ASSOCIATED COLLOIDAL FLOCCULANTS UNDER WIDE pH VARIATION

ISAMU KASHIKI AND AKIRA SUZUKI

Department of Chemistry, Hokkaido University, Hakodate 041

Key Words: Solid Liquid Separation, Polyelectrolyte, Colloid, Ion Dissociation, Quartz Sand

The influence of pH on the operating conditions of polycation/polyanion mixed ACFs was studied. Water clarification experiments on quartz sand suspensions under varying pH were carried out by using ACFs formed from polyelectrolytes. In the case of an ACF where polycation and polyanion were both strongly ionizable polyelectrolytes, the variation of pH produced no significant effect except for a charge reversal of the suspended solid at the isoelectric point (i.e.p.). Sudden change in the flocculating efficiency takes place at the point where the polycation and the polyanion which are to form an ACF are equal in number of ionizable functional groups ($n_c = n_a$). In the case of an ACF containing weak polyelectrolyte(s), the situation appeared to be quite different; the pH showed appreciable effects not only at the i.e.p. but also at a point far from the i.e.p. It was found, however, that the results can be explained in quite the same manner as before, if we take into account the variation in degree of dissociation of weak polyelectrolyte(s); the pH where the sudden change in the flocculating efficiency was observed simply corresponds to the point where the polycation and the polyanion are the same in number of really ionized functional groups.

Introduction

Earlier, we proposed a new type of flocculant (associated colloidal flocculant, ACF),³⁻⁵⁾ where we presented a wide variety of ACFs and a simple condition necessary for them to work effectively. An ACF can be defined as a flocculant that is hardly soluble in water, so that it is dispersed in relatively large colloidal particles through molecular association, and thereby has the ability to flocculate suspended solids. In the preceding paper,⁶⁾ a detailed study of the working mechanism of a polycation/polyanion mixed-type ACF was extended with a special view to applying ACFs to practical use. However, that work was exclusively concerned with suspensions around neutral pH. This paper describes a necessary condition for polycation/polyanion mixed-type ACFs to work effectively on suspensions under wide variation of pH. Not only the electrical charge density on the surface of suspended solids but also the degree of dissociation of ionizable functional groups on polyelectrolytes is expected to vary greatly with pH, particularly where the polyelectrolytes are weak ones. The sign and the amount of charges on the two kinds of polyelectrolytes and the suspended solids play a decisive part in the previously presented theory of the conditions required for ACFs to work effectively.^{4,6)} Accordingly, the theory may not directly apply to a case including wide pH variation, without

appropriate modification.

1. Experimental

1.1 Flocculant

The polyelectrolytes used to prepare ACF were methyl glycol chitosan (MGCh), potassium polyvinyl sulfate (PVS_K) and sodium polyacrylate (NaPA). MGCh and PVS_K are strong cationic and anionic polyelectrolytes because their cationic and anionic characters derive from the completely ionizable quaternary ammonium iodide and potassium sulfate groups, respectively; the last is a weak, anionic polyelectrolyte, of which the anionic character comes

Fig. 1. Conductometric determination of the number of ionizable functional groups in NaPA

from the incompletely ionizable sodium carboxylate groups. These three polyelectrolytes were obtained from Wako Pure Chemical Industries (Japan) and used with no further purification. The number of ionizable functional groups in the polymers was determined by an electro-conductance titration method. An example is given in Fig. 1, where 5 ml of 0.1 wt% NaPA solution was mixed with 10 ml of 0.001 N NaOH solution, and the mixture was titrated with 0.002-N HCl solution. The figure shows the relation between the conductivity (arbitrary unit) and the added volume. In the first stage, the neutralization reaction takes place between NaOH and HCl ($O-V_1$). This is followed by the neutralization between carboxylate in NaPA and HCl (V_1-V_2). At V_2 the neutralization is completed, and thereafter the added HCl remains unreacted. From this result we can estimate the ionizable group concentration of the 0.1 wt% NaPA solution as 9.92×10^{-3} N. We can also estimate the purity and the degree of neutralization of the original NaPA as 92.2 and 95.2%, respectively. Attention should be paid to the fact that the concentration thus obtained does not always agree with that determined by the colloid titration method.⁶⁾ The former is based on the number of ionizable functional groups in polymers, the latter on the number of really ionized functional groups. In the case of weak electrolytes, these two values do not in general agree.

