

Effect of the Parent Solution Concentration on the Flocculation Performance of PAAm Flocculants and the Relation Between the Optimal Parent Solution Concentration and Critical Concentrations

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ABSTRACT: Flocculation performance of three kinds of polyacrylamide (PAAm), linear-PAAm, Al(OH)₃-PAAm hybrid, and star-PAAm, in kaolin suspensions have been investigated by Spectrophotometer. It was found that the flocculation performance of the polymer flocculant is enhanced at the beginning and then impaired with increasing parent solution concentration (C_p) and an optimal parent solution concentration (C_{op}) exists, which is directly proportional to both critical concentrations of C^* and C_s of the polymer in the dilute aqueous solution, and can be roughly ex-

pressed by an empirical formula, $C_{op} = 3.1 \times 10^{-3} + 643.1C_s$. The findings suggests that flocculation performance of a given polymer is dependent on both of the interchain association and the chain contact of the polymer chains in the parent solution and in the kaolin suspension, respectively. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1585–1592, 2007

Key words: polyacrylamide; flocculant; polymer solution; critical concentration

INTRODUCTION

It is well known that polyacrylamide (PAAm), which is a water-soluble polymer, is widely used in waste water treatment as flocculants.^{1,2} The flocculation performance of PAAm flocculants primarily depends on the sort of flocculants, ionic-PAAm or nonionic-PAAm,³ ionic content,^{4,5} molecular weight,⁶ dose,⁷ the type of waste water and their suspensions' concentrations,^{8,9} and also on some operation processes such as the shear rate.¹⁰

At present, the charge neutralization and bridging are two main of mechanisms during the flocculation process.¹¹ In spite of mechanisms, the solution properties of PAAm flocculants have remarkable influence on the flocculation performance.^{12,13}

The solution properties of polymer are affected by the chain dimension and chain shape in solutions.^{14–16} The polymer solution concentration is one of the factors to affect the chain dimension and chain shape in solution.

Generally, polymer chain expands, shrinks, contacts, associates, overlaps, and entangles when the polymer solution concentration changes. Furthermore, the solution properties of polymer, such as the

viscosity, will change with the polymer solution concentration. However, the change of viscosity or other solution properties is always not linear; thus, several critical concentrations^{17–21} exist from extremely dilute solution to concentrated solution of a polymer. One of these critical concentrations is C^* at which the polymer coils start to overlap, as reported by de Gennes.²² Several expressions of C^* have been proposed to be related to the chain dimensions.²³ Usually, C^* is expressed as follows,

$$C^* = \frac{3M}{4\pi N_A R_G^3} \quad (1)$$

where N_A , M , and R_G are the Avogadro constant, molecular weight, and the radius of gyration, respectively. Using the Fox–Flory equation

$$[\eta] = \frac{\phi' R_G^3}{M} \quad (2)$$

where $\phi' = 6^{3/2} \phi$ and $\phi = 2.5 \times 10^{23}$ (mL/g),²⁴ we have

$$C^* = \frac{1.23}{[\eta]} \quad (3)$$

In general,²⁵ eq. (3) is approximately written as

$$C^* = \frac{1}{[\eta]} \quad (3')$$

It means that C^* is inversely proportional to the intrinsic viscosity ($[\eta]$), which represents the chain dimension or the segment density of the chain coil in solutions; namely, the higher the $[\eta]$ of polymer solu-

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tion, the larger the chain dimension, and lower the segment density of the chain coil and C^* .

Recently, another critical concentration (C_s) called the dynamic contact concentration is proposed according to the experimental results from eximer fluorescence spectroscopy,²⁶ dynamic light scattering,²⁷ and size exclusion chromatography.²⁸ Cheng and co-workers²⁹ deduced an expression for C_s , on the basis of a cluster formation model as follows,^{29–31}

$$C_s = \frac{0.001}{2K_m} = \frac{0.003}{K_H[\eta]} \quad (4)$$

where K_m and K_H are association constant and Huggins constant, respectively. The value of K_H , from Huggins viscosity equation,³² mainly depends on the polymer/solvent system, i.e., both the sort of polymer and the quality of the solvent.³³

It is interesting to research the relation between the two kinds of basic parameters, one of which reflects the characteristic of flocculation performance such as the optimal dose⁷ and parent solution concentration of flocculants, and the other reflects the solution properties of a polymer flocculant, such as different critical concentrations C^* and C_s . Both parameters should be related because the polymer solution concentration used in flocculation process is very dilute.

In this work, the flocculation performance of three kinds of PAAm flocculants in kaolin suspensions with different parent solution concentration (C_p) are examined, and the optimal parent solution concentration (C_{op}), at which the flocculation performance is the best, exists. The relation between the C_{op} of PAAm flocculants in flocculation process and the dynamic contact critical concentration (C_s) in aqueous solution will be explored.

