Single-point determination of limiting viscosity numbers of polyacrylamides in water and 1 M sodium chloride solution

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Several methods of calculation of the limiting viscosity number (intrinsic viscosity), $[\eta]$, from a single viscosity measurement for polymer solutions have been applied in this paper for polyacrylamide–water and polyacrylamide–1 M NaCl. It is shown that various forms of the Kraemer and Huggins equations, singly or combined, can be used successfully for single-point determinations of limiting viscosity numbers.

(Keywords: polyacrylamide; limiting viscosity number; single-point determination of limiting viscosity number; high conversion)

INTRODUCTION

The limiting viscosity number, $[\eta]$, of polymer solutions is determined from the extrapolation to zero concentration of $\ln \eta_{\mathrm{rel}}/C$ against concentration C, using the Kraemer[1] equation or of (η_{sp}/C) vs. C, using the Huggins equation[2]:

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

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

in which

$$\eta_{\mathrm{sp}}=\eta_{\mathrm{rel}}-1 \qquad (3)$$

$$\eta_{\mathrm{rel}}=\eta/\eta_0=t/t_0 \qquad (4)$$

$$[\eta]=\lim_{C\to 0}(\eta_{\mathrm{sp}}/C)=\lim_{C\to 0}(\ln \eta_{\mathrm{rel}}/C) \qquad (5)$$

where $[\eta]$ = the limiting viscosity number, or intrinsic viscosity, η_{sp} = specific viscosity, η = viscosity of solution, η_0 = viscosity of solvent, t = flow time of the polymer solution in the viscometer, t_0 = flow time of pure solvent in the viscometer, η_{rel} = relative viscosity of solution compared with the solvent $=(t/t_0)$, C = concentration of polymer solution (g/100 cm^3), k' = Huggins' constant, and k'' = Kramer's constant.

The experimental procedure underlying the determination of the value of $[\eta]$ can become time-consuming. To overcome this difficulty, several workers[3–9] have suggested alternative methods for calculating $[\eta]$ from a single viscosity measurement at a known concentration, C. The methods involve use of the following equations:

$$[\eta]=\frac{\eta_{\mathrm{sp}}}{C}\frac{N}{\eta_{\mathrm{sp}}+N} \qquad (6)$$

from Hart[3];

$$[\eta]=\frac{\eta_{\mathrm{sp}}+\gamma \ln \eta_{\mathrm{rel}}}{(1+\gamma)C} \qquad (7)$$

from Maron[4];

$$[\eta]=\left(\frac{2^{\frac{1}{2}}}{C}\right)(\eta_{\mathrm{sp}}-\ln \eta_{\mathrm{rel}})^{1/2} \qquad (8)$$

from Soloman and Ciuta[5];

$$\frac{C}{\eta_{\mathrm{sp}}}=-k'''C+\frac{1}{[\eta]} \qquad (9)$$

from Soloman and Grottesman[6];

$$\frac{\eta_{\mathrm{sp}}}{C}=[\eta]+\tfrac{1}{3}[\eta]^2C \qquad (10)$$

from Gillespie and Hulme[7];

$$[\eta]=\left(\frac{1}{C}[2(\eta_{\mathrm{sp}}-\ln \eta_{\mathrm{rel}})]^{1/2}\right)\left(1-\frac{\eta_{\mathrm{sp}}^2}{12}\right) \qquad (11)$$

from Varma and Sengupta[8] (for extremely good polymer–solvent systems); and

$$\eta_{\mathrm{sp}}/C=[\eta]+k[\eta]\eta_{\mathrm{sp}} \qquad (12)$$

from Schulz and Blaschke[9], which is another form of equation (6). In these equations N = Hart's constant, γ = Maron's constant, k''' = Soloman and Gottesman's constant, and k = Schulz and Blaschke's constant.

