with an accuracy in relative viscosity better than several per cent; b) one parameter of the equation, namely, intrinsic viscosity is readily determined from measurements in dilute solutions. The other two parameters, k_L and b , are best determined by numerical computing employing the optimisation method; c) even though the physical meaning of the constants k_L and b is not clear so that the equation seems to be purely empirical, in practice it still can be a valuable aid for the description of the rheological behaviour of polymeric system.

REFERENCES

1. Debye P.: *J. Chem. Phys.* 14, 636 (1946).
2. Rouse P. E.: *J. Chem. Phys.* 21, 1272 (1953).
3. Allen V. R., Fox T. G.: *J. Chem. Phys.* 41, 337 (1964).
4. Williams M. C.: *AIChE J.* 12, 1064 (1966); *ibid* 13, 534, 955 (1967).
5. Imai S.: *Rep. Progr. Polym. Phys. Jap.* 9, 117 (1966).
6. Vand V.: *J. Phys. Coll. Chem.* 52, 277 (1948).
7. Martin A. F.: Meeting of American Chemical Society (Memphis, April 20 to 24, 1942).
8. Baker F.: *J. Chem. Soc.* 103, 1653 (1913).
9. Ferry J. D., Foster E. L., Browning V., Sawyer W. M.: *J. Colloid Interface Sci.* 6, 377 (1951).
10. Johnson M. F., Evans W. W., Jordan I., Ferry J. D.: *J. Colloid Interface Sci.* 7, 498 (1952).
11. Ferry J. D., Grandine L. D., Udy D. C.: *J. Colloid Interface Sci.* 8, 529 (1953).
12. Landel R. F., Berge J. W., Ferry J. D.: *J. Colloid Interface Sci.* 12, 400 (1957).
13. Fox T. G., Gratch S., Loshaek S.: *Rheology*, Vol. 1 (F. Eirich, Ed.), Chap. 12. Academic Press, New York 1956.

14. Chou L., Zakin J. L.: *J. Colloid Interface Sci.* 25, 547 (1951).
15. Onogi S., Kobayashi T., Kojima Y., Taniguchi Y.: *J. Appl. Polym. Sci.* 7, 847 (1963).
16. Onogi S., Kimura S., Kato T., Masuda T., Miyanaga N.: *J. Polym. Sci.* 15, 381 (1966).
17. Lyons P. F., Tobolsky A. V.: *Polym. Eng. Sci.* 10, 1 (1970).
18. Rodriguez F.: *Polym. Lett.* 10, 455 (1972).
19. Meyerhoff G.: *Z. Phys. Chem. (Frankfurt am Main)* 4, 335 (1955).
20. Večeřa M., Synek L.: *This Journal* 24, 3402 (1959).
21. Moore W. R., Edge G. D.: *J. Polym. Sci.* 47, 469 (1960).
22. Heller W.: *J. Colloid Interface Sci.* 9, 547 (1954).
23. Kataoka T., Ueda S.: *J. Polym. Sci. A-2*, 5, 973 (1967).
24. Williams M. L., Landell R. F., Ferry J. D.: *J. Amer. Chem. Soc.* 77, 3701 (1955).
25. Bucche F.: *Physical Properties of Polymers*, p. 61. Interscience, New York 1962.
26. Pezzin G.: *J. Appl. Polym. Sci.* 10, 21 (1966).
27. Brandrup J., Immergut F. M.: *Polymer Handbook* III, 71. Interscience, New York 1966.

Translated by L. Kopecká.