1.2 Suspended solid

Quartz sand was used to prepare the suspensions for water clarification. It was from the same batch as in the previous work.⁴⁾ The average particle size measured by an air-permeability method was $2.39 \mu\text{m}$. This particular material was selected because of its strong surface-negative character in water; it may remain negative even when the pH is decreased to as low as 2 or so.¹⁾

1.3 Water clarification

Suspensions of quartz sand were prepared as follows. To soak the surface of the solid particles thoroughly with water, 1 g of the powder was boiled with ca. 40 ml of water in a 200 ml flask. An amount of dilute HCl or NaOH solution was added so as to adjust the final pH in the suspension to an expected value. Further, an appropriate amount of water was added so as to form finally a 100 ml suspension when combined with a prearranged amount of polymer solutions to be added later. Then, a prearranged amount of NaPA or PVSK solution was added and the resultant suspension was allowed to stand in a constant-temperature water bath (30°C) for some time. Upon reaching thermal equilibrium, an appropriate amount of MGCh solution was added to obtain a final 100 ml suspension containing 1 g of the solid. Five minutes later the suspension was poured into a graduated 100 ml cylinder of 30 mm diameter and

allowed to stand for an additional 5 min to settle the flocs just formed. Subsequently, a known volume of the sample was taken from the supernatant. The solid concentration, T , of the sample was determined by turbidimetry. Relative solid concentration, T/T_0 , was employed to assess the efficiency of the ACF just formed in the tested suspension, where T_0 refers to T in the absence of polyelectrolytes. The final pH of the suspension was also measured.

1.4 Assessment of degree of colloid formation

This was done by measuring the intensity of light of 500 nm wavelength scattered toward 90° by colloidal particles which were formed between NaPA and MGCh. The measurement was conducted with a spectrofluorometer (FP-550, Japan Spectroscopic Co.).

2. Results and Discussion

2.1 ACFs composed of two strong polyelectrolytes

Figure 2 shows the result of clarification experiments on quartz sand suspensions under varying pH by PVSK-MGCh, which refers to an ACF formed by the combination of PVSK and MGCh. Two such combinations were used. One was of $n_c = 5.1 \mu\text{mol}$ and $n_a = 5.0 \mu\text{mol}$ (open circles), and the other was of $n_c = 5.0 \mu\text{mol}$ and $n_a = 5.1 \mu\text{mol}$ (closed circles). These two curves, in spite of the small difference in composition, behave in entirely opposite ways. Both undergo sudden changes, and they intersect at $\text{pH} = 2.1$. Quartz is known to take its isoelectric point around this pH ($\equiv \text{pH}_i$).¹⁾ Therefore, the sudden changes should be attributed to the charge reversal from negative to positive taking place around the pH_i with decreasing pH. Apart from the pH_i , nothing significant occurs in either curve.

Based on our previous discussions,^{4,6)} these results can be interpreted as follows. Both PVSK and MGCh are strong polyelectrolytes. Accordingly, their numbers of ionized functional groups may remain constant as n_a and n_c even if the pH is varied. Thus, in the case of the result shown by the open circles, the number of ionized, cationic groups is greater than

Fig. 2. Water clarification of quartz sand suspensions by PVSK-MGCh under varying pH

that of anionic groups. Therefore, in this case we can expect to obtain a positive ACF according to the Paneth-Fajans rule. This is the reason why PVSK-MGCh ($n_a = 5.0$, $n_c = 5.1$) is effective at $\text{pH} > \text{pH}_i$, and ineffective at $\text{pH} < \text{pH}_i$, for in the former pH range the quartz sand is expected to charge negatively, and in the latter positively. The result shown by the closed circles can be explained in an exactly analogous manner. Thus, we conclude that a necessary condition for an ACF composed of two strong polyelectrolytes to work effectively is:

$$n_c > n_a \quad (\text{for a negative solid}) \quad (1)$$

or

$$n_c < n_a \quad (\text{for a positive solid}) \quad (2)$$

It is worth noting that only one kind of ACF is enough to treat both negative and positive suspended solids, where what is only necessary is to select an appropriate mixture ratio of polyelectrolytes. In general, oxide-type solids undergo a charge reversal on the variation of pH. Therefore, the adaptability of the ACF to this situation may be a particular advantage over conventional polymer flocculants.

Attention may be paid to the fact that in the above discussion we tacitly neglected the amount of polymers adsorbed on the solid. However, this amount is in general negligible, as compared with that consumed for colloid formation. For a more exact discussion, this must be taken into account. A detailed study of this point has been presented elsewhere.⁶⁾

2.2 ACFs containing weak polyelectrolyte(s)

1) Relation between T/T_0 and pH at constant n_a and n_c **Figure 3** shows the results of experiments on the water clarification of quartz sand suspensions by various NaPA-MGCh mixtures under varying pH, where the amount of anionic polymer (NaPA) contained in 100 ml suspension, n_a , was kept constant at $50 \mu\text{mol}$ on the basis of the number of ionizable functional groups of the polymer. In each series of experiments, the added amount of MGCh, n_c , was kept constant while the pH was varied.

