

## Study of the interactions between hydrophobically modified polyacrylamide and poly(*N*-isopropylacrylamide) in water by polymer solvent method

Ming Duan<sup>1,2</sup>, Dong mei Ren<sup>3</sup>, Xing qi Hu<sup>1</sup> (✉)

<sup>1</sup>State Key Laboratory of Oil/Gas Reservoir Geology and Exploitation, Southwest Petroleum Institute, Chengdu, Sichuan, 610500, China

<sup>2</sup>Department of Material Science and Technology, Southwest Petroleum Institute, Chengdu, Sichuan, 610500, China

<sup>3</sup>Department of Computer Science, Southwest Petroleum Institute, Chengdu, Sichuan, 610500, China

E-mail: [mduan@swpi.edu.cn](mailto:mduan@swpi.edu.cn); Fax: 86-28-8303-2852

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### Summary

The hydrophobic interactions between poly(*N*-isopropylacrylamide), PNIPAM, and hydrophobically modified polyacrylamide, HMPAM, have been investigated by means of the polymer solvent viscometry method in dilute solutions. When HMPAM aqueous solution is used as a solvent, a divergence from linearity between the reduced viscosities of PNIPAM (as a solute) and  $C_{\text{PNIPAM}}$  is observed. While PNIPAM aqueous solution is used as a solvent, the linearity is better and the intrinsic viscosity of HMPAM is higher than that in 0.1 M NaCl. The magnitude of mutual interaction parameter  $K_{\text{AB}}$  suggests the presence of the hydrophobic interaction between HMPAM and PNIPAM, which is dependent on the hydrophobic groups content of HMPAM and temperature. Especially, as temperature increases from 25 to 30 °C, the degree of hydrophobic interactions is enhanced, as is reflected in the Huggins coefficient  $K_{\text{H}}$  of HMPAM increase from 1.954 to 7.987.

### Introduction

Over the past two decades, interactions between heterogeneous macromolecules and formation of polymer-polymer complexes have attracted much attention [1]. They possess unique properties that are essentially different from those of the initial components and were applied in mobility control, enhanced oil recovery and other fields. Most of past studies were focused on such complex systems as Coulomb attraction [2], hydrogen bond attraction [3], Van der Waals attraction [4], antigen-antibody interaction [5] and ion interaction [6]. Only a few literatures [7-9] reported that the hydrophobic interactions between hydrophobically modified water-soluble polymer and poly(*N*-isopropylacrylamide) (PNIPAM) in aqueous solution existed and the two polymer mixed solutions exhibited a thermothickening behavior, which could solve a major drawback of thickener, a loss of viscosity under heating.

Many experimental methods have been used to investigate polymer-polymer interactions in solution [10]. Among these experimental methodologies, viscometry has proved to be a simple and reliable technique [11-16].

In general, for ternary system formed by polymer A/polymer B/solvent, two experimental methods have been followed: (1) measurement of the reduced viscosity of a mixture of two polymers A and B as a solute in a single solvent ((A+B)<sub>solute</sub>/solvent). (2) measurement of the reduced viscosity of a mixture of polymer A as a solute in solution containing a constant concentration of polymer B (A<sub>solute</sub>/(B+solvent)), which is the "polymer solvent" method[11]. The latter is more reliable as it reflects changes in the molecular dimensions of polymer A at a constant concentration of polymer B. H.Y. Yang details the advantages of the method [17].

The present paper, a continuation of our previous investigations [9], attempts to investigate the hydrophobic interactions between hydrophobically modified polyacrylamide (HMPAM) and PNIPAM by the polymer solvent viscometry method, and further reveal the thermothickening mechanism.

## Experimental

### Materials

HMPAM, which was previously reported [18], was prepared by radical copolymerization of acrylamide (AM), *p*-vinylbenzyltrimethylammonium chloride (VBDMOAC) and acrylic acid (AA). For comparison, AM-AA copolymer (PAM) was prepared under identical experimental condition.

PNIPAM was prepared by a homopolymerization process, which has been described in detail in another paper [9].

The characteristics of the model polymer are given in Table 1.