EXPERIMENTAL

Materials

The polymer flocculants used in this study are linear-PAAm, $\text{Al}(\text{OH})_3$ -PAAm hybrid, and star-PAAm, which were synthesized in our previous work. The $\text{Al}(\text{OH})_3$ -PAAm hybrid was prepared from *in situ* polymerization of acrylamide with $\text{Al}(\text{OH})_3$ colloid induced by $\text{NaHSO}_3/(\text{NH}_4)_2\text{S}_2\text{O}_8$ initiator system.³⁴ The star-PAAm was synthesized using Ce^{4+} and 1, 2, 3-propanetriol or pentaerythritol as initiator systems.³⁵ Various samples with different intrinsic viscosities (or different molecular weights) were obtained by different polymerization conditions. Kaolin clay (1250 mesh) was kindly supplied by XinYang Company, Taiyuan, China.

Intrinsic viscosity measurement

The polymer flocculants samples were dissolved entirely in distilled water with 1.0 mol/L NaCl at 45°C, and then filtered. Intrinsic viscosity ($[\eta]$) mea-

surement of PAAm sample was conducted with an Ubbelohde viscometer at $30 \pm 0.02^\circ\text{C}$. The flux-times were recorded with an accuracy of ± 0.05 s. Extrapolation from data obtained for several concentrations of solution was used to evaluate $[\eta]$ by the Huggins equation, $\eta_{sp}/C = [\eta] + k_H[\eta]^2 C$. The representative η_{sp}/C - C curves for each kind of polymer flocculants samples were shown in Figure 1. The $[\eta]$ and Huggins constant of all samples used were listed in Table I. Therefore, in this study the molecular weights of samples are expressed by $[\eta]$ obtained for 1.0 mol/L NaCl aqueous solution at 30°C.

Light transmission measurement

Flocculants parent solutions were prepared by the way that PAAm samples were dissolved entirely in distilled water without added salt at 45°C. Kaolin clay was dispersed in the tap water with pH = 7.6 and without added salt at room temperature. The flocculation performance of PAAm samples conducted in a 100-mL stoppered graduated cylinder.³³ The kaolin suspension was placed in the cylinder, then the flocculant parent solution was added, and the cylinder was inverted 10 times. After mixing, the cylinder was set upright in a residence time of 5 min. Then, the light transmission of the clean supernatant was measured with a Spectrophotometer (Spectrophotometer-722, Shanghai Third Analytical Instruments Factory, China) at 680 nm wavelength, which is the maximum absorbance.

RESULTS AND DISCUSSION

Intrinsic viscosity and Huggins constant of PAAm flocculants

Polymerization conditions and results of all flocculants used are listed in Table I. Figure 1 gives the rep-

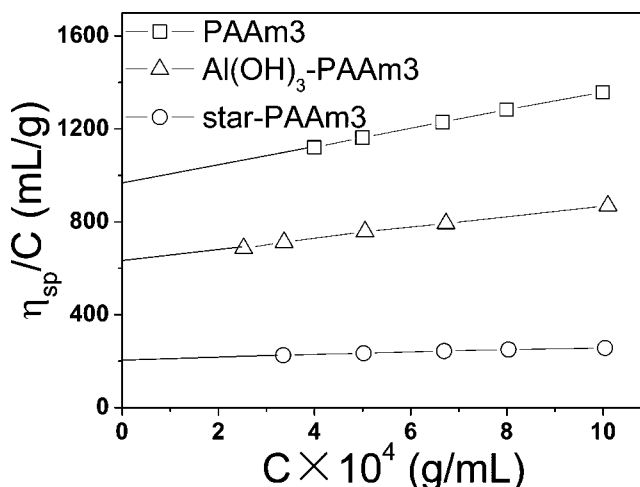


Figure 1 η_{sp}/C - C curves of linear-PAAm, $\text{Al}(\text{OH})_3$ -PAAm, and star-PAAm in 1.0 mol/L NaCl aqueous solution respectively, at 30°C.

TABLE I
Polymerization Conditions and Results of Polymer Flocculants Used

Sample	Initiator1/2/AAm ^c	Temperature (°C)	Time (h)	[η] (mL/g)	K_H	$C_{op} \times 10^3$ (g/mL)
linear-PAAm1	0.02/0.04/100	80	8	766	0.474	8.5
linear-PAAm2	0.02/0.04/100	70	8	844	0.417	8.0
linear-PAAm3	0.02/0.04/100	60	8	961	0.433	7.0
linear-PAAm4	0.02/0.04/100	50	8	1181	0.392	6.0
Al(OH) ₃ -PAAm1 ^a	0.07/0.14/100	40	8	376	0.593	12.0
Al(OH) ₃ -PAAm2 ^a	0.06/0.12/100	40	8	465	0.625	11.0
Al(OH) ₃ -PAAm3 ^a	0.05/0.1/100	40	8	631	0.601	9.1
Al(OH) ₃ -PAAm4 ^a	0.04/0.08/100	40	8	813	0.531	8.2
Al(OH) ₃ -PAAm5 ^a	0.03/0.06/100	40	8	941	0.511	7.0
star-PAAm1 ^b	0.155/0.0136/100	47.5	16	152	1.018	14.8
star-PAAm2 ^b	0.155/0.0136/200	47.5	16	177	0.939	14.5
star-PAAm3 ^b	0.155/0.0136/300	47.5	16	213	0.989	12.0
star-PAAm4 ^b	0.155/0.0136/400	47.5	16	273	1.055	10.0
star-PAAm5 ^b	0.155/0.0136/500	47.5	16	298	1.047	9.6

