NOTE

Empirical Viscosity-Concentration Relationship for Polymer Solutions

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Viscometry is a very popular method for obtaining information on the size and structure of polymer molecules in solution. In order to obtain polymer parameters from viscosity measurement of solutions, it is necessary to establish a viscosity-concentration relationship.

The viscosity of a dilute solution of a neutral polymer may be expressed as a power series of concentration:

$$\eta_r \equiv \eta/\eta_0 = 1 + [\eta]c + k_1[\eta]^2c^2 + k_2[\eta]^3c^3 + \dots \quad (1)$$

where η_0 and η are, respectively, the solvent viscosity and the solution viscosity, η_r is the relative viscosity, c is the concentration expressed in grams of polymer per unit volume of solution, and $[\eta]$, k_1 , and k_2 are constants independent of c . The linear-term coefficient $[\eta]$ is called the intrinsic viscosity which is one of the most important sources of information on the size and shape of polymer molecules. Thus, the method for evaluating $[\eta]$ has been intensively studied by many investigators since the beginning of polymer science.

The higher order terms in eq 1 naturally become insignificant at low concentrations. Thus, we may approximate eq 1 by either of the following forms:

$$\eta_{sp}/c \equiv (\eta_r - 1)/c = [\eta] + k_1[\eta]^2c \quad (2)$$

$$\eta_{sp}/c = [\eta] + k_1[\eta]\eta_{sp} \quad (3)$$

where η_{sp} is the specific viscosity. Equations 2 and 3 are, respectively, the Huggins and the Schulz-

Blaschke equations,^{1,2} and k_1 is usually referred to as the Huggins constant. These equations suggest that if a series of accurate data is available at sufficiently low concentrations, the plots of η_{sp}/c against c and η_{sp} both give straight lines and $[\eta]$ is readily obtained from their intersections with the ordinate, $c=0$ or $\eta_{sp}=0$. These procedures are, however, not generally practical, for the experimental uncertainty in the η_{sp}/c ratio becomes impractically large at "sufficiently" low concentrations. Thus, neither eq 2 nor 3 is strictly valid at most practical concentrations, and a nonlinear extrapolation of the plots of η_{sp}/c against c and η_{sp} is needed for evaluating $[\eta]$.

It is widely recognized that an exponent-type equation is often useful for describing a physical quantity when the power series equation becomes impractical. In the present case of polymer solution viscosity, the old Baker equation³ is an example:

$$\eta_r = (1 + ac)^k \quad (4)$$

where a and k are constants. Sakurada⁴ has shown that this equation is valid at relatively high concentrations with $k=3\sim 4$ for polystyrene, poly(methyl methacrylate) and polyisobutylene and that $[\eta]$ is obtainable according to $[\eta]=ak$. At sufficiently high concentrations where $ac \gg 1$, eq 4 yields

$$\eta_r^{1/k} = ac \quad (5)$$

We note that this equation represents a concentration scaling for the viscosity.⁵