**Table 1.** Details on chemical composition of polymers

Polymer Code	Feed ratio	<sup>a</sup> Product's composition	<sup>b</sup> [ $\eta$ ] (dL g <sup>-1</sup> )
	AM/AA/VBDMOAC (mol%)		
PAM	85:15:0	84.09:15.91:0	10.859
HMPAM-0.25	84.75:15:0.25	86.54:13.07:0.39	11.604
HMPAM-0.75	84.25:15:0.75	86.93:12.15:0.92	8.657

<sup>a</sup>Elemental analysis

<sup>b</sup>in 0.1 M NaCl at 25 °C

### Sample Preparation and Viscosity Measurements

HMPAM and PNIPAM stock solutions were prepared by dissolving the proper amount of polymer in distilled water, respectively. HMPAM solutions should be neutralized with NaOH (final pH = 7-8). The final solutions of desired concentration were prepared by diluting the stock solutions with distilled water and mixing in a thermostatic waterbath shaker(25 °C) for about 12 h. Before measurements, polymer solutions were left without agitation for at least one day to reach equilibrium.

Their viscosities were measured by a Ubbelohde dilution viscometer at 25 ± 0.1 °C. The capillary diameter is 0.57 mm. Four successive dilutions of the polymer solution were made by use of various solvents, respectively. Intrinsic viscosities ([ $\eta$ ]) were obtained from the Huggins equation [19] as shown below.

$$\frac{\eta_{sp}}{c} = [\eta] + K_H [\eta]^2 c \quad (1)$$

where  $\eta_{sp}$  refers to the specific viscosity and  $K_H$  is the Huggins coefficient.

### Results and discussion

For the “polymer solvent” method, namely,  $A_{\text{solute}}/(B+\text{solvent})$ , the intrinsic viscosity  $[\eta_A]_B$  was obtained from Eq.(2)[14].

$$\begin{aligned} [\eta_A]_B &= \lim_{C_A \rightarrow 0} \frac{\eta_{sp}(C_A, C_B)}{C_A} = \lim_{C_A \rightarrow 0} \frac{\eta(C_A, C_B) - \eta(C_B)}{C_A} \\ &= \lim_{C_A \rightarrow 0} \frac{t(C_A, C_B) - t(C_B)}{C_A} \end{aligned} \quad (2)$$

where  $C_A$ ,  $C_B$  refer to the concentration of polymer A and B in mixture, respectively,  $t(C_A, C_B)$  and  $t(C_B)$  are the flow time of a mixture of  $A_{\text{solute}}/(B+\text{solvent})$  and  $(B+\text{solvent})$ .

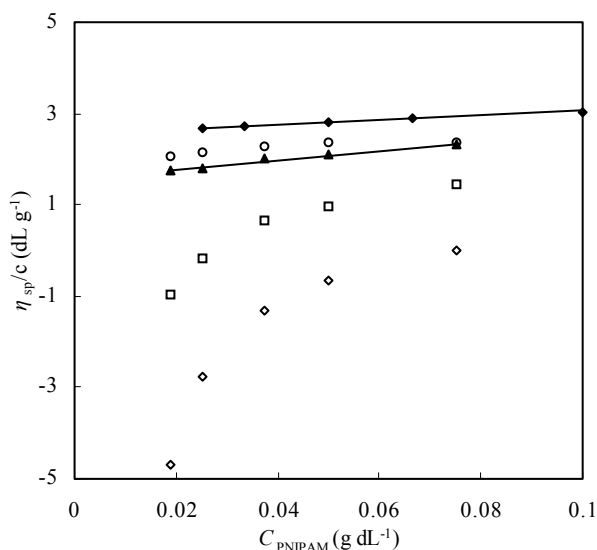
The Huggins mutual interaction parameter  $K_{AB}$  was obtained from Eq. (3)[14].

$$K_{AB} = \frac{[\eta_A]_B (1 + [\eta_B] C_B + K_B [\eta_B]^2 C_B^2) - 1}{2[\eta_B] C_B} \quad (3)$$

where  $[\eta_A]_B$  is the intrinsic viscosity of polymer A in solution containing a constant concentration of polymer B,  $[\eta_A]$ ,  $[\eta_B]$  are the intrinsic viscosity of polymer A and B in a pure solvent, and  $K_B$  is the Huggins coefficient of polymer B in a pure solvent.  $K_{AB}$  can be applied to estimate the intensity of interaction between polymer A and B.

