Estimation of the limiting viscosity number and Huggins constant of polyacrylamides in water and 1M aqueous sodium chloride

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Four procedures have been checked to estimate the limiting viscosity number (intrinsic viscosity) $[\eta]$ and the Huggins constant k' accurately. The four equations involved are named after Huggins, after Nagy, Kelen and Tudos, and after Chee (two equations). Viscometric data for polyacrylamide samples, up to high conversion, in distilled water and 1 M NaCl solution, were analysed by the above-mentioned methods, the accuracies of which are compared. The variation of Huggins constant k' with respect to percentage conversion and intrinsic viscosity $[\eta]$ was also studied.

(Keywords: polyacrylamide; Huggins constant; limiting viscosity number; branching)

INTRODUCTION

Dilute solution viscometry is a relatively simple and reliable technique for the determination of the molecular weights of polymers. The method is often based on the use of the Mark–Houwink equation, which relates the limiting viscosity number (or intrinsic viscosity) $[\eta]$ to the molecular weights, usually the viscosity average, $\bar{M}_v$, but sometimes the weight or number average, $\bar{M}_w$ or $\bar{M}_n$, respectively.

The Mark–Houwink relations of polyacrylamides (PAM) in water and in some aqueous salt solutions have been established by several workers[1], but few have considered the variation of the Huggins constant k' with the type of solvent[2].

The limiting viscosity number $[\eta]$ is conventionally determined using the Huggins equation[3] derived for non-electrolyte polymers and given as:

$$\eta_{sp}/C = [\eta] + k'[\eta]^2 C \qquad (1)$$

$$\eta_{sp} = (t - t_0)/t_0 \qquad (2)$$

In these equations, η_{sp} = specific viscosity, t = flow time of the polymer solution, t_0 = flow time of pure solvent, C = concentration of polymer solution (usually in units of g/100 cm^3), k' = Huggins constant, and $[\eta]$ = limiting viscosity number, or intrinsic viscosity.

A simple plot of (η_{sp}/C) *versus* C according to equation (1) yields a straight line whose intercept and slope are $[\eta]$ and $k'[\eta]^2$, respectively. Since the variance of the (η_{sp}/C) quantity is not a constant, the values of $[\eta]$ and k' obtained in this way are highly biased. To overcome this shortcoming, several alternative methods have been reported by Nagy, Kelen and Tudos (NKT)[4] and Chee[5] to enhance the determined precision of $[\eta]$ and k'. All of these methods involve least-squares analysis but different error structures are involved.

In this work, the precision of four reported methods have been checked for polyacrylamide samples prepared at different conversions, in distilled water and in 1 M NaCl solution.

The polyacrylamide (PAM) samples were prepared in our own laboratories by the aqueous-phase radical polymerization of acrylamide (M) at 50 or 70°C, using the initiator, 4,4'-azobis-4-cyanopentanoic acid (ACV) and reaction conditions are also reported.

Detailed information on the statistical calculations involved in these four methods has been reported by Chee[5]. Here, simply the mathematical form of the equations is considered.

Conventional Huggins equation[3]

$$\frac{t - t_0}{t_0 C} = [\eta] + k'[\eta]^2 C \qquad (3)$$

NKT equation[4]

$$\frac{t - t_0}{C(\tau - C)t_0} = \frac{[\eta]}{\tau} + \left(k'[\eta]^2 + \frac{[\eta]}{\tau}\right)\frac{C}{\tau - C} \qquad (4)$$

where τ is equal to the sum of the lowest and highest concentrations of any series of results.

Quadratic form of Huggins equation[5]

$$\eta_{sp} = [\eta]C + k'[\eta]^2 C^2 \qquad (5)$$

Error-in-variables method (EVM). This method, which accepts the presence of error in all variables, has been developed by Chee[5]. The residual of flow time, r, is defined as the difference between the observed and estimated flow times, $\hat{t}$, respectively:

$$r = t - \hat{t} = t - t_0 - t_0[\eta]C - t_0 k'[\eta]^2 C^2 \qquad (6)$$

According to the principle of least squares, S, the sum of

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the weighted squares of the residual, becomes:

$$S = \sum wr^2 = \text{a minimum} \qquad (7)$$

where w is equal to $1/\sigma^2(r)$ or $1/V(r)$, and $\sigma^2(r)$ and $V(r)$ are the square of the standard deviation of r and the variance in r, respectively.

