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Dilute solution properties of hydrophobically associating polyacrylamide: fitted by different equations

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Abstract

In this paper six different equations were used to fit the data of dilute solution of both nonionic (PBAM3) and ionic (PBAMS) hydrophobically associating polyacrylamide with and without the addition of NaCl. The results showed that Fedors equation was the most accurate equation to describe the dilute solution properties of these kinds of polymers. The lower value of the polymer concentration parameter (C_m) in Fedors equation was corresponded to the higher value of the constant k in Schulz–Blaschke equation for PBAM3 system. Two types of polymers had anti-polyelectrolyte effect. In dilute solution the PBAMS polymer chains had a more extended conformation than those of PBAM3 due to the existence of ionic groups.

Keywords: Hydrophobically associating polyacrylamide; Dilute solution; Fedors equation

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1. Introduction

Hydrophobically associating water-soluble polymers are synthetic water-soluble polymers containing a small proportion of hydrophobic groups usually in the form of pendent side chains or terminal groups, which are of increasing interest for a wide variety of industrial applications such as: flocculants, thickening agents in oil recovery, latex paints, cosmetics due to the advantage both the polyelectrolyte and the hydrophobic groups effect [1–5].

Most researchers focused the studies of this kind of polymers on the semi-dilute solution properties. For the dilute solution, the Huggins equation was the most common one used to determine the intrinsic viscosity and the Huggins constant, which could then be used to study the hydrodynamic volume of polymer chains and the interaction between different polymer chains or between polymer chains and the solvent [6–8]:

$$\frac{\eta_{sp}}{C} = [\eta] + k_H[\eta]^2C \tag{1}$$

where $[\eta]$ is intrinsic viscosity (dl/g), η_{sp} is the specific viscosity and η_{sp}/C is the reduced viscosity (η_{red}).

Usually it was combined with the Kraemer equation to get the intrinsic viscosity [7,8]:

$$\frac{\ln \eta_r}{C} = [\eta] - \beta[\eta]^2C \tag{2}$$

where η_r is the relative viscosity and β is a constant.

It was reported that the Schulz–Blaschke equation (S–B equation, Eq. (3)) [9] and the Fouss equation (Eq. (4)) [10, 11] also could to some extent be applied to study the dilute solution properties of hydrophobically associating water-soluble polymers.

$$\frac{\eta_{sp}}{C} = [\eta] + k[\eta]\eta_{sp} \tag{3}$$

where k is a constant corresponded to the interaction between different polymer chains. For coil-like polymer molecules, $k = k_H - (3A_2M/[\eta])f(\alpha)$, which includes the thermodynamic term k_H and hydrodynamic term

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$(3A_2M/[\eta])f(\alpha)$ [12]:

$$\frac{C}{\eta_{sp}} = A\sqrt{C} + \frac{1}{[\eta]} \quad (4)$$

where A is constant related with the dielectric constant of solvent.

Martin–Staudinger–Heauer equation (M–S–H equation) was used for polymer solution with moderate concentration [13]. But it was never used for hydrophobically associating water-soluble polymer solutions in the literatures.

$$\lg\left(\frac{\eta_{sp}}{C}\right) = \lg[\eta] + \left(\frac{k_m}{2.3}\right)[\eta]C \quad (5)$$

where k_m is Martin's constant.

Fedors [14] found that the equation developed and applied to viscosities of aqueous suspensions could be used to fit a wide variety of experimental data of water-soluble polymers. From a great deal of measurements Fedors found that this equation is generally applicable for η_r value from 1 to about 100.

$$\frac{1}{2(\eta_r^{1/2} - 1)} = \frac{1}{[\eta]}\left(\frac{1}{C} - \frac{1}{C_m}\right) \quad (6)$$

where C_m is polymer concentration parameter.

In this paper, these six equations would firstly be used to linearize the viscometric data obtained from dilute solution of both nonionic and anionic hydrophobically associating polyacrylamide with arylalkyl group, and to be compared to get the most accurate one by the linear regression coefficients. Then the intrinsic viscosity and related parameters calculated from the equation would be used to get the information about the behavior of the polymer chains in dilute solution with and without the addition of NaCl.