However, methods involving the use of equations (6)–(12) are not of general application, but have been applied only to specific polymer–solvent systems. We assess in this paper the accuracy of the above methods specifically for polyacrylamide (PAM)–water and PAM–1 M NaCl solution.

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EXPERIMENTAL

Viscometry

Viscometric measurements were carried out in aqueous solution at 25±0.02°C using an Ubbelohde dilution viscometer. For the two systems, polyacrylamide–water and polyacrylamide–1 M NaCl solution, several samples which were prepared in a 5–100% conversion polymerization were used[10].

Table 1 Viscometry data for PAM–1 M NaCl and PAM–water systems (t_0 = 169.5 and 77.0 s, respectively)

PAM–1 M NaCl			PAM–water		
Sample No.	10*C* (g/100 cm^3)	Flow time (s)	Sample No.	10*C* (g/100 cm^3)	Flow time (s)
1	0.66	465.0	I[a]	0.66	372.5
	0.50	375.6		0.50	307.5
	0.40	331.0		0.40	273.5
	0.33	293.4		0.33	251.0
2	1.00	687.8	II	0.80	226.3
	0.66	471.0		0.60	181.0
	0.50	384.0		0.40	141.8
	0.40	332.4		0.20	106.6
	0.33	302.6			
3	1.00	663.0	III	0.80	227.2
	0.66	465.5		0.60	181.7
	0.50	378.5		0.40	142.0
	0.40	330.4		0.20	107.0
				0.13 (3)	96.0
4	0.66	443.0	IV	0.80	219.5
	0.50	357.6		0.60	177.3
	0.40	313.5		0.40	140.0
				0.13 (3)	95.6
5	1.00	544.4	V	0.80	211.5
	0.66	391.0		0.60	168.5
	0.50	324.8		0.40	135.8
	0.40	289.0		0.20	104.0
	0.33	266.0			
6	1.00	471.2	VI	0.80	206.5
	0.66	354.0		0.60	167.2
	0.50	303.2		0.40	132.0
	0.33	254.0		0.20	101.8
7	1.00	494.6	VII	0.80	192.2
	0.66	363.5		0.60	157.2
	0.50	305.0		0.40	127.0
	0.40	273.0		0.20	99.3
	0.33	254.0			
8	0.66	346.0			
	0.50	295.0			
	0.33	246.2			

[a] t_0 for this sample is 162 s

The solutions were made up without any mechanical agitation (other than shaking by hand), or heating, and flow times were measured using a stopwatch accurate to ±0.2 s. Several measurements were made of each flow time, and the average flow time was recorded. For each sample, the plots of η_{sp}/C *versus* C and $\ln \eta_{rel}/C$ *versus* C were made. If, by extrapolation by eye to zero concentration, a common intercept was obtained, then the limiting viscosity number was equal to this common intercept.

If a common intercept is not obtained by the above extrapolations, a common practice is to report a mean $[\eta]$ value, with values of k' and k'' calculated from the two slopes (procedure (a)). In this paper, however, an alternative procedure was followed whereby the two above lines were 'forced' to give a common $[\eta]$ value. Values of k' and k'' were then calculated from the 'forced' slopes, but usually biasing the results towards the Kraemer method which gives an extrapolation of least error (procedure (b)).

In practice, the values of $[\eta]$ found by procedures (a) and (b) were in close agreement.

RESULTS AND DISCUSSION

Table 1 lists the viscosity data for both systems, PAM–1 M NaCl solution and PAM–water, respectively.

Determination of $[\eta]$ *and related constants using multi-point data for equations* (*1*), (*2*), (*9*) *and* (*12*)

In applying equations (1), (2), (9) and (12) to single-point determinations of $[\eta]$, it was first necessary to calculate the constants involved in these equations by analysis of multi-point data. So equations (1), (2), (9) and (12) were used and $\ln \eta_{rel}/C$ vs. C, η_{sp}/C vs. C, C/η_{sp} vs. C and η_{sp}/C vs. η_{sp} respectively, were plotted to obtain the corresponding $[\eta]$ values and associated constants. The results are presented in *Tables 2* and *3* for both PAM–1 M NaCl and PAM–water systems and are compared, for reference, with results from procedure (b).