EXPERIMENTAL

The experimental procedures used in viscometry measurements have been described previously[6].

RESULTS AND DISCUSSION

The viscometric data of polyacrylamide samples in distilled water and polyacrylamide samples in 1 M NaCl solution at 25°C have been listed in *Tables 1* and *2*, and these data are used for the present purpose.

Table 3 shows the results of two samples produced by the methods discussed in the preceding section for these particular systems. The precision of each estimate is calculated by the value of the standard deviation. The ratio of $\sigma[\eta]/[\eta]$ and $\sigma k'/k'$ for better estimates are also calculated. A common procedure in many laboratories is to plot (η_{sp}/C) *versus* C and the intercept, drawn by eye, at zero concentration is $[\eta]$, the limiting viscosity number, and the corresponding slope is $k'[\eta]^2$. This method is clearly not considered further in this paper.

It should be mentioned that the Huggins, NKT and quadratic methods contain three different models of error structure. Accordingly, the estimates of $[\eta]$ and k' from these three methods are noticeably different. The quadratic method, which shows the lowest standard deviations of $[\eta]$, t and k', is the most efficient of these methods. So for the iterative (EVM) method, the first approximations, $[\eta]$ and k', were estimated by the quadratic method.

Table 1 Viscosity data of PAM: polymerization to high conversion at 50°C

Sample no.	Conversion (%)	Concentrations (g/100 cm³)	Flow times (s)
1	5.1	0.066, 0.050, 0.040, 0.033	465.0, 375.0, 331.0, 293.4
2	18.7	0.100, 0.066, 0.050, 0.040, 0.033	687.8, 471.0, 384.0, 332.4, 302.6
3	32.2	0.100, 0.066, 0.050, 0.040	663.0, 465.5, 378.5, 330.4
4	61.0	0.066, 0.050, 0.040, 0.033	443.0, 357.6, 313.5, 280.0
5	65.0	0.100, 0.066, 0.050, 0.040, 0.033	544.4, 391.0, 324.8, 289.0, 266.0
6	72.7	0.100, 0.066, 0.050, 0.033	471.2, 354.0, 303.2, 254.0
7	76.7	0.100, 0.066, 0.050, 0.040, 0.033	494.6, 363.5, 305.0, 273.0, 254.0
8[a]	87.3	0.066, 0.050, 0.033	346.0, 295.0, 246.2
9[b]	61.0	0.066, 0.050, 0.040, 0.033	372.5, 307.5, 273.5, 251.0
10	45.3	0.080, 0.060, 0.040, 0.020	226.3, 181.0, 141.8, 106.6
11	75.0	0.080, 0.060, 0.040, 0.020, 0.013	227.2, 181.7, 142.0, 107.0, 96.0
12	93.0	0.080, 0.060, 0.040, 0.013	219.5, 177.3, 140.0, 95.6
13	98.0	0.080, 0.060, 0.040, 0.020	211.5, 168.5, 135.8, 104.0
14	101.0[d]	0.080, 0.060, 0.040, 0.020	206.5, 167.2, 132.0, 101.8
15[c]	–	0.080, 0.060, 0.040, 0.020	192.2, 157.6, 127.0, 99.3

[a] For samples 1–8, polymerization conditions involved $[ACV] = 1.78 \times 10^{-4}$ mol dm^{-3} and $[M]_0 = 0.563$ mol dm^{-3}. Viscosity measurements at 25°C in 1 M NaCl solution and $t_0 = 169.5$ s
[b] For sample 9, polymerization conditions identical with those for 1–8[a]. Viscosity measurements at 25°C in distilled water and $t_0 = 162.0$ s
[c] For samples 10–15, polymerization conditions involved $[ACV] = 2.5 \times 10^{-4}$ mol dm^{-3}, $[M] = 3.5$ mol dm^{-3}. Viscosity measurements at 25°C in distilled water and $t_0 = 77.0$ s
[d] Theoretical maximum value is 100, hence some water was retained despite extensive drying *in vacuo* at 50°C