2. Experimental

2.1. Materials

Details on the synthesis and the process of the copolymers were given in Ref. [15]. The composition of copolymers used in this paper are: PBAM3-poly (arylalkyl acrylamide/acrylamide), AM/AAM (mole ratio) = 99.5/0.5, SDS, 1.5 g/dl; PBAMS poly (arylalkyl acrylamide/acrylamide/2-acrylamido-2-methyl-1-propanesulfonic acid), AM/AAM/AMPS (mole ratio) = 74.25/0.75/25, SDS, 2 g/dl. NaCl is analytically pure grade agents used without further purification.

2.2. Viscosity measurements

Viscometric measurements of polymer solutions were carried out by a 0.6 mm Ubbelohde capillary viscometer at 30.0 ± 0.1 °C. The kinetic energy and shear rate were found to be negligible. The density of solution was thought to be approximately the same as that of pure water. All aqueous solutions were made up in double-distilled water. Salt solutions were made up by adding quantitative solid NaCl into aqueous solutions directly and stirred to solve NaCl. All solutions were filtered by sand filter and kept overnight before measurement. The solutions were kept about 10 min prior to the measurements for temperature equilibrium.

3. Results and discussion

3.1. Nonionic PBAM3 copolymers

After measuring the relative viscosity (η_r), the viscometric data of polymer dilute solutions with different polymer concentration could be linearized by different equations. The linear regression correlation coefficients (C_{LR}) of different equations could be used to evaluate the degree of linear fitting. Table 1 gave the linear regression correlation coefficients of different equations for PBAM3 aqueous solutions of different concentration. As can be seen from Table 1 the degree of linear fitting of the Fedors equation was the best, then that of the S–B equation. It's very interested to see that with increasing polymer concentration, the C_{LR} of the other four equations increased.

The intrinsic viscosities calculated by different equations were listed in Table 2. The results showed that although the C_{LR} of different equations were different, the intrinsic viscosity values calculated from different equations were closed to each other. Because of the best fitting results of the Fedors equation, the $[\eta]_{Fedors}$ would be used to describe the behavior of macromolecular chains. From Table 2, we can see that with increasing the polymer concentration, the $[\eta]_{Fedors}$ increased, which means the hydrodynamic volume of polymer chains increased.

Table 2 also listed the parameter k calculated by S–B equation and the polymer concentration parameter (C_m) from Fedors equation. The higher the polymer concentration, the higher the k value is, which means that the interaction between different molecules becomes stronger. The tendency of $[\eta]_{Fedors}$ and k indicate that although the polymer solutions are dilute, the inter-molecule association still occur. The meaning of C_m in Fedors equation is unknown for water-soluble polymer systems. The calculated

Table 1
The linear regression correlation coefficients of different equations for PBAM3 dilute solution of different concentration

Concentration (g/dl)	Huggins	Kraemer	Fouss	S–B[a]	M–S–H[b]	Fedors
0.036	0.8255	0.635	0.8177	0.849	0.8218	0.9992
0.1	0.9257	0.9116	0.9555	0.9973	0.8873	0.9988
0.2	0.9377	0.9784	0.9901	0.9984	0.9813	0.9994

[a] The results of Schulz–Blaschke equation.
[b] The results of Martin–Staudinger–Heauer equation.

Table 2
The intrinsic viscosity calculated by different equations, the polymer concentration parameter (C_{m}) and the constant k of the PBAM3 solution with different polymer concentration

Concentration (g/dl)	Huggins	Kraemer	Fouss	S–B[a]	M–S–H[b]	Fedors	k	C_{m}
0.036	9.8617	9.8660	9.9010	9.8902	9.8810	10.0301	0.5876	2.1213
0.1	11.004	11.812	11.6690	12.2087	12.1056	12.3475	1.8361	1.2445
0.2	16.7092	17.7877	16.6555	18.4882	17.5886	18.1920	2.5690	0.3597

[a] The results of Schulz–Blaschke equation.
[b] The results of Martin–Staudinger–Heauer equation.

results show the lower C_{m} corresponds to the higher k, that is to say the lower C_{m} means the stronger interaction between different molecules.

