

CONDUCTIVITY BEHAVIOR OF IONIC $\text{Al}(\text{OH})_3$ -POLYACRYLAMIDE HYBRIDS IN AQUEOUS SOLUTIONS*

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Abstract The conductivity behavior of $\text{Al}(\text{OH})_3$ -acrylamide hybrid polyacrylamide (hybrid PAAM) in distilled water was studied. A discontinuity phenomenon of the conductivity (k) versus concentration (c) curve of the hybrid PAAM in a certain concentration regime is found. This phenomenon is dependent on the molecular weight of the hybrid PAAM and on the particle size and content of the $\text{Al}(\text{OH})_3$ colloid in the hybrid PAAM. This phenomenon was accounted for assuming ionization of the hybrid PAAM.

Keywords Ionic hybrid polyacrylamide, Viscosity, Conductivity

INTRODUCTION

Polyacrylamide (PAAM) is one of the widely used organic flocculants for wastewater. Many studies were performed on modified PAAM such as partially hydrolyzed PAAM (HPAAM)^[1], cationic PAAM^[2], binary composition of anionic and cationic PAAM^[3], HPAAM/anionic surfactant SDS complex^[4], sodium alginate-g-PAAM^[5], star-PAAM^[6], HPAAM/aluminum sulfate mixture^[7] and poly(acrylamide-co-acrylic acid)/inorganic coagulant^[8] to obtain more effective flocculants for the treatment of various kinds of wastewaters. In our previous study^[9] a new kind of $\text{Al}(\text{OH})_3$ -acrylamide hybrid polyacrylamide was synthesized by *in situ* polymerization using $\text{Al}(\text{OH})_3$ colloid and acrylamide monomer, which has much better flocculent behaviors, such as high sedimentation rate and dense flocs compared to pure PAAM due to the combination of organic polymer flocculant and inorganic flocculant. In addition, it is well known that the performance of ionic flocculants in wastewater is often affected by the charge density of polymer chains^[10–12] which will be changed by the concentration and pH of the dilute solution because of the changing conductivity of aqueous solutions. In the present study, conductivity behaviors of hybrid PAAM in aqueous solution were investigated. A discontinuity phenomenon of the conductivity (k) versus concentration (c) curve of the hybrid PAAM is demonstrated and discussed in relation to the molecular weight of hybrid PAAM, the particle size of $\text{Al}(\text{OH})_3$ colloid in the hybrid PAAM and the content of $\text{Al}(\text{OH})_3$ colloid used in the preparation of hybrid PAAM.

EXPERIMENTAL

Materials

Acrylamide (chemically pure grade) was purchased from Shanghai Chemical Co., other agents were analytically pure grade. All compounds were used without further purification.

Preparation and Characterization

$\text{Al}(\text{OH})_3$ colloidal solution was prepared by dropwise addition of an appropriate amount of aqueous ammonium carbonate to aqueous aluminum chloride with vigorous stirring. The acrylamide was dissolved in $\text{Al}(\text{OH})_3$

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colloidal solution, and then polymerized *in situ* by the redox system $((\text{NH}_4)_2\text{S}_2\text{O}_8\text{-NaHSO}_3)$ under the nitrogen atmosphere at a definite temperature for 8 h. All the products were precipitated and extracted with acetone, then dried in a vacuum oven to constant weight at 60°C. The aqueous solution of $\text{Al}(\text{OH})_3$ -polyacrylamide hybrid is homogeneous and transparent without any precipitate, but the mixture of PAAm solution and $\text{Al}(\text{OH})_3$ colloidal solution is a flocculent system. The TGA curves of hybrid PAAm show that it has a higher initial hydrolysis temperature and a higher mid-hydrolysis temperature at 212 and 521°C, (half-weight loss) compared with 200 and 450°C for the blend of $\text{Al}(\text{OH})_3$ /PAAm, and with 198 and 400°C for the pure PAAm, respectively. According to its solubility and heat-resistance behavior, $\text{Al}(\text{OH})_3$ -polyacrylamide hybrid was considered as an ionic $\text{Al}(\text{OH})_3$ -acrylamide hybrid with an ionic bond between the SO_4^{2-} anion at the end of PAAm chain and the cationic surface of $\text{Al}(\text{OH})_3$ colloid particle, *i.e.* a new type of ionomer which has an ionic group at one end of the chain. Their synthesis and characteristics were described in detail in our previous work^[9]. The particle size of $\text{Al}(\text{OH})_3$ colloid in the hybrid PAAm was measured by a Transmission Electron Microscope (JEM-1200EX).