Fig. 3. Water clarification of quartz sand suspensions by NaPA-MGCh under varying pH

For every series, the flocculating power of NaPA-MGCh suddenly decreased with decreasing pH around the pH_i in exactly the same fashion as the case shown by the open circles in Fig. 2. Unlike that case, however, the result of each series was still influenced by pH even if its value is different from the pH_i . Every series showed redeterioration in clarifying efficiency with increasing pH according to the S-shaped curve on the right side of the figure. We can define a critical flocculation pH, pH_f , for each series as the inflection point of the corresponding S-shaped curve, as indicated by the dotted arrows in Fig. 3. This sort of definition has a close analogy to that of the end-point of titration in analytical chemistry. These pH_f values tend to increase with increasing n_c .

Similar result can be obtained with various added amounts of NaPA. The cases of $n_a = 30$ and $70 \mu\text{mol}$ were carried out in this work.

2) Relation between colloid formation and flocculating ability We have already stated^{4,6)} that the flocculating ability of a cation/anion mixture comes from colloid formation between the two kinds of ions, and this is in fact the principle of ACF.^{4,5)} **Figure 4** shows that the flocculating ability of NaPA-MGCh produced by pH variation ($\text{pH} > \text{pH}_i$) comes from colloid formation as well. Light of 500 nm wavelength with a constant intensity was passed through mixtures of NaPA and MGCh solutions at a constant mixture ratio ($n_a = 5.0 \mu\text{mol}$ and $n_c = 0.5 \mu\text{mol}$ in 100 ml mixture) under varying pH. The intensity of light scattered toward 90° against the incident beam was measured by a spectrofluorometer. The measured mixtures of NaPA and MGCh were just ten times as dilute as the cases represented by the open squares in Fig. 3, but in this case quartz sand was absent. Dilution was necessary, because the Tyndallometric instrument used was too sensitive for a mixture with the original polymer concentrations. According to the study by Huizenga *et al.*,²⁾ dilution of a polyelectrolyte solution may not result in a significant change in degree of dissociation.

Fig. 4. Variation of colloid amount in NaPA/MGCh mixture with pH

As shown in Fig. 4, gradual addition of HCl and lowering of pH caused a sudden increase in the intensity of scattered light around $\text{pH}=4.8$, indicating a sudden increase in the amount of colloid formed around this point. At this same pH ($=\text{pH}_f$), NaPA-MGCh having the same mixture ratio starts to work effectively with decreasing pH, as shown by the open squares in Fig. 3. This strongly supports the idea that the flocculating power of NaPA-MGCh comes from the colloid formation between the two electrolytes.

3) Relation between T/T_0 and n_c at constant pH From the results obtained in 2.2.1, we can obtain the relation between T/T_0 and n_c at a constant pH for each n_a . Some experimental difficulties would have been encountered in the adjustment of pH if we had tried to obtain the same relation directly from a

Fig. 5. Relation between T/T_0 and n_c at $\text{pH}=4$

Fig. 6. Relation between T/T_0 and n_c at $\text{pH}=5$

Fig. 7. Relation between T/T_0 and n_c at $\text{pH}=6$

water-clarification experiment at an exactly constant pH. The relations obtained indirectly are presented in Figs. 5, 6 and 7 for the cases of $\text{pH}=4$, 5 and 6, respectively. For every case, a smooth reverse S-shaped curve can be drawn through the data. The inflection point of each curve indicated with a dotted arrow refers to a corresponding critical value of n_c , n_{cf} , over which the ACF of NaPA-MGCh works effectively at the constant pH.

4) A necessary condition for an ACF containing weak polyelectrolyte(s) to work effectively Figure 8 shows plots of n_{cf} vs. n_a for the results in Figs. 5, 6 and 7. The plots give three straight lines; the slope, β , decreases with decreasing pH. At $\text{pH} > \text{pH}_f$ (i.e., for the positive solid), NaPA-MGCh is effective under the condition that

$$n_c > n_{cf} \quad (\text{for positive solids}) \quad (3)$$

It can be easily seen that this n_{cf} corresponds to n_a in Eq. (1). However, this n_{cf} depends not only on n_a but also on pH. NaPA is an anionic, weak polyelectrolyte. Therefore, the number of its really ionized functional groups depends not only on n_a but also on pH. This may be the reason why n_{cf} depends on pH. The pH influences the degree of dissociation of a weak polyelectrolyte. Therefore, we conclude that at the point of $n_c = n_{cf}$ the cationic and anionic, really ionized functional groups of the two polyelectrolytes which are to form an ACF must be equal in number:

$$n_{cf} = \alpha n_a \quad (4)$$

or in the case of an ACF composed of two weak polyelectrolytes:

$$\alpha_c n_{cf} = \alpha_a n_a \quad (5)$$

where α is the degree of dissociation, and the subscripts, c and a , indicate the cationics and the anionics respectively.