The addition of NaCl will increase the polarity of solutions and change the behavior of PBAM3 molecules. The C_{LR} of different equations for the 0.036 g/dl PBAM3 NaCl solutions were listed in Table 3. One can directly observe that the sequence of fitting accuracy is: Fedors > S–B > Huggins > M–S–H > Fouss > Kraemer. That is to say the Fedors equation is the most moderate equation for nonionic hydrophobically associating polymer, PBAM3, both with and without the addition of NaCl.

The variation of the reduced viscosity versus the PBAM3 concentration with different NaCl concentration was shown in Fig. 1. The polymers had an anti-polyelectrolyte behavior in salt solutions, i.e. the reduced viscosity value decreased with decreasing the concentration of polymer solution due to the contraction of polymer chains, which is caused by the intra-molecular hydrophobic association between hydrophobic groups [16].

With the increase of NaCl concentration, the η_{red} of different PBAM3 solutions firstly decreased, then increased and kept almost unchanged in high NaCl concentration (see Fig. 2). But the η_{red} of high polymer concentration solution kept almost unchanged with increasing NaCl concentration. The variation of $[\eta]_{\mathrm{Fedors}}$ with increasing NaCl concentration for a given polymer concentration solution was similar to that of the η_{red} (see Table 3). With increasing NaCl concentration the polarity of solution increased, which resulted the stronger intra-molecular hydrophobic association and more contracted polymer chains. But the higher polarity would cause different molecules aggregating together, resulting the increase of hydrodynamic volume ($[\eta]_{\mathrm{Fedors}}$). The calculated lower C_{m} of PBAM3 NaCl solution still corresponds to the higher k.

3.2. Anionic PBAMS copolymers

The viscometric data of anionic hydrophobically associating water-soluble polymer PBAMS with different concentration were also fitted by six different equations. The C_{LR} of different equations were listed in Table 4. The results showed that for PBAMS dilute aqueous solutions the Fedors equation was still the most moderate one, and then the Kraemer equation, the Huggins equation, the S–B equation and the M–S–H equation. For PBAMS NaCl solutions, the C_{LR} of different equations (see Table 5) showed the sequence of accuracy is: Fedors > S–B > M–S–H > Huggins ≈ Fouss ≈ Kraemer. So the Fedors equation can also accurately describe the dilute solution behavior for both the aqueous and salt solutions of ionic hydrophobically associating polymer PBAMS.

For ionic hydrophobically associating polymers, there exists hydrophobic association effect and electrostatic repulsion effect simultaneously inside the polymer chains, so the properties of PBAMS dilute solutions were different to those of PBAM3. The data of $[\eta]_{\mathrm{Fedors}}$, C_{m} from the Fedors equation and k from the S–B equation for PBAMS aqueous solutions (listed in Table 4) showed that $[\eta]_{\mathrm{Fedors}}$ was obviously bigger than that of PBAM3, due to the existence of ionic group which introduced the electrostatic repulsion force and made the polymer chains extended. Compared with the data in Table 2, one can observe that the inter-molecular hydrophobic association occurred in very

Table 3
The C_{LR} of different equations, C_{m}, $[\eta]_{\mathrm{Fedors}}$ and k of the 0.036 g/dl PBAM3 dilute solutions with addition of different concentration of NaCl

NaCl concentration (mol/l)	C_{LR}						$[\eta]_{\mathrm{Fedors}}$	k	C_{m}
	Huggins	Kraemer	Fouss	S–B[a]	M–S–H[b]	Fedors			
0.01	0.9445	0.6038	0.9010	0.9639	0.9466	0.9994	8.1253	0.6705	0.4376
0.05	0.9850	0.8734	0.9822	0.9794	0.9790	0.9995	7.764	0.79	0.2066
0.10	0.9727	0.9579	0.9633	0.9922	0.9817	0.9996	6.9061	1.266	0.1526
0.30	0.9645	0.6782	0.9289	0.9786	0.9668	0.9996	8.547	0.7429	0.3926
1.00	0.9839	0.8530	0.9742	0.9858	0.9824	0.9996	8.4246	0.760	0.2448

[a] The results of Schulz–Blaschke equation.
[b] The results of Martin–Staudinger–Heauer equation.