#### *Viscosity behavior of PNIPAM in various solvents*

The variation of the reduced viscosity ( $\eta_{sp}/c$ ) of PNIPAM (solute) in various solvents versus PNIPAM concentration ( $C_{\text{PNIPAM}}$ ) is presented in Figure 1. The results obtained from Eq. (2) and (3) are tabulated in Table 2. The correlation coefficient  $R^2$ , obtained from linear match by the Huggins equation, shows the linear dependence. Combining Figure 1 and  $R^2$  in Table 2, both in 0.1 M NaCl and in 0.025 g dL<sup>-1</sup> PAM/0.1 M NaCl mixed solution, the relations between  $\eta_{sp}/c$  and  $C_{\text{PNIPAM}}$  are linear because the  $R^2$  values are close to 1. For the latter, the intrinsic viscosity  $[\eta]$  of PNIPAM is lower due to excluded volume effect between unlike polymers. While in all HMPAM-0.75/0.1 M NaCl mixed solution, an unexpected result is obtained that the linearity between  $\eta_{sp}/c$  and  $C_{\text{PNIPAM}}$  is too bad to calculate  $[\eta]$  of PNIPAM. The plausible value of  $K_{AB}$ , 0.872, indicates the presence of a specific interaction between PNIPAM and HMPAM, since it significantly higher than the common value of 0.2 to 0.3 for those general unlike polymers system [20].



**Figure 1.** Reduced viscosity of PNIPAM(solute)  $\eta_{sp}/c$  in various solvents as a function of  $C_{PNIPAM}$  at 25 °C. (◆) 0.1 M NaCl, (▲) 0.025 g dL<sup>-1</sup> PAM/0.1 M NaCl, (○) 0.025 g dL<sup>-1</sup> HMPAM-0.75/0.1 M NaCl, (□) 0.05 g dL<sup>-1</sup> HMPAM-0.75/0.1 M NaCl, (◇) 0.075 g dL<sup>-1</sup> HMPAM-0.75/0.1 M NaCl

**Table 2.** Viscometric data for PNIPAM in various solvents at 25 °C

Solute	Solvent	R <sup>2</sup>	$[\eta]$ (dL g <sup>-1</sup> )	$K_H$	$K_{AB}$
PNIPAM	0.1 M NaCl	0.989	2.551	0.778	—
	0.025 g dL <sup>-1</sup> PAM/0.1 M NaCl	0.985	1.583	4.053	-0.364
	0.025 g dL <sup>-1</sup> HMPAM/0.1 M NaCl	0.721	2.020	1.329	0.872
	0.05 g dL <sup>-1</sup> HMPAM/0.1 M NaCl	0.852	-1.254	—	—
	0.075 g dL <sup>-1</sup> HMPAM/0.1 M NaCl	0.797	-4.987	—	—

#### *Viscosity behavior of HMPAM in various solvents*

When PNIPAM/0.1 M NaCl mixed solution is used as a solvent, all the relations between the reduced viscosities and the polymer (solute) concentrations are linear and follow the Huggins equation. The results are presented in Table 3.

#### *Effect of the hydrophobic groups content of HMPAM on viscosity behavior*

As seen from Table 3, when PNIPAM/0.1M NaCl mixed solution is used as a solvent, all HMPAM samples show a higher  $[\eta]$  than that in 0.1 M NaCl. However, for PAM, which is not hydrophobically modified, a slight decrease in  $[\eta]$  is observed in PNIPAM/0.1M NaCl mixed solution, compared to that in 0.1 M NaCl. This trend is similar to that observed for PNIPAM in PAM/0.1 M NaCl mixed solution, which indicates the excluded volume effect between PAM and PNIPAM is dominant.