Viscosity Average Molecular Weight

The sample was dissolved in distilled water at 45°C, and then filtered. Viscosity measurement of the solution was conducted with an Ubbelohde type viscometer at $(30 \pm 0.02)^\circ\text{C}$. The reproducibility of the reduced viscosity was checked and found to be within $\pm 1\%$. The intrinsic viscosities $[\eta]$ of all samples were obtained by the extrapolation method. The viscosity average molecular weights (M_v) of all samples were estimated using the Mark-Houwink equation at θ conditions, $[\eta]_\theta = k_\theta M_v^{0.5}$, where k_θ equals to $0.2088 \text{ cm}^3/\text{g}$ calculated according to the van Krevelen method^[13] and the $[\eta]_\theta$ value of each sample was calculated using the Qian *et al.* method^[14].

Conductivity Measurement

The solution conductivity of samples were measured by a DDS-11A conductometer at $(30 \pm 1)^\circ\text{C}$ with magnetic stir.

Measurement of Degree of Hydrolysis

The degree of hydrolysis (α) of PAAm was determined by acid-base titration^[15]. $\alpha = n_{\text{-COOH}}/n_{\text{PAAm}}$ (mole ratio).

RESULTS AND DISCUSSION

Influence of Molecular Weight on Conductivity

Figure 1 shows the k versus c curves of hybrid PAAm with different molecular weights (with same particle size 150 nm and same dosage 5.67 wt% of $\text{Al}(\text{OH})_3$ colloid), the $\text{Al}(\text{OH})_3$ colloid and PAAm ($M_v = 4.81 \times 10^6$) in distilled water. As can be seen from Fig. 1, the k values of the hybrid PAAm are much larger and lower than that of pure PAAm and $\text{Al}(\text{OH})_3$ colloid, respectively. Obviously, this is because $\text{Al}(\text{OH})_3$ is an inorganic electrolyte, while neutral PAAm is a polymer only with a few hydrolyzed carboxyl groups on the chain. It is interesting to note that the shape of k versus c curves of PAAm hybrid is significantly different from that of PAAm or inorganic electrolyte $\text{Al}(\text{OH})_3$, which display a discontinuity behavior in their k versus c curves, *i.e.*, the k value decreases quickly at the beginning, maintains a slow decrease (discontinuity) and a fast decrease again with decreasing concentration of the hybrid PAAm. This discontinuity of the k versus c curve is considered to be due to the ionization of the hybrid PAAm in certain concentration regime. If the concentration, at which the k value starts to enter the discontinuity, is denoted as c_k , the c_k value increases with decreasing M_v of the hybrid PAAm. This means that the hybrid PAAm with lower molecular weight in distilled water ionizes easily *i.e.*, ionizing even at higher concentration. Apparently, this is because the inter-chain interaction (or entanglement) is weaker in the ionic hybrid PAAm with low M_v than that with high M_v . In Fig. 1, however, higher k values of the hybrid PAAm with larger M_v are similar to pure PAAm (See Fig. 2). This is attributed to the higher carboxyl group content on each chain in pure PAAm with larger M_v .