^a 5.76 wt % Al(OH)₃ content.

^b Ce⁴⁺ and pentaerythritol as initiator system.

^c Initiator1/2/AAm = NaHSO₃/(NH₄)₂S₂O₈/AAm monomer(wt/wt/wt) for linear-PAAm and Al(OH)₃-PAAm; Initiator1/2/AAm = Ce⁴⁺/pentaerythritol/AAm monomer(wt/wt/wt) for star-PAAm.

representative η_{sp}/C - C curves for three kinds of polymer flocculants, linear-PAAm, Al(OH)₃-PAAm, and star-PAAm solutions. From Figure 1, straight lines of η_{sp}/C versus C could be obtained even for Al(OH)₃-PAAm sample when NaCl solution, 1.0 mol/L NaCl, was used as solvent. Thus, their [η] values and Huggins constants (K_H) are all obtained according to Huggins equation. K_H reflects the property of polymer-solvent system. Usually, linear polymers in good solvents have K_H less than 0.5 and branching polymers have much high K_H values.³³ Therefore, the K_H values of three kinds of polymer flocculants in Table I are quite reasonable. K_H value of Al(OH)₃-PAAm star

like is located between the values of the linear-PAAm and the star-PAAm.

Effect of parent solution concentrations C_p on flocculation performance of PAAm flocculants

Figures 2(a) and 2(b) show a typical variation of the flocculation performance with the dose (C_d) of linear-PAAm1 and linear-PAAm4 samples respectively, for a series of flocculant parent solution concentrations (C_p) in 2×10^{-2} g/mL kaolin suspensions. The light transmission (T) goes up at the beginning and then comes down with increasing C_d for all T - C_d curves of

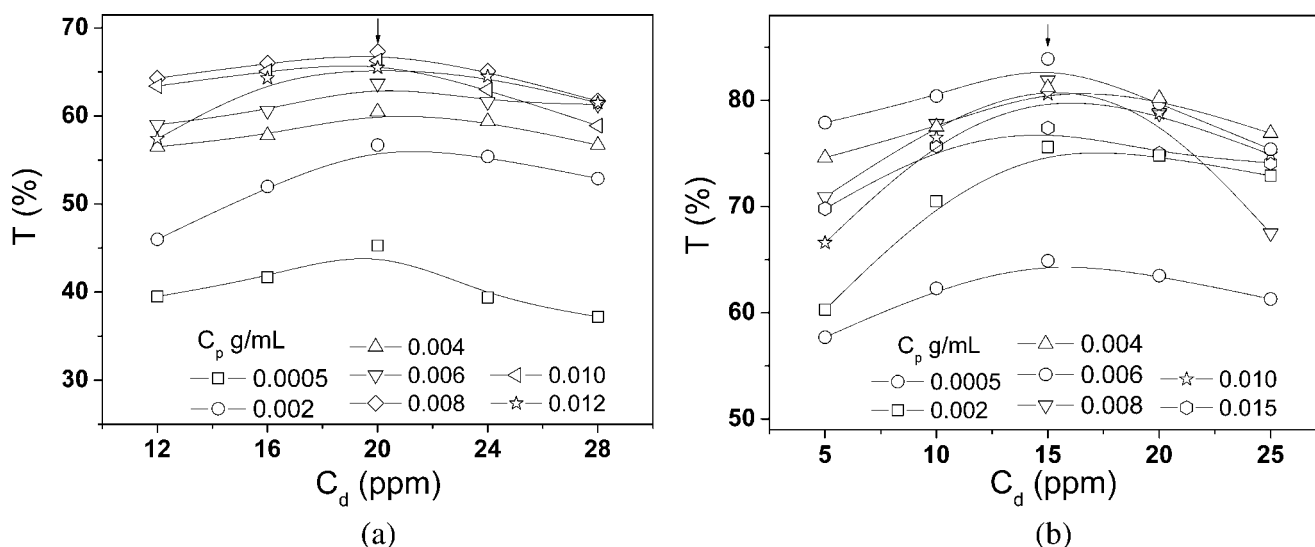


Figure 2 (a) Variation of flocculation performance of linear-PAAm1 with C_d for different C_p in 2×10^{-2} g/mL kaolin suspensions. (b) Variation of flocculation performance of linear-PAAm4 with C_d for different C_p in 2×10^{-2} g/mL kaolin suspensions.