Table 2 Viscosity data of PAM: polymerization to low conversion and propionamide (S) as transfer agent at 50 and 70°C[a,b]. Viscosity measurements in distilled water at 25°C and $t_0 = 143.7$ s

Sample no.	Conversion (%)	Concentrations (g/100 cm³)	Flow times (s)
50-1[c]	15.61	0.08, 0.04, 0.02, 0.01	378.3, 243.5, 187.6, 163.9
50-2[d]	12.63	0.08, 0.04, 0.02, 0.01	295.2, 210.3, 174.2, 158.0
50-3[e]	10.04	0.08, 0.04, 0.02, 0.01	252.0, 192.5, 167.0, 135.0
50-4[f]	11.36	0.100, 0.050, 0.025, 0.020, 0.012(5)	262.8, 197.8, 169.3, 164.0, 156.3
50-5[g]	14.36	0.20, 0.10, 0.08, 0.05	390.4, 245.5, 222.0, 190.3
70-1[c]	12.67	0.200, 0.100, 0.050, 0.040, 0.025	1182.8, 488.6, 287.0, 251.1, 206.0
70-2[d]	11.85	0.200, 0.100, 0.050, 0.040, 0.025	638.0, 325.5, 220.0, 202.4, 178.3
70-3[e]	14.70	0.200, 0.100, 0.050, 0.040, 0.025	417.3, 257.3, 193.8, 182.8, 168.0
70-4[f]	11.68	0.100, 0.050, 0.040, 0.025	234.0, 186.1, 177.1, 164.3
70-5[g]	8.70	0.200, 0.100, 0.050, 0.040, 0.025	295.0, 212.0, 175.7, 169.0, 159.2
70-6[h]	9.20	0.200, 0.100, 0.050	229.0, 185.0, 163.7

[a] Samples 50-1 to 50-5, and 70-1 to 70-6 were prepared at 50°C and 70°C, respectively
[b] $[ACV]^{1/2}/[M] = 6.32 \times 10^{-3}$ dm$^{3/2}$ mol$^{-1/2}$ in all experiments at 50°C and 1.58×10^{-3} dm$^{3/2}$ mol$^{-1/2}$ in all experiments at 70°C
[c] $[M] = 2.500$ mol dm^{-3} and $[S] = 0.000$ mol dm^{-3}
[d] $[M] = 2.286$ mol dm^{-3} and $[S] = 0.400$ mol dm^{-3}
[e] $[M] = 2.000$ mol dm^{-3} and $[S] = 0.883$ mol dm^{-3}
[f] $[M] = 1.857$ mol dm^{-3} and $[S] = 1.125$ mol dm^{-3}
[g] $[M] = 1.714$ mol dm^{-3} and $[S] = 1.365$ mol dm^{-3}
[h] $[M] = 1.630$ mol dm^{-3} and $[S] = 1.837$ mol dm^{-3}

Table 3 Comparison of the precision of various methods for estimating limiting viscosity numbers and Huggins constants for polyacrylamide–water system

Sample no.	Method	$[\eta]$ (100 cm³/g)	$\sigma[\eta])$ (100 cm³/g)	$\sigma[\eta]/[\eta]$	k'	$\sigma(k')$	$\sigma k'/k'$	$\sigma(t)$ (s)
9	Huggins	13.529	0.711	0.052	0.503	0.126	0.250	1.1_{96}
	NKT	13.392	0.656	0.049	0.529	0.154	0.291	1.1_{26}
	Quadratic	13.374	0.658	0.049	0.531	0.091	0.171	1.1_{21}
	EVM	13.514	1.358	0.100	0.505	0.249	0.493	1.1_{82}
70-6	Huggins	2.737	0.074	0.027	0.159	0.066	0.415	0.3
	NKT	2.747	0.052	0.019	0.147	0.072	0.490	0.2_{6}
	Quadratic	2.759	0.047	0.017	0.138	0.038	0.275	0.2_{487}
	EVM	2.758	0.041	0.015	0.139	0.034	0.245	0.2_{488}