Influence of Particle Size of $\text{Al}(\text{OH})_3$ Colloid on Conductivity

Figure 3(a) shows the k versus c curves of the hybrid PAAm with different particle size of $\text{Al}(\text{OH})_3$ colloid in the ionic hybrid PAAm (amount of $\text{Al}(\text{OH})_3$ colloid: 5.67 wt%, $M_v = 6.77 \times 10^6$, 6.6×10^6 and 4.41×10^6 , respectively) in distilled water. The discontinuity phenomenon is also displayed. The c_k values increase with

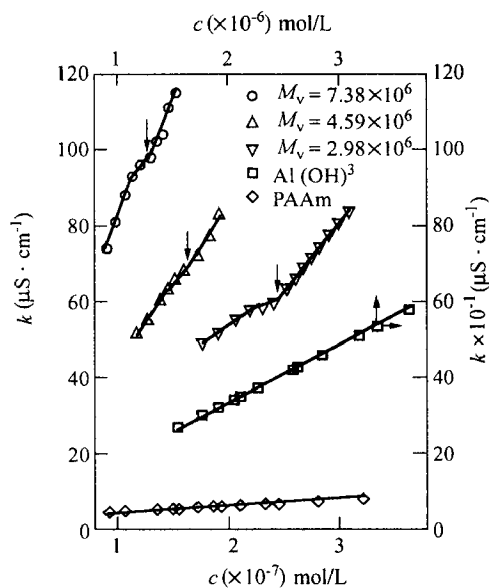


Fig. 1 Variation of k versus c curves of the ionic hybrid PAAm with M_v (the content and particle size of the $\text{Al}(\text{OH})_3$ colloid are 5.67 wt% and 150 nm, respectively). Straight lines are for $\text{Al}(\text{OH})_3$ and pure PAAm samples, respectively

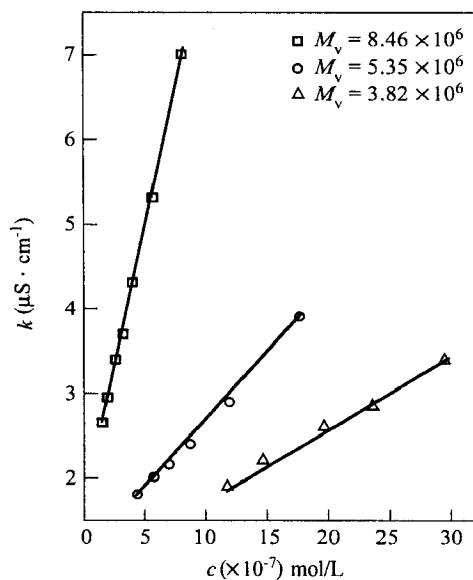


Fig. 2 Effect of molecular weight of PAAm on the conductivity ($M_v = 8.46 \times 10^6$, 5.35×10^6 , 3.82×10^6 with degree of hydrolysis (α): 3919, 2381 and 1660, respectively)

increasing particle size of the $\text{Al}(\text{OH})_3$ colloid in the hybrid PAAm because of weak electrostatic action between large positive particles of $\text{Al}(\text{OH})_3$ colloids and the ends of chains with negative charge of PAAm in hybrids^[16]. The largest c_k of the sample with particle size of 185 nm $\text{Al}(\text{OH})_3$ colloid is attributed to both the weak electrostatic action and low M_v , *i.e.*, the molecular weight effect which has been mentioned above. The large k values of the sample with small particle size such as 78 nm are due to more nakedness of the $\text{Al}(\text{OH})_3$ colloid particle itself, leading to easy ionization (see Fig. 3b). On the other hand, in the ionic hybrid PAAm, more nakedness of the $\text{Al}(\text{OH})_3$ colloid particle with small particle size is caused by less PAAm chains on the particle of $\text{Al}(\text{OH})_3$ colloid due to less initiators, as compared with the $\text{Al}(\text{OH})_3$ colloid particle with large particle size under the same polymerization conditions.