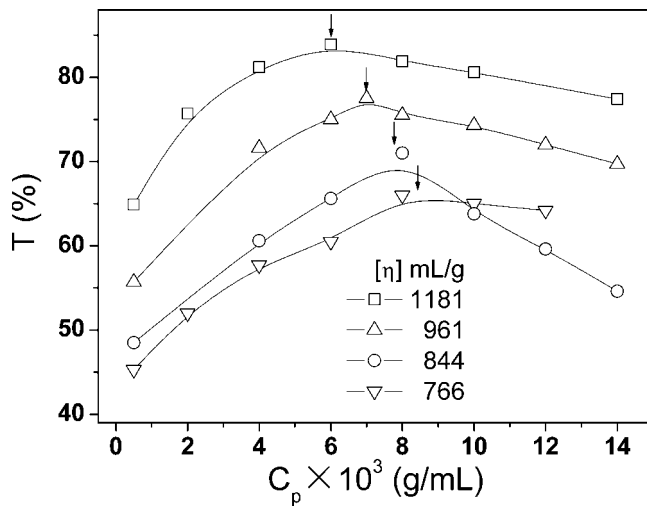


Figure 3 Effect of C_p on flocculation performance of linear-PAAm at C_{od} in 2×10^{-2} g/mL kaolin suspensions.

each C_p of the two samples. The optimal dose (C_{od}),⁷ at which the light transmission is larger and the dose is lower, exists for each T - C_d curve. The C_{od} values are almost the same for the same flocculant sample, such as $C_{od} = 20$ ppm for linear-PAAm1 and $C_{od} = 15$ ppm for linear-PAAm4. It is consistent with the C_{od} value, which decreases with increasing $[\eta]$ of the flocculant in our previous study. Surprisingly, the T values of a flocculant sample changes with C_p from 0.0005 to 0.015 g/mL at the same C_d . In other words, the T - C_d curve of a given flocculant still depends on C_p .

Figure 3 shows the effect of C_p on T value of four linear-PAAm samples at each optimal dose, C_{od} . From Figure 3, the light transmission of each floccu-

lant sample increases at the beginning and then decreases with increasing C_p . Also, a maximum light transmission (T_{max}) for each flocculant sample reveals at C_p , which is called the optimal parent solution concentration (C_{op}) and marked by arrowheads in Figure 3. It leads us to consider that low or high parent solution concentration C_p at the optimal dose C_{od} does not gain the best flocculation efficiency except for at C_{op} . Again from Figure 3, the C_{op} value seems to be inversely proportional with $[\eta]$ of flocculants samples.

Figure 4(a, b) show the typical variation of the flocculation performance with the dose (C_d) of $\text{Al}(\text{OH})_3$ -PAAm3 and $\text{Al}(\text{OH})_3$ -PAAm4 samples for a series of flocculant parent solution concentrations (C_p) in 2×10^{-2} g/mL kaolin suspensions, respectively. From Figure 4 the phenomena are the same as in Figure 2, such as, different T values of a given $\text{Al}(\text{OH})_3$ -PAAm flocculant with different C_p . The C_{od} values are approximately equal to 25 ppm for $\text{Al}(\text{OH})_3$ -PAAm3 and 30 ppm for $\text{Al}(\text{OH})_3$ -PAAm4.

Figure 5 shows the effect of C_p on T value of five $\text{Al}(\text{OH})_3$ -PAAm samples at each optimal dose, C_{od} . Figure 5, similar to Figure 3, displays the same trend of change of T - C_p curves. T_{max} exists at the C_{op} and also displays that the higher the $[\eta]$ of the sample, the higher the T value and lower the C_{op} will be.

Figure 6(a, b) show the typical variation of the flocculation performance with the dose (C_d) of star-PAAm2 and star-PAAm3 samples for a series of flocculant parent solution concentrations (C_p) in 2×10^{-2} g/mL kaolin suspensions, respectively. In Figure 6, the similar phenomena exist as in Figures 2 and 4. But, C_{od} values of two star-PAAm samples are nearly the same 20 ppm, it is probably because that they