The average values of k' are 0.348 and 0.334, for the PAM–1 M NaCl solution and PAM–distilled water systems respectively. These values compare favourably with the corresponding constants determined by a statistical method equal to 0.345±0.024 and 0.329±0.024, respectively. *Tables 2* and *3* show that the error in

Table 2 Limiting viscosity numbers using various equations: PAM–1 M NaCl solution system

		Values using (1)			Values using (2)			Values using (9)			Values using (12)		
Sample No.	$[\eta]$ (100 cm^3/g) obtained by procedure (b)	$[\eta]$ (100 cm^3/g)	Error (%)	$-k''$	$[\eta]$ (100 cm^3/g)	Error (%)	k'	$[\eta]$ (100 cm^3/g)	Error (%)	k'''	$[\eta]$ (100 cm^3/g)	Error (%)	k
1	17.90	17.60	−1.7	0.126	18.20	+1.7	0.375	19.37	+8.2	0.200	20.00	+11.7	0.194
2	18.80	18.50	−1.6	0.146	20.00	+6.4	0.263	23.08	+22.8	0.139	20.00	+6.4	0.128
3	19.10	18.60	−2.6	0.166	20.10	+5.2	0.240	22.88	+19.8	0.142	22.00	+15.2	0.124
4	15.80	16.00	+1.3	0.100	15.50	−1.9	0.540	19.32	+22.3	0.250	19.30	+22.1	0.259
5	14.60	14.50	−0.7	0.152	14.70	+0.7	0.342	17.03	+16.6	0.190	16.70	+14.4	0.175
6	13.40	13.30	−0.7	0.181	13.70	+2.2	0.218	15.01	+12.0	0.148	14.10	+5.2	0.180
7	12.80	12.50	−2.3	0.141	13.10	+2.3	0.353	14.92	+16.6	0.212	13.40	+4.7	0.271
8	11.80	12.00	+1.7	0.104	11.70	−0.8	0.450	13.56	+14.9	0.285	12.00	+1.7	0.297
Average value				0.140			0.348			0.196			0.204

Table 3 Limiting viscosity numbers using various equations: PAM–water system

Sample No.	$[\eta]$ (100 cm^3/g obtained by procedure (b)	Values using (1)			Values using (2)			Values using (9)			Values using (12)		
		($[\eta]$ (100 cm^3/g)	Error (%)	$-k''$	$[\eta]$ (100 cm^3/g)	Error (%)	k'	$[\eta]$ (100 cm^3/g)	Error (%)	k'''	$[\eta]$ (100 cm^3/g)	Error (%)	k
I	13.70	14.00	+2.2	0.085	13.30	−2.9	0.548	14.28	+4.2	0.300	14.20	+3.6	0.302
II	17.40	17.30	−0.6	0.158	17.50	+0.6	0.272	18.76	+7.8	0.150	18.00	+3.4	0.178
III	17.30	17.10	−1.1	0.171	17.80	+2.9	0.253	18.40	+6.4	0.152	18.20	+5.2	0.180
IV	17.00	16.80	−1.2	0.180	17.20	+1.2	0.253	18.20	+7.0	0.180	18.30	+7.6	0.138
V	15.90	15.90	0	0.163	15.90	0	0.291	16.47	+3.6	0.183	16.20	+1.9	0.169
VI	14.50	14.50	0	0.131	14.50	0	0.386	15.29	+5.4	0.225	14.60	+0.7	0.233
VII	13.00	12.90	−0.8	0.118	13.70	+5.3	0.333	14.43	+11.0	0.200	14.15	+8.8	0.208
Average value				0.144			0.334			0.199			0.201