Influence of Content of $\text{Al}(\text{OH})_3$ Colloid on Conductivity

Figure 4 shows the k versus c curves of the hybrid PAAm with different contents of $\text{Al}(\text{OH})_3$ colloid in the ionic hybrid PAAm (particle size of $\text{Al}(\text{OH})_3$ colloid = 150 nm, $M_v = 6.6 \times 10^6$, 6.53×10^6 and 8.79×10^6 , respectively) in distilled water. The discontinuity phenomenon is also offered. The c_k values decrease with decreasing content of the $\text{Al}(\text{OH})_3$ colloid in the hybrid PAAm because of the increase of the PAAm chain number on the particle of $\text{Al}(\text{OH})_3$ colloid due to the same initiator and less $\text{Al}(\text{OH})_3$ colloid dosage in the polymerization. The inter-chain interaction (or entanglement) increases when the amount of PAAm chains on the particle of $\text{Al}(\text{OH})_3$ colloid increases, thus the hybrid PAAm is difficult to ionize *i.e.*, the c_k values decrease with the decreasing content of the $\text{Al}(\text{OH})_3$ colloid in the hybrid PAAm. Of course, the lowest c_k of the sample with $M_v = 8.79 \times 10^6$, is attributed to both strong inter-chain interaction and high M_v , *i.e.*, molecular weight effect which has been mentioned above. Apparently, the reason for the decrease of k values with decreasing content of $\text{Al}(\text{OH})_3$ colloid in the hybrid PAAm is the same as that of c_k .

Viscosity Study of Hybrid PAAm

Figure 5(a) shows the variation of the η_{sp}/c versus c curve of the ionic hybrid PAAm and pure PAAm with $M_v = 2.98 \times 10^6$, 6.6×10^6 , 7.38×10^6 and 4.81×10^6 , respectively. Figure 5(b) shows the influence of particle size of

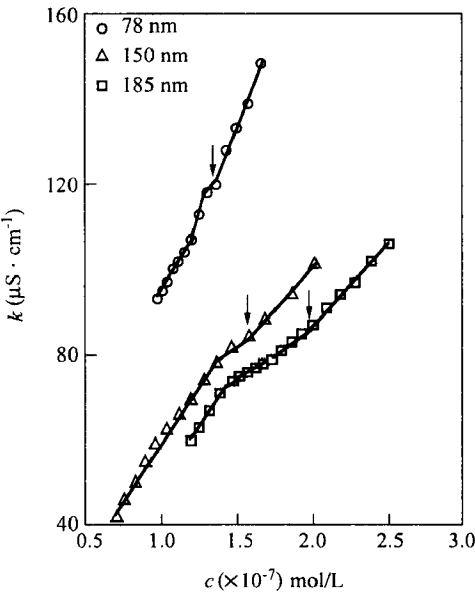


Fig. 3a Variation of k versus c curves of the ionic hybrid PAAm with the particle size of $\text{Al}(\text{OH})_3$ colloid
The content of the $\text{Al}(\text{OH})_3$ colloid in the ionic hybrids is 5.67 wt%; M_v of the samples: 4.41×10^6 , 6.6×10^6 , 6.77×10^6 , respectively from bottom line to the top line

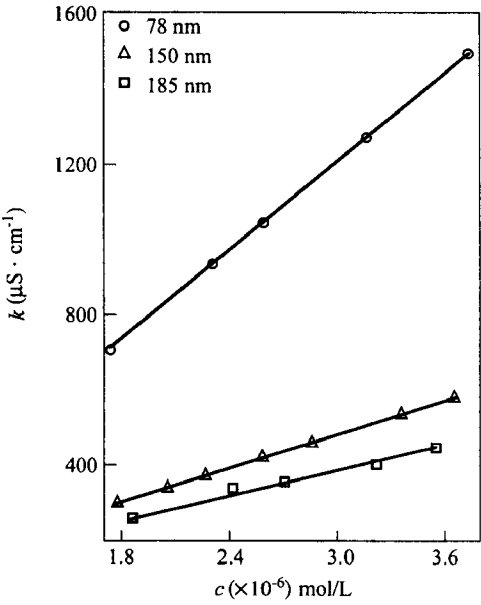


Fig. 3b Variation of k versus c curves of $\text{Al}(\text{OH})_3$ colloid with different particle sizes: 185, 152, 78 nm respectively from bottom line to the top line