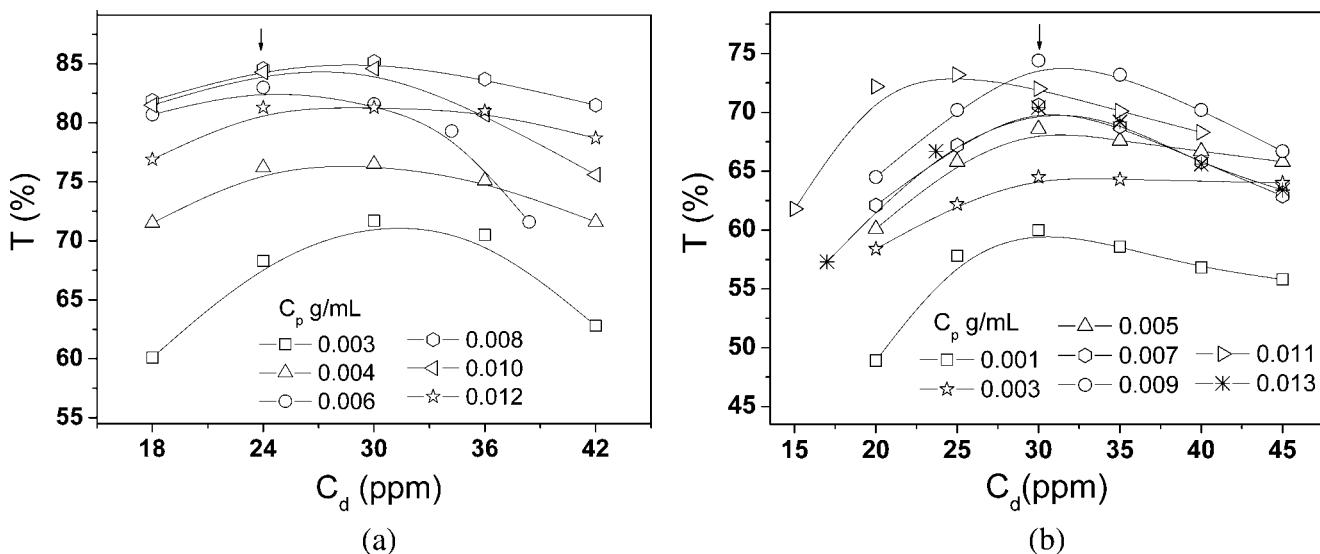


Figure 4 (a) Variation of flocculation performance of $\text{Al}(\text{OH})_3$ -PAAm3 with C_d for different C_p in 2×10^{-2} g/mL kaolin suspensions. (b) Variation of flocculation performance of $\text{Al}(\text{OH})_3$ -PAAm4 with C_d for different C_p in 2×10^{-2} g/mL kaolin suspensions.

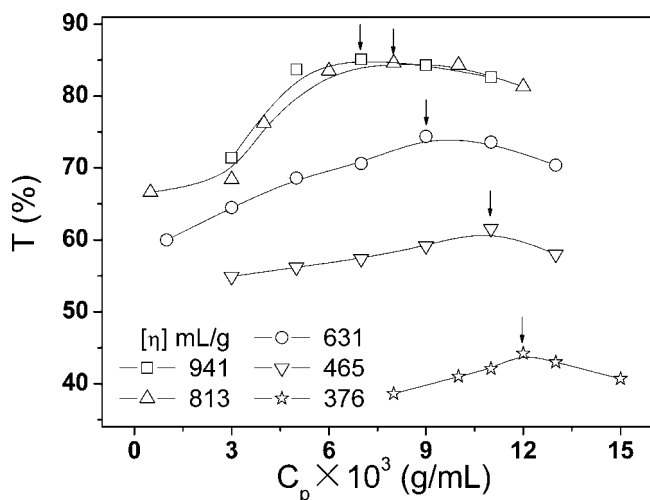


Figure 5 Effect of C_p on flocculation performance of $\text{Al}(\text{OH})_3$ -PAAm at C_{od} in 2×10^{-2} g/mL kaolin suspensions.

have close $[\eta]$ values or deficient data points in corresponding concentration regions.

Figure 7 shows the effect of C_p on T value of five star-PAAm samples at each optimal dose, C_{od} . Figure 7, similar to Figures 3 and 5, displays the same trend of change of T - C_p curves, the higher $[\eta]$ of the sample, the higher T value and the lower C_{op} will be except for star-PAAm4 and star-PAAm5.

The last column in Table I gives the approximate values of C_{op} of all flocculant samples from Figures 3, 5, and 7. It is clear that the value of C_{op} decreases roughly with the increasing $[\eta]$ of flocculant sample. It means that the optimal parent solution concentra-

tion C_{op} is less for the flocculant with higher molecular weight.

In the flocculation process, the adsorption-bridging action between flocculant chains and colloid particles occurs simultaneously during the mixing of the flocculant parent solution and the Kaolin suspension. Thus, the shape of the flocculant chains that enter the Kaolin suspension will greatly affect the flocculation process and the flocculation performance. A polymer chain in solutions could present various shapes, such as expanded, associated, shrank, entangled and so on. According to the bridging mechanism, the flocculants chains with proper interchain association in the parent solution should be good for flocculation. The solution concentration is one of simplest methods to control the interchain association directly. That is, the increase of the parent solution concentration (C_p) would enhance the flocculation performance of the polymer flocculant. But, excessive association of the flocculants in the parent solution or even in Kaolin suspensions is equal to the decrease of the amount of the flocculants. Therefore, the flocculation performance of the polymer flocculant rises at the beginning and then decreases with the increasing parent solution concentration (C_p). So, an appropriate concentration of the parent solution for fitting proper chain-association is necessary to reach the best flocculation efficiency. This appropriate concentration in the flocculation process is just optimal parent solution concentration C_{op} , i.e., C_{op} exists reasonably. As we know, the interchain association of a given polymer in solutions is dependent on its molecular weight. Generally, high molecular weight links to a low association concentration of a polymer in solutions.^{15,21}