Insertion of Eq. (4) or (5) in Eq. (3) makes clear the fact that the slope, β , must simply correspond to α or α_a/α_c . It is known about a polyelectrolyte that the degree of dissociation is almost independent of its

Fig. 8. Plots of n_{cf} vs. n_a

Fig. 9. Degree of dissociation of NaPA under varying pH

concentration.²⁾ This is in conformity with the fact that the plot of n_{cf} vs. n_a gives a straight line for a given pH, as shown in Fig. 8. It is somewhat difficult and laborious to determine the degree of dissociation for a polyelectrolyte. Huizenga *et al.*²⁾ made such determinations for NaPA at various pH values by measuring the mobility of the ions in an electric field. The results are presented in Fig. 9 by the squares and the solid line. The open circles show values from the slope, β , in Fig. 8. Shown by the closed circles are the data obtained on the assumption that Eq. (4) also holds at the point $\text{pH} = \text{pH}_f$ in Fig. 3. Both types of circles can be represented by a single (dotted) line. Some discrepancy is observed between our data and those of and Huizenga. However, this may be acceptable since the two data sets were generated by fundamentally different methods. Acceptable agreement between the two data sets in turn suggests that the above assumption is acceptable. Thus we obtain a necessary condition for an ACF containing weak polyelectrolyte(s) under varying pH:

$$n_c > (\alpha_a/\alpha_c)n_a \quad (\text{for a negative solid}) \quad (6)$$

or

$$n_c < (\alpha_a/\alpha_c)n_a \quad (\text{for a positive solid}) \quad (7)$$

Attention should be paid to the fact that this is nothing but a wide generalization of the Paneth-Fajans rule to include a colloid formed from weak polyelectrolytes. That is to say, a positive ACF will be formed under the condition of Eq. (6), and a negative one under that of Eq. (7). The former can work on a negative solid, and the latter on a positive one.

Conclusion

A study of the condition necessary for polycation/polyanion mixed-type ACFs to work was carried out on suspensions under widely varied pH. The conclusions are as follows.

(1) Where an ACF is composed of two strong polyelectrolytes, pH variation produces no remarkable effect different from operation under constant pH, except for charge reversal of the suspended solid. In this case, the necessary condition is that if the suspended solid is negative, the ACF must be positive ($n_c > n_a$), and *vice versa* (Eqs. (1) or (2)). Flocculation experiments using this type of ACFs may be utilized to determine the isoelectric point of an oxide-type solid.

(2) In the case of an ACF containing weak polyelectrolyte(s), the situation is complicated by variation of the degree of dissociation with pH, as well as by charge reversal. In this case, the condition must be modified to fit Eq. (6) or (7). These relations may be applied also to determining the degree of dissociation of a weak polyelectrolyte.

(3) A particular advantage of a polycation/polyanion mixed ACF is that a single kind of ACF is enough to treat both negative and positive solids, the only necessary change being the adjustment of the mixture ratio.

Acknowledgment

The authors wish to express their thanks to Mr. M. Tagami for his assistance in the experiments. This work was partially supported by a Grant-in-Aid for Scientific Research No. 61550687 from the Ministry of Education, Science and Culture.

Nomenclature

n	= number of ionizable functional groups	[μmol]
n_{cf}	= critical flocculation value of n_c	[μmol]
pH_i	= pH giving isoelectric point of a solid	[—]
pH_f	= critical flocculation pH	[—]
T	= solid concentration in supernatant	[g/m^3]
T_0	= T in the absence of flocculant	[g/m^3]
α	= degree of dissociation	[—]
β	= slope of the line in Fig. 8	[—]

<Subscripts>

a	= anionics
c	= cationics

Literature Cited

- 1) Churaev, N. V., I. P. Sergeeva, V. D. Sobolev and B. V. Derjaguin: *J. Colloid Interface Sci.*, **84**, 451 (1981).
- 2) Huizenga, J. R., P. F. Grieger and F. T. Wall: *J. Am. Chem. Soc.*, **72**, 2636 (1950).
- 3) Kashiki, I. and A. Suzuki: *Kagaku Kogaku Ronbunshu*, **8**, 722 (1982).
- 4) Kashiki, I. and A. Suzuki: *Ind. Eng. Chem. Fundam.*, **25**, 120 (1986).
- 5) Kashiki, I., A. Suzuki and K. Gotoh: *Kagaku Kogaku Ronbunshu*, **8**, 73 (1982).
- 6) Suzuki, A. and I. Kashiki: *Ind. Eng. Chem. Research*, **26**, 1464 (1987).