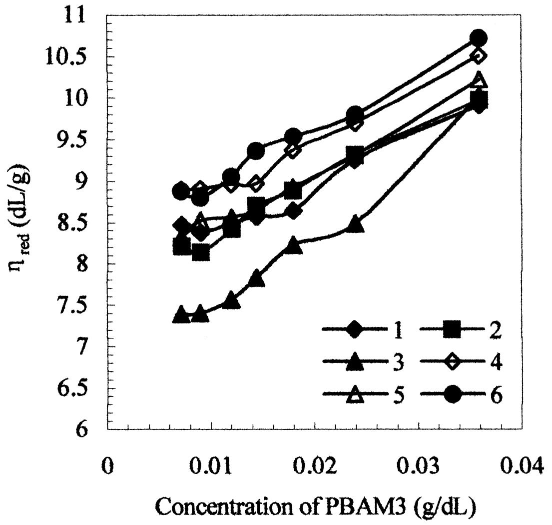

Fig. 1. The reduced viscosity of the PBAM3 dilute solution with addition of different concentration of NaCl as a function of polymer concentration. NaCl concentration (mol/l): (1) 0.01, (2) 0.05, (3) 0.10, (4) 0.30, (5) 0.50, (6) 1.0.

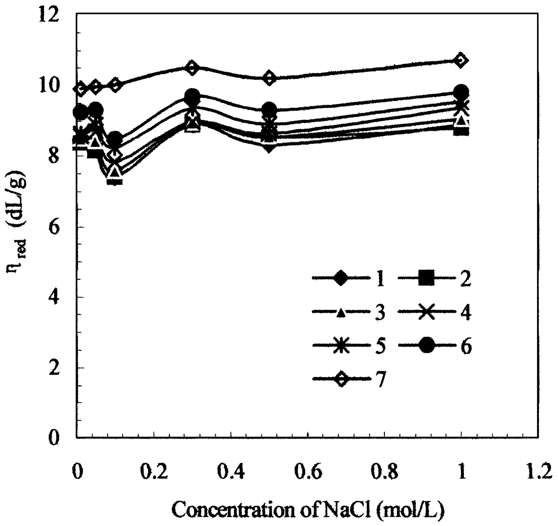

Fig. 2. The reduced viscosity of the PBAM3 solution with different polymer concentration as a function of the NaCl concentration. (Polymer concentration (g/dl): (1) 0.007, (2) 0.009, (3) 0.012, (4) 0.014, (5) 0.018, (6) 0.024, (7) 0.036).

low PBAMS concentration, so the hydrodynamic volume increased abruptly after PBAMS concentration was bigger than 0.03 g/dl. The *k* value of 0.025 g/dl PBAMS aqueous solution was closed to the value of common linear polymers in good solvent, then decreased with the increasing PBMAS concentration, which may be due to the increase of the molecular weight of complex macromolecules. It's very interested that the values of C_m were all negative and not related with the *k* value, which was never reported in the literatures. The accurate descriptions need to be studied further.

The variation of the reduced viscosity versus the PBAMS concentration with addition of different concentration of NaCl (see Fig. 3) shown the PBAMS also had an obvious anti-polyelectrolyte behavior, and the increasing amplitude of the reduced viscosity with increasing the polymer concentration was bigger than that of PBAM3 NaCl solution.

With the increase of NaCl concentration, the η_{red} of solutions with different PBAMS concentration decreased and kept almost unchanged in high NaCl concentration (see Fig. 4). And the higher the PBAMS concentration, the more obviously the reduced viscosity dropped with increasing NaCl concentration. The variation of the $[\eta]_{Fedors}$ and the η_{red} with increasing NaCl concentration for a given polymer concentration solution was similar. The addition of NaCl would shield the electrostatic repulsion effect and reinforce the hydrophobic association effect, resulting the contraction of the polymer chains and the decrease of both the $[\eta]_{Fedors}$ and the η_{red}. The increased *k* value means that the interaction between polymer chains and water was weakened due to the contraction of chains. There did not exist the direct relationship between the C_m value and the *k* value.