Table 4 The maximum and average percentage errors in $[\eta]$ values determined by single-point procedures for the PAM–1 MnNaCl and PAM–water systems using data of *Table 1*

System		Equation number							
		(13)	(14)	(16)	(8)	(9)	(10)	(11)	(12)
PAM– 1 M NaCl	Max. % error	9.50	10.48	9.62	8,80	17.58	11.30	78.70	16.44
	Ave. % error	2.75	3.12	2.94	3.15	7.42	3.29	14.64	6.78
PAM– water	Max. % error	6.89	8.26	7.55	7.00	14.15	8.00	37.2	13.92
	Ave. % error	3.09(48)	3.09(70)	3.09(59)	3.25	5.13	2.97	10.94	5.28

$[\eta]$ values using equations (9) and (12) are relatively high compared with the $[\eta]$ value found by procedure (b). Equation (7) was not used for multi-point or single-point determination of $[\eta]$ since it is based on the assumption that a common intercept is always obtained by Huggins' and Kraemer's plots[11]. This was not generally true in our experiments.

Single-point determination of $[\eta]$

The average values of k' and k'' in Kraemer's and Huggins' equations, respectively, are known (*Tables 2* and *3*) and the value of η_{rel} (or η_{sp}) is known for each single concentration, C (*Table 1*). Thus $[\eta]$ can be calculated as the positive root of the quadratic equations for each single point:

$$[\eta]_K = \frac{(1+4k''\ln\eta_{rel})^{1/2}-1}{2k''C} \tag{13}$$

for Kraemer's equation and

$$[\eta]_H = \frac{(1+4k'\eta_{sp})^{1/2}-1}{2k'C} \tag{14}$$

for Huggins' equation. Also the average value of the limiting viscosity number from these equations was calculated:

$$[\eta]_{av} = \frac{[\eta]_K+[\eta]_H}{2} \tag{15}$$

where $[\eta]_K$ and $[\eta]_H$ are the $[\eta]$ values obtained from Kraemer's and Huggins' equations, respectively. So, the average of the positive roots of the two equations (13) and (14) yields:

$$[\eta]_{av} = \frac{[\eta]_K+[\eta]_H}{2} = \frac{1}{4k''k'C}[k''(1+4k'\eta_{sp})^{1/2}+ k'(1+4k''\ln\eta_{rel})^{1/2}-(k'+k'')] \tag{16}$$

By applying the average values of k'' and k' to equation (16), an average limiting viscosity number was calculated for each set of values of η_{sp}, η_{rel} and C.

Single-point determinations of $[\eta]$ were calculated using equations (13), (14) and (16), average values of the appropriate constants shown in *Tables 2* and *3*, and the data of *Table 1*. The average modulus percentage error in values of $[\eta]_K$, $[\eta]_H$ and $[\eta]_{av}$ are compared with the values of $[\eta]$ found by procedure (b), $[\eta]_b$, in *Table 4*.

Single-point calculations were not performed using equation (6), since this equation is simply another form of (12). Equations (8)–(12) with average values of the constants involved as necessary were also used for single-point determination.

The results in *Table 4* indicate that compared with procedure (b) for obtaining $[\eta]$, Kraemer's and Huggins' equations, used singly or in a combined form, can be used successfully for single-point determinations.

Equation (8) has a general limitation, that $(k'+k'')$ must be equal to 0.5. Equation (8) can be used for a single-point determination since for the PAM–water system $(k'+k'')$ is 0.478 and for PAM–1 M NaCl is 0.488 which gives slightly better results. Equation (10) is Huggins' equation with k' equal to 1/3 and gives better results for the PAM–water system, where k' is 0.334 than for the PAM–1 M NaCl system for which k' is 0.348. Equation (11) cannot be used for polyacrylamide solutions, especially at higher polymer concentrations.

Equations (9) and (12), both of which involve constants, are subject to considerable error and are therefore not recommended for single-point determination.

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