**Table 3.** Viscometric data for HMPAM in various solvents (T=25 °C)

Polymer Code	$C_{\text{PNIPAM}}$ (g dL <sup>-1</sup> )	$[\eta]$ (dL g <sup>-1</sup> )	$K_{\text{H}}$	$R^2$	$K_{\text{AB}}$	$\Delta[\eta]$ (dL g <sup>-1</sup> )
HMPAM-0.75	0.075	17.320	1.954	0.989	3.764	8.663
	0.050	16.367	2.244	0.991	4.530	7.710
	0.025	17.522	1.868	0.990	9.089	8.865
	0	8.657	11.175	0.981		
HMPAM-0.25	0.075	11.715	0.557	0.996	0.605	0.111
	0.050	12.719	0.468	0.991	0.979	1.115
	0.025	13.257	0.455	0.987	1.716	1.653
	0	11.604	0.818	0.995		
PAM	0.075	9.528	0.389	0.993	0.184	-1.331
	0.050	10.014	0.380	0.999	0.202	-0.845
	0.025	10.041	0.366	0.997	-0.105	-0.818
	0	10.859	0.293	0.992		

Why do the two polymers exhibit opposite behaviors in the same solvent? Many literatures [14,17,21] have reported that an increase in  $[\eta]$  generally arises from the attractive interaction between two polymers, for the case between HMPAM and PNIPAM can be the hydrophobic interaction. Many investigations [7,24,25] had demonstrated that the molecules of PNIPAM have moderate hydrophobic character. As PNIPAM adding to the HMPAM aqueous solution, the hydrophobic interactions between HMPAM and PNIPAM in water spontaneously occur and result in the attachment of PNIPAM molecule to the hydrophobic groups on HMPAM chain.

On the other hand, as for HMPAM, below the critical aggregation concentration  $C^*$ , intramolecular hydrophobic associations lead to a collapse of the polymer chain [22,23]. In the case, all HMPAM concentration is lower than  $C^*$  ( $C^*$  for HMPAM-0.25  $\approx 0.35$  g dL<sup>-1</sup>,  $C^*$  for HMPAM-0.75  $\approx 0.15$  g dL<sup>-1</sup>). Therefore, the intramolecular associations can be present, and lead to the intrinsic viscosity decrease with increasing the hydrophobe content (as shown in Table 3). The aforementioned attachment of PNIPAM can break the original intramolecular associations of HMPAM and make the polymer chain extended, leading to an increase in  $[\eta]$ . Therefore, the higher the hydrophobic groups content of HMPAM, the larger the increment  $\Delta[\eta]$  ( $= [\eta]_{\text{B}} - [\eta]_{\text{A}}$ ), at the same time, the larger the intensity of interaction between HMPAM and PNIPAM from the magnitude of the mutual interaction parameter  $K_{\text{AB}}$ .

#### *Effect of the concentration of polymer solvent on viscosity behavior*

As shown in Table 3, the decrement  $\Delta[\eta]$  of PAM gradually increases with increasing PNIPAM concentration  $C_{\text{PNIPAM}}$ , which is due to the excluded volume effects between the two polymers. This effect should be enhanced with increasing polymer concentration. As a result,  $[\eta]$  of PAM becomes much lower at the higher concentration of PNIPAM. By contrast the results in Table 3 show that although there is a small difference in the variation of the increment  $\Delta[\eta]$  versus  $C_{\text{PNIPAM}}$  between HMPAM-0.25 and HMPAM-0.75 ( $\Delta[\eta]$  for HMPAM-0.25 decreases with increasing PNIPAM concentration, while that for HMPAM-0.75 have an upturn at  $C_{\text{PNIPAM}}=0.075$  g dL<sup>-1</sup>), all  $K_{\text{AB}}$  decrease with increasing PNIPAM concentration. This can be explained that the combined effects of hydrophobic interaction (attractive) and excluded volume (repulsive). With  $C_{\text{PNIPAM}}$  increasing, the repulsive interaction is

enhanced, leads to a decrease of the attractive interaction, reflected in the decrease of  $K_{AB}$ .