4. Discussion

The Huggins equation and the Kraemer equation are always used to describe the dilute solution properties of linear soft polymers in good solvent. As for hydrophobically associating water-soluble polymers, the inter-molecular hydrophobic association plays a very important role

Table 4
The C_{LR} of different equations, and the C_m, $[\eta]_{Fedors}$ and *k* of the PBAMS aqueous solution with different polymer concentration

PBAMS concentration (g/dl)	C_{LR}						$[\eta]_{Fedors}$	*k*	C_m
	Huggins	Kraemer	Fouss	S–B[a]	M–S–H[b]	Fedors			
0.025	0.7948	0.9256	0.9075	0.7951	0.8128	0.9973	58.1359	0.3509	−0.0403
0.030	0.3334	0.9888	0.4364	0.3519	0.3343	0.9987	78.125	0.02449	−0.1224
0.035	0.0114	0.9189	0.0480	0.0044	0.0113	0.9973	101.01	0.0316	−0.0537
0.040	0.7816	0.9173	0.8276	0.6801	0.776	0.9966	103.0386	0.0345	−0.0775
0.050	0.9189	0.9474	0.9476	0.9897	0.9711	0.9962	106.383	0.0693	−0.1858

[a] The results of Schulz–Blaschke equation.
[b] The results of Martin–Staudinger–Heauer equation.

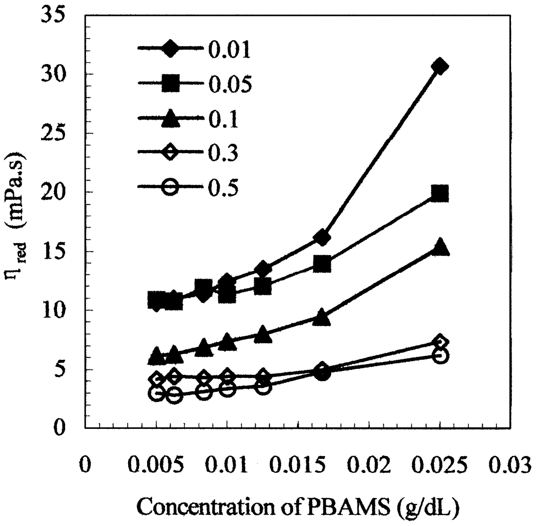

Fig. 3. The reduced viscosity of the PBAMS dilute solution with addition of different concentration of NaCl as a function of polymer concentration.

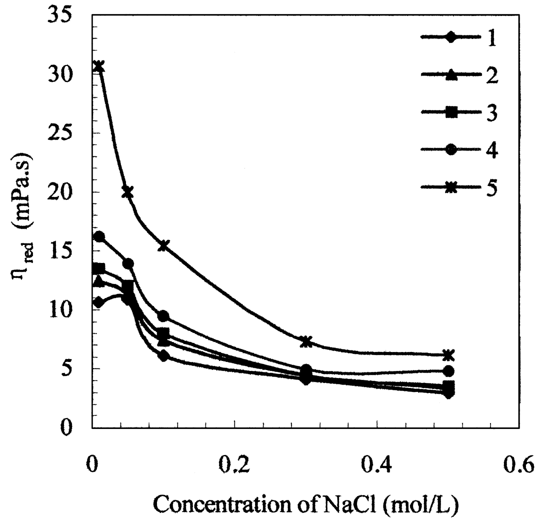

Fig. 4. The reduced viscosity of the PBAMS solution with different polymer concentration as a function of the NaCl concentration. (Polymer concentration (g/dl): (1) 0.005, (2) 0.01, (3) 0.0125, (4) 0.0167, (5) 0.025).

resulting the polymer chains contracting. So the actual condition deviate the real condition of the Huggins equation. By approximately processing, the Huggins equation could be derived from the S–B equation [12], so the accuracy of the S–B equation is higher, which was testified by the experimental results.