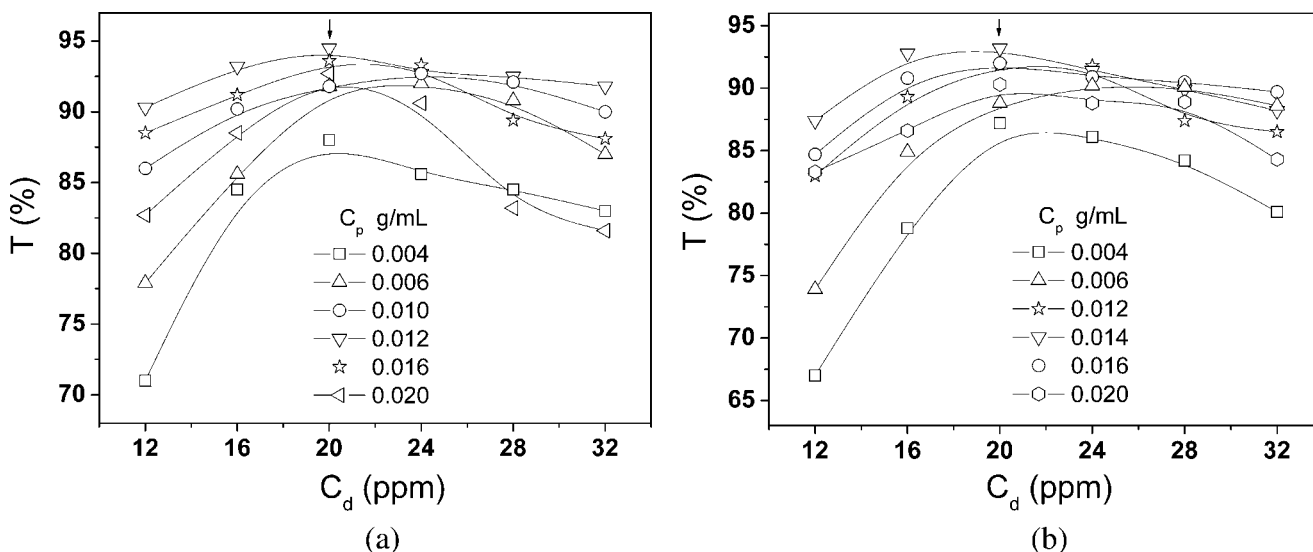


Figure 6 (a) Variation of flocculation performance of star-PAAm2 with C_d for different C_p in 2×10^{-2} g/mL kaolin suspensions. (b) Variation of flocculation performance of star-PAAm3 with C_d for different C_p in 2×10^{-2} g/mL kaolin suspensions.

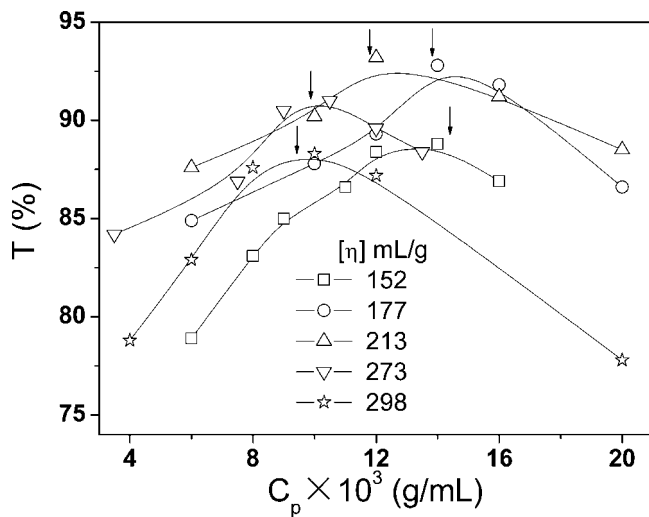


Figure 7 Effect of C_p on flocculation performance of star-PAAm at C_{od} in 2×10^{-2} g/mL kaolin suspensions.

This is why C_{op} is also negatively proportional to the $[\eta]$ of the flocculant.