*Effect of temperature on viscosity behavior*

**Table 4.** Viscometric data for HMPAM-0.75, PNIPAM, PAM at 25 °C and 30 °C

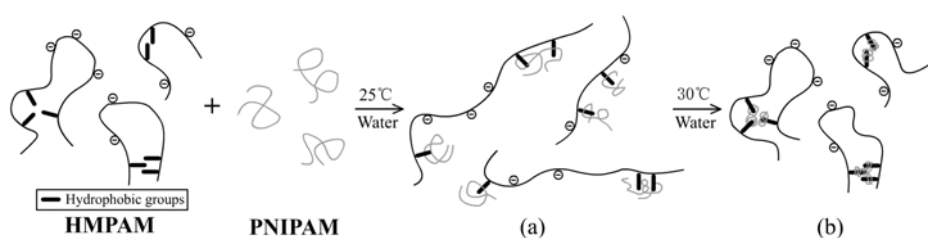
Solute	Temperature (°C)	Solvent	$[\eta]$ (dL g <sup>-1</sup> )	$K_H$
HMPAM-0.75	25	0.1 M NaCl	8.658	11.176
	30	0.1 M NaCl	9.292	9.034
	25	0.075 g dL <sup>-1</sup> PNIPAM/0.1 M NaCl	17.320	1.954
	30	0.075 g dL <sup>-1</sup> PNIPAM/0.1 M NaCl	8.290	7.587
PNIPAM	25	0.1 M NaCl	2.551	0.778
	30	0.1 M NaCl	1.355	5.023
PAM	25	0.075 g dL <sup>-1</sup> PNIPAM/0.1 M NaCl	9.528	0.389
	30	0.075 g dL <sup>-1</sup> PNIPAM/0.1 M NaCl	10.172	0.325

The influence of temperature on the intrinsic viscosity and the Huggins coefficient is listed in Table 4. In general, the intrinsic viscosities of most polymers slightly increase with increasing temperature, as shown for instance for the case of HMPAM-0.75 in 0.1 M NaCl or PAM in 0.075 g dL<sup>-1</sup> PNIPAM/0.1 M NaCl. However, both for PNIPAM in 0.1 M NaCl and for HMPAM-0.75 in 0.075 g dL<sup>-1</sup> PNIPAM/0.1 M NaCl, a decrease in  $[\eta]$  is observed while temperature increases from 25 to 30 °C. Besides, the Huggins coefficient  $K_H$  becomes greater, indicating a lowering of the solvent quality, in good agreement with the temperature-sensitive property of PNIPAM, which has been attributed to the disruption of hydrogen bonds between water molecules and the amide groups on PNIPAM chain by an increase in solution temperature and the enhancement of the hydrophobicity of PNIPAM [25]. As for HMPAM-0.75,  $[\eta]$  decreases from 17.320 to 8.290 dL g<sup>-1</sup>, indicating the polymer chain contracts. On the other hand,  $K_H$  dramatically increases from 1.954 to 7.587, meaning an increasing of the degree of hydrophobic interaction because the magnitude of the Huggins coefficient can be used to assess the degree of hydrophobic interaction. One explanation for these is that PNIPAM molecules adsorbed on HMPAM become hydrophobic groups, leading to an increase of the hydrophobe content of HMPAM. Thus, the degree of intramolecular associations is enhanced and  $[\eta]$  is even lower than that in 0.1 M NaCl.

### Conclusions

The viscosity behavior of different polymer in a series of concentrated PNIPAM aqueous solution has demonstrated that the intrinsic viscosity  $[\eta]$  of PAM slightly decreases with PNIPAM concentration ( $C_{PNIPAM}$ ) increasing, which is a result of the polymer chain shrink by the excluded volume effect between PAM and PNIPAM. On the contrary, the intrinsic viscosity of HMPAM in the presence of PNIPAM is significantly higher than that in pure salt solution, which is a result of the formation of the complexes (in Scheme 1a) between the two polymers by the hydrophobic interactions and the disruption of the intramolecular associations of HMPAM. On the other hand, the intensity of this interaction is dependent on the hydrophobic groups

content of HMPAM and temperature. The higher the hydrophobic groups content of HMPAM, the larger the intensity of the interaction, reflected in the increase of the mutual interaction parameter  $K_{AB}$ . With temperature increasing, the temperature-sensitive property of PNIPAM leads to an enhancement of the hydrophobicity of PNIPAM and a contraction of polymer chain [25,26]. This behavior can result in an increase of the hydrophobe content of HMPAM/PNIPAM complex and further enhance the intramolecular associations, as shown in Scheme 1b.



**Scheme 1.** Schematic representation of (a) the complexes formed between HMPAM and PNIPAM and (b) the intramolecular associations by an increase in temperature

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