The Fouss equation was commonly used to describe the viscometric properties of polyelectrolyte dilute solution. To some extent it can also be used for ionic hydrophobically associating water-soluble polymers [10,11]. However, the PBAM3 and PBAMS copolymers had an obvious anti-polyelectrolyte effect due to the inter- or intra-molecular hydrophobic association. So the linear fitting results was not the best.

The M–S–H equation is a very good empirical equation for concentrated polymer solutions. The results showed to some extent this equation could be used to describe the properties of dilute solution of hydrophobically associating water-soluble polymers, especially for high polymer concentration solutions.

The Fedors equation was firstly applied to the viscosity of Newtonian suspensions of rigid particles, and then be used to describe the viscosity of dilute to moderately concentrated polymer solutions [13,17]. Ghimici [18] testified that this equation could be used to describe the viscometric properties of polyelectrolyte solution in a wide concentration range. Dragan [11] used it for cationic hydrophobically modified polyelectrolyte solution and got very good results. However, up to date, there are less data, as we aware, on the application of this equation to the intrinsic viscosity determination of both uncharged and charged hydrophobically associating water-soluble polymers solutions with and without the addition of inorganic salt.

By using scaling approach, Dobrynin [19] proposed that in dilute solution the polymer chains of hydrophobically modified polyelectrolyte could form the structure of necklaces or crew-cut micelles. Potemkin [20] studied the telechelic associating polymers with phase equilibrium theory and confirmed that the hydrophobic groups could aggregate together to form finite size clusters. In our study, for PBAM3 and PBAMS system, the existence of rigid hydrophobic arylalkyl groups in the polymer chains led the

Table 5
The C_{LR} of different equations, C_m, $[\eta]_{Fedors}$ and k of the 0.025 g/dl PBAMS solution with addition of different concentration of NaCl

NaCl concentration (mol/l)	C_{LR}						$[\eta]_{Fedors}$	k	C_m
	Huggins	Kraemer	Fouss	S–B[a]	M–S–H[b]	Fedors			
0							58.1395	0.3509	0.0403
0.01	0.9718	0.9749	0.9660	0.9992	0.9571	0.9993	9.149	3.1907	0.0413
0.05	0.9043	0.8951	0.9042	0.9865	0.9332	0.9965	9.7752	2.2393	0.0659
0.10	0.9424	0.9590	0.9903	0.9995	0.9864	0.9995	5.2743	4.9062	0.0389
0.30	0.8384	0.8276	0.8196	0.9658	0.8671	0.9957	3.8834	5.4189	0.0764
0.50	0.9669	0.9665	0.9531	0.9840	0.9699	0.9937	2.5407	9.5308	0.0424

[a] The results of Schulz–Blaschke equation.

[b] The results of Martin–Staudinger–Heauer equation.

hydrophobic group associating together forming the relative rigid clusters or coils, to some extent which were like the isolated rigid particles. So the Fedors equation exhibited very good linear fitting degree for two systems with and without NaCl. Detailed relationship will be studied in a forthcoming research by theoretical methods and light scattering techniques.

5. Conclusions

The data of dilute solution of both nonionic and ionic hydrophobically associating polyacrylamide with and without the addition of NaCl were fitted by six different equations. The results showed that Fedors equation was the most accurate one to describe the dilute solution properties of these kinds of polymers. The lower value of the polymer concentration parameter (C_m) in Fedors equation corresponded to the high value of the constant k in Schulz–Blaschke equation for nonionic PBAM3 polymer. But for anionic PBAMS polymer system, there did not have any direct relationship between the two parameters. The other five equations could to some extent be used for hydrophobically associating water-soluble polymers dilute solution. Two types of polymers had anti-polyelectrolyte effect. With decreasing the polymer concentration, the reduced viscosities and the intrinsic viscosities of polymer aqueous and NaCl solutions decreased. The introduction of ionic groups into polymer resulted a more extended chain structure in dilute solutions, so the hydrodynamic volume of PBAMS was obviously bigger than that of PBAM3. The very good linear fitting degree of the Fedors equation for PBAM3 and PBAMS system may be due to the relative rigidity of clusters or coils made up of rigid hydrophobic arylalkyl groups in the polymer chains, which to some extent were like the isolated rigid particles.

Acknowledgements

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