The results indicate that the quadratic form of the Huggins equation (5) gives the best estimated values of $[\eta]$ and k' since this equation gives the lowest $(\sigma[\eta]/[\eta])$, $(\sigma k'/k')$ and $\sigma(t)$, except for two samples, 70-5 and 70-6, where the EVM method gives the best estimates. In these latter two samples, the relative viscosities (t/t_0) are relatively small. In contrast to the analysis and conclusion of Chee[5], the present authors conclude that the EVM method for PAM is more accurate than the quadratic form only when the limiting viscosity number is less than 4.00 (100 cm³/g)*. Otherwise the EVM method is the worst of the four available methods. This conclusion was confirmed by use of equations when the variance of $[\eta]$ and k' were shown to be a function of $[\eta]$, and the relatively high value of $[\eta]$ gave high values of $\sigma[\eta]$ and $\sigma k'$ (ref. 5).

The Huggins original or conventional equation, equation (1), and the NKT equation, equation (2), are only marginally different in predicting the values of $[\eta]$ and k' from sets of data as shown in *Table 3*, but both methods are usually better than the EVM method for $[\eta] > 4.00$ (100 cm³/g). The current work shows that the NKT method does not increase the reliability of $[\eta]$ and k' in contrast to previous suggestions[4].

Further discussion of the Huggins constant k'

Determination of the Huggins constant k' for many polymer systems have been made over many years. Attempts have been made by several research groups to clarify the theoretical significance of k', but a completely quantitative interpretation has not yet been formulated. Even under theta conditions, many different values of k' have been reported[7] for flexible-chain polymers.

Experimental results relating to the constant k' may be summarized as follows[7]: (a) a polymer shows a higher value of k' in a poor solvent than in a good solvent; (b) k' has a value of about 0.5 in an ideal solvent; (c) the magnitude of k' may be influenced by the branching or the molecular weight distribution of the polymer; (d) k' is very sensitive to the formation of polymer micelles or aggregates of polymer molecules; (e) an effect of the shear rate on k' is observed; (f) some of the above features for flexible-chain polymers differ from those for stiff-chain polymers.

Current results reveal a large variation of k' *versus* both percentage conversion and $[\eta]$. However, the variation of k' with respect to percentage conversion and $\bar{M}_w$ (or $[\eta]$) is complicated and difficult to explain. Values of k' previously determined by Munk *et al.*[2] for PAM in distilled water vary between 0.17 and 0.41, which are in good agreement with the present results. In the case of the results for 1 M NaCl solution, however, the variation of k' determined by Munk *et al.*[2] is negligible, in contrast to values of the present work.

For polyacrylamide samples, k' values may be affected by: (1) branching, which is believed to take place during polymerization; (2) molecular weight distribution; (3) intra- and intermolecular hydrogen bonds; (4) ionic strength—the k' values are expected to be different in distilled water and in 1 M NaCl solution; (5) the history of the solution used in viscometry measurements, since the precise history affects the extent of hydrogen bonding.

The present results relating to the variation of k' with parameters such as percentage conversion, $[\eta]$ and $\bar{M}_w$ for polyacrylamides presumably reflect the complex nature of these polymer molecules in solution, such as hydrogen bonding, and the kinetic processes governing the final shape of the molecules, such as the gel effect and branching for high-conversion polyacrylamides.

REFERENCES

1 Kulicke, W. M., Kniewske, R. and Klein, J. *Prog. Polym. Sci.* 1982, **8**, 373
2 Munk, P. A., Williams, P. and Hoffman, D. E. *Macromolecules* 1980, **13**, 871
3 Huggins, M. L. *J. Am. Chem. Soc.* 1942, **64**, 2716
4 Nagy, T. T., Kelen, T. and Tudos, F. *Polymer* 1978, **19**, 1360
5 Chee, K. K. *J. Appl. Polym. Sci.* 1985, **30**, 2607
6 Rafi'ee Fanood, M. H. and George, M. H. *Polymer* submitted for publication
7 Sakai, T. *J. Polym. Sci. (A-2)* 1968, **6**, 1535

*The sample that was used by Chee[5] was a commercial poly(vinyl chloride) in tetrahydrofuran and it had a limiting viscosity number of 1.0 (100 cm³/g) at 25°C (ref. 4)