Effect of parent solution concentrations C_p on flocculation performance in different concentrations of kaolin suspensions

Figure 8 shows the variation of the flocculation performance with the dose (C_d) of $\text{Al}(\text{OH})_3$ -PAAm3 sample for a series of flocculant parent solution concentrations (C_p) in 3×10^{-2} g/mL kaolin suspensions. In Figure 8, the trend of T - C_d curves of $\text{Al}(\text{OH})_3$ -PAAm3 at different C_p is exactly the same as in Figure 4(a) in 2×10^{-2} g/mL kaolin suspensions. But T values are much lower and C_{od} values are much higher in 3×10^{-2} g/mL kaolin suspensions than in 2×10^{-2}

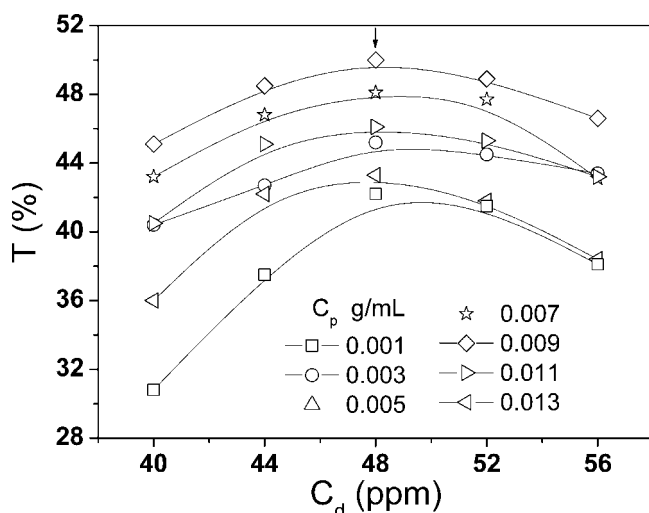


Figure 8 Variation of flocculation performance of $\text{Al}(\text{OH})_3$ -PAAm3 with C_d for different C_p in 3×10^{-2} g/mL kaolin suspensions.

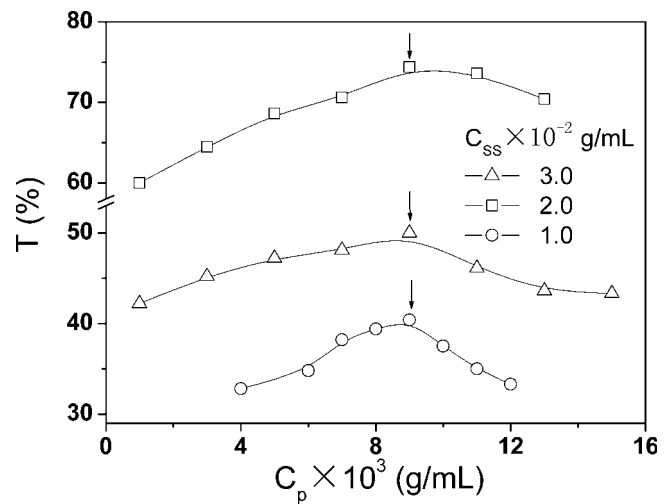


Figure 9 Effect of C_p on flocculation performance of $\text{Al}(\text{OH})_3$ -PAAm3 at C_{od} in kaolin suspensions with different kaolin solid contents.

g/mL, because kaolin suspensions are more unwieldy due to higher kaolin solid contents in the suspension.

Figure 9 shows the effect of C_p on the flocculation performance of $\text{Al}(\text{OH})_3$ -PAAm3 samples in kaolin suspensions with three different suspensions solid contents (C_{ss}) at their optimal dose (C_{od}), respectively. In Figure 9, the optimal parent solution concentrations (C_{op}) of $\text{Al}(\text{OH})_3$ -PAAm3 in kaolin suspensions at different C_{ss} are almost the same, i.e., $C_{op} = 0.009$ g/mL though the light transmission at the each C_{od} at the same C_p are different. It means that C_{op} of a flocculant is independent on C_{ss} of Kaolin suspension.

Relation between C_{op} and C^* or C_s

According to the results above, the flocculation performance of PAAm depends on the parent solution concentration C_p of flocculants in spite of the kind of polymer flocculants and the amount of Kaolin in the Kaolin suspensions, and an optimal parent solution concentration C_{op} exists for each C_p of a given flocculant.

Figure 10 shows the relation between C_{op} and the critical concentrations C^* and C_s , which can be calculated by eqs. (3') and (4), respectively. In Figure 10(a), the C^* dependence of C_{op} is exactly the same for linear-PAAm and $\text{Al}(\text{OH})_3$ -PAAm samples, but different from star-PAAm sample, i.e., the C^* dependence of C_{op} for star-PAAm is less than that for linear-PAAm and $\text{Al}(\text{OH})_3$ -PAAm. It probably attributes to the chain shape of the star-PAAm, which seems to be associated chains or "self-association" due to the star structure, compared to linear-PAAm and $\text{Al}(\text{OH})_3$ -PAAm. Figure 10(b) shows the plots of C_{op} versus C_s of three kinds of PAAm with different $[\eta]$. From Figure 10(b), it can be seen that a master curve with posi-