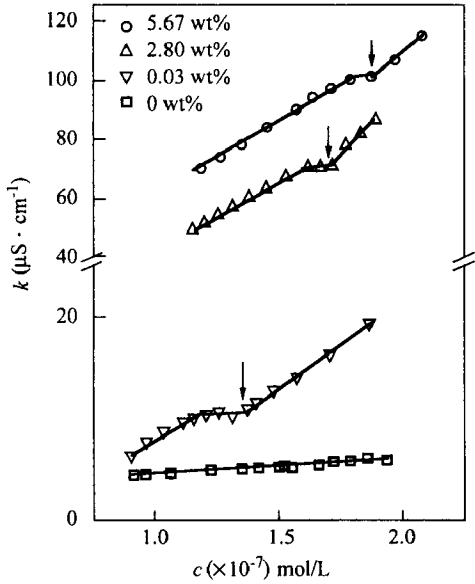


Fig. 4 Variation of k versus c curves of the ionic hybrid PAAm with the content of $\text{Al}(\text{OH})_3$ colloid
The particle size of $\text{Al}(\text{OH})_3$ colloid and M_v of samples: 150 nm, 4.81×10^6 , 8.79×10^6 , 6.53×10^6 and 6.6×10^6 , respectively from bottom line to the top line

$\text{Al}(\text{OH})_3$ colloid, 78 and 150 nm, respectively, on the $\eta_{sp}/c \sim c$ curve of the ionic hybrid PAAm. Figure 5(c) displays the effect of content of $\text{Al}(\text{OH})_3$ colloid (0, 2.8 and 5.67 wt%) on the η_{sp}/c versus c curve of the ionic hybrid PAAm. All the η_{sp}/c versus c curves in Fig. 5 inflect downwards at certain concentration except for pure

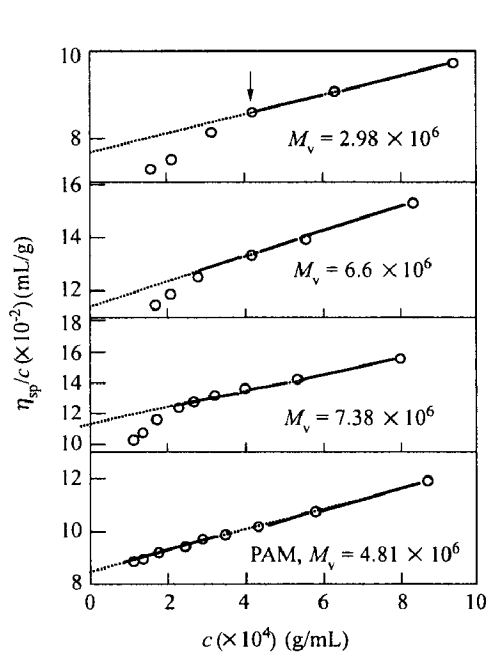


Fig. 5a Variation of downturn phenomenon of the η_{sp}/c versus c curves of the ionic hybrid PAAm and pure PAAm with respect to M_v . The content and the particle size of $\text{Al}(\text{OH})_3$ colloid are 5.67 wt% and 150 nm, respectively.

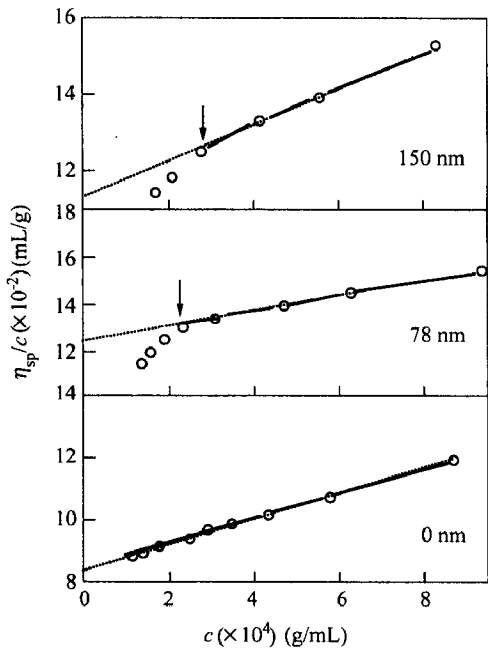


Fig. 5b Variation of downturn phenomenon of the η_{sp}/c versus c curves of the ionic hybrid PAAm with the particle size of $\text{Al}(\text{OH})_3$ colloid: 0, 78 and 150nm. The content of the $\text{Al}(\text{OH})_3$ colloid in the ionic hybrid PAAm: 5.67 wt%; M_v of the samples: 4.81×10^6 , 6.77×10^6 and 6.6×10^6 , respectively from bottom line to the top line