Table I. Viscosity data used for testing the validity of eq 6

1. Polystyrene ($M=600,000$) in toluene at 30°C. Data of Weissberg, Simha, and Rothman.⁶

2. Poly(4-vinylbiphenyl) ($M=706,500$) in benzene at 30°C. Data of Utracki, Simha, and Eliezer⁸

c^a	η_r	η_{sp}	η_{sp}/c^a	$\eta_{sp}/\eta_r^{0.28}$	c^a	η_r	η_{sp}	η_{sp}/c^a	$\eta_{sp}/\eta_r^{0.28}$
0.091	1.199	0.199	2.1868	0.1891	0.2333	1.234	0.234	1.003	0.2206
0.3384	1.872	0.872	2.5768	0.7316	0.2979	1.304	0.304	1.0205	0.2822
0.5602	2.616	1.616	2.8847	1.2345	0.4179	1.441	0.441	1.0553	0.3981
0.6367	2.922	1.922	3.0187	1.4235	0.5268	1.577	0.577	1.0953	0.5079
0.7236	3.336	2.336	3.2283	1.6671	1.4943	3.067	2.067	1.3833	1.5103
0.8469	3.872	2.872	3.3912	1.9659	1.756	3.604	2.604	1.4829	1.8186
0.9196	4.205	3.205	3.4852	2.1437	2.317	4.84	3.84	1.6573	2.4693
1.1824	5.653	4.653	3.9352	2.8648	2.9324	6.449	5.449	1.8582	3.2334
1.2671	6.143	5.143	4.0589	3.0936	3.7595	9.147	8.147	2.167	4.3837
1.3795	6.954	5.954	4.3161	3.4593	4.6617	12.817	11.817	2.5349	5.7853
1.6554	9.065	8.065	4.8719	4.3505	4.8344	13.747	12.747	2.6367	6.1194
1.8512	10.747	9.747	5.2652	5.0131	6.1664	21.54	20.54	3.331	8.6954
2.0692	13.033	12.033	5.8153	5.8636	8.1869	37.712	36.712	4.4842	13.286
2.2626	15.206	14.206	6.2786	6.6299	11.123	84.271	83.271	7.4864	24.06
2.5454	19.008	18.008	7.0747	7.8952					
2.909	24.748	23.748	8.1636	9.6702					
3.3939	39.799	33.799	9.9587	12.5102					

^a c is expressed in gram per 100 cm³ of solution.

Figure 1. η_{sp}/c vs. c , η_{sp} , and $\eta_{sp}/\eta_r^{0.28}$ plots for polystyrene ($M=600,000$) in toluene at 30°C: Δ , η_{sp}/c vs. c ; $\circ$, η_{sp}/c vs. $\eta_{sp}/\eta_r^{0.28}$; $\times$, η_{sp}/c vs. η_{sp} . Data of Weissberg, Simha, and Rothman.⁶

NEW EMPIRICAL EQUATION

As mentioned above, eq 3 is valid at sufficiently low concentrations, while eq 5 is valid at sufficiently high concentrations. Thus, we may expect that a hybrid form of these two equations is applicable over a very wide range of concentration:

$$\eta_{sp}/c = [\eta] + (k_1[\eta]\eta_{sp}/\eta_r^\gamma) \quad (6)$$

This equation reduces to eq 2 or 3 when c approximate to zero or η_r to unity, and it reduce to following equation

$$\eta_r^\gamma = k_1[\eta]c \quad (7)$$

when the first term $[\eta]$ is negligible in comparison with the second term.

Tests of eq 6 were made using the two series of data shown in Table I, which were obtained by Weissberg, Simha, and Rothman^{6,7} for solutions of polystyrene in toluene and by Utracki, Simha, and Eliezer^{8,7} for solutions of poly(4-vinylbiphenyl) in benzene. These data are plotted in Figures 1 and 2 against c , η_{sp} , and $\eta_{sp}/\eta_r^{0.28}$, each corresponding to eq 2, 3, and 6. The γ value of 0.28 was chosen so as

to make the plot as straight as possible. As can be readily seen from these figures, only the present equation 6 yields straight lines throughout the entire range from sufficiently low concentration extend to $c = 10 \text{ g } 100 \text{ cm}^{-3}$, and $\eta_r = 100$.

Also, similar results were obtained, though not reproduced here, for solutions of polystyrene in methyl ethyl ketone, poly(1-vinylnaphthalene) in benzene, and poly(2-vinylnaphthalene) in benzene. The best fit value of γ was again 0.28 for each system. Thus, the present analysis seems to suggest that η_r of concentrated solutions is generally proportional to $([\eta]c)^{3.5}$.

The two constants $[\eta]$ and k_1 in eq 6 are essentially the parameters characteristic of dilute solutions and are obtainable from the viscosity data at low concentrations. Hence, if γ is a universal constant, we may with the aid of eq 6, predict the viscosity η_r for concentrated solutions from the data for dilute solutions.

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Figure 2. η_{sp}/c vs. c , η_{sp} , and $\eta_{sp}/\eta_r^{0.28}$ plots for poly(4-vinyl biphenyl) ($M = 706,500$) in benzene at 30°C . Δ , η_{sp}/c vs. c ; $\circ$, η_{sp}/c vs. η_{sp} ; $\times$, η_{sp}/c vs. $\eta_{sp}/\eta_r^{0.28}$. Data of Utracki, Simha, and Eliezer.⁸

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