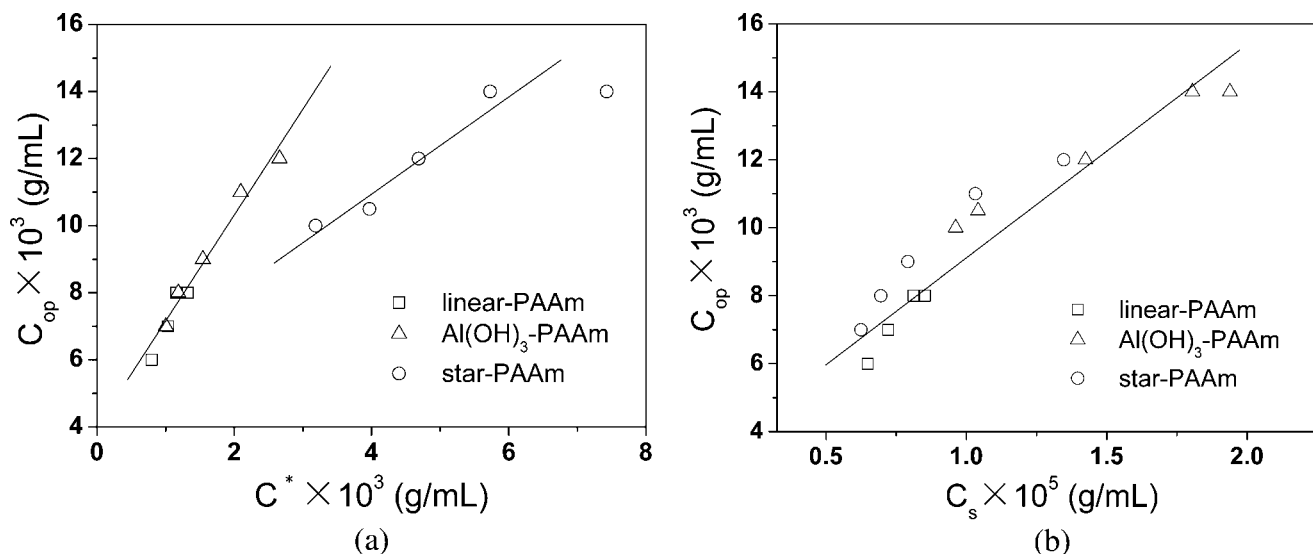


Figure 10 (a) Relation between C_{op} and the critical concentration C^* . (b) Relation between C_{op} and the critical concentration C_s .

tive relation between C_{op} and C_s presents approximately. Therefore, the C_s is better than the C^* to be related the C_{op} because chain shape parameters, K_m and K_H , are included in C_s [eq. (4)].

According to literature,²⁹ C_s of a polymer solution is a particular critical concentration at which the inter-chain interactions starts to appear. Oppositely, the polymer chain as an isolated single chain exists when $C \leq C_s$. In Figure 10(a, b), the C_{op} is a little larger than C^* , and 100 times more than C_s . But, the real concentration of flocculants in kaolin suspensions is just a little larger than C_s because the volume of the cylinder for kaolin suspensions is 100 mL and the dose is between 0.05 mL and 2 mL. That is, C_p is 100 times more than C_d , but C_d is close to C_s .

According to the data points in Figure 10(b), a linear relation between C_{op} value and C_s value could be expressed as follows,

$$C_{op} = 3.1 \times 10^{-3} + 643.1C_s \quad (5)$$

Equation (5) could be used to predict the optimal parent solution concentration (C_{op}) of the flocculants before experiments for a given flocculant to achieve the optimal flocculation performance without pretest.

CONCLUSIONS

Effect of the parent solution concentration C_p of flocculants on the flocculation performance of flocculants of linear-PAAm, $Al(OH)_3$ -PAAm, and star-PAAm in kaolin suspensions with different suspension concentrations was investigated. The flocculation performance of the flocculant is enhanced at the beginning and then impaired with increasing C_p . An optimal

parent solution concentration C_{op} of the flocculant exists, at which a maximum light transmission of the clean supernatant takes place when the flocculant parent solution with C_{op} is added into the kaolin suspensions. The value of C_{op} is larger than the value of the overlap critical concentration C^* , and much larger than the value of the dynamic contact critical concentration C_s of the polymer in solutions. In fact, the real concentration of flocculant, in the kaolin suspension during the flocculation process is much less than C^* but still larger than the C_s to obtain the maximum light transmission. That is, both of the interchain association and the chain contact of a given polymer flocculant in the parent solution and in the kaolin suspension respectively, are very important to achieve the best flocculation performance of the given polymer flocculant. The optimal parent solution concentration C_{op} of the flocculant of a given poly acrylamide flocculant could be predicted roughly by the empirical formula, $C_{op} = 3.1 \times 10^{-3} + 643.1C_s$.

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