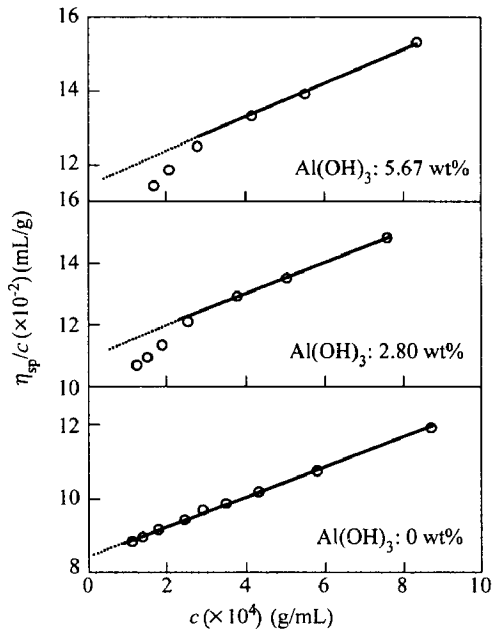


Fig. 5c Variation of downturn phenomenon of the η_{sp}/c versus c curves of the ionic hybrid PAAm with the content of $\text{Al}(\text{OH})_3$ colloid: 0, 2.8, 5.67 wt%. The particle size of the $\text{Al}(\text{OH})_3$ colloid: 150 nm and M_v of samples: 4.81×10^6 , 6.53×10^6 and 6.6×10^6 , respectively from bottom line to the top line

PAAm. If the concentration at the inflection point is denoted as c_d , the c_d value increases with decreasing M_v of the ionic hybrid PAAm and with increasing particle size or content of $\text{Al}(\text{OH})_3$ colloid in the hybrid PAAm with almost the same M_v . Interestingly, the variation of c_d is in good agreement with that of c_k with M_v of the hybrid PAAm and content and particle size of $\text{Al}(\text{OH})_3$ colloid in the hybrid PAAm. Apparently, this result indicates that the ionization of the hybrid PAAm alters the k versus c curve and also affects the η_{sp}/c versus c curve of the hybrid PAAm in distilled water. It leads us to consider that ionization reduces the M_v of the hybrid PAAm, and then depresses the η_{sp}/c value, and then reveals the downturn phenomenon of the η_{sp}/c with decreasing concentration even at high relative viscosity ($\eta_r \geq 1.3$). However, this is opposite to the behavior of ion containing polymer (common ionomer) or polyelectrolyte. An upturn phenomenon of η_{sp}/c of ion containing polymer or polyelectrolyte occurs when their concentrations go down^[17]. This is because the M_v of the ion containing polymer or polyelectrolyte does not change as in their ionization. Instead, the chain coil of ion containing polymer or polyelectrolyte expands due to large electrostatic repelling action through ionization.

CONCLUSIONS

Conductivity behaviors of $\text{Al}(\text{OH})_3$ -acrylamide hybrid polyacrylamide (hybrid PAAm) have been investigated in aqueous solutions. The conductivity discontinuity phenomenon of the conductivity (k) versus concentration (c) curves of the hybrid PAAm was found and it is mainly attributed to the ionization of the hybrid PAAm. The conductivity behavior in aqueous solution is very complicated. With increasing M_v of the hybrid PAAm the incipient concentration (c_k) of the discontinuity phenomenon decreases and the conductivity (k) increases, respectively; with increasing particle size, c_k increases and k decreases respectively; and with increasing content of the $\text{Al}(\text{OH})_3$ colloids in the hybrid PAAm both c_k and k increase.

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