Abstract

The adsorption of hydrophillic polymers on the mercury electrode by tensammetric measurement was compared with the results of turbidity measurement to silver halide grains. It was found experimentally that the results from the both measurements agree well for adsorption character. Therefore, it is considered that the turbidity measurement has close connection to the adsorption character of hydrophillic polymers on silver halide crystals.

§ 1. Introduction

Gelatin has been used for making photographic emulsion as a protective colloid for nearly one hundred years, and is yet still indispensable; the light sensitive silver halide crystals of a photographic emulsion are suspended in gelatin.

One of the most important property of gelatin, utilized in emulsion making, is the excellent protective action for silver halide. For the period of mixing of silver nitrate and alkali halide solutions, gelatin prevents the coaguration and gives very finely divided silver halide crystals, and under suitable conditions, it allows the growth of the crystals.

In the field of photographic chemistry, protective action and the growth of silver halide crystals are mainly investigated by means of turbidity measurements. Evva reported that the turbidity due to a suspension of silver halide particles in water, is proportional to the particle size up to a certain limited value. According to the modified method of Evva, the author reported on the estimation of the protective action of several synthetic polymers by turbidity measurements.

In conclusion, it becomes clear that the behavior of polymers on the growth of silver chloride crystals was largely dependent on the adsorption character of the polymers on the silver chloride crystals.

On the other hand, it is well known that the adsorption character of surface active agents including water soluble polymers is indicated on the tensammetric curve in the a.c. polarography.

Therefore, it seemed interesting to measure the tensammetric data of some polymers and compared them with the characters, which were measured by the turbidity measurements described above.

§ 2. Experimental

1. Material

1-1. Polymers

a) Polyvinyl alcohol used was a product of KOHBUNSHI KAGAKU K.K. “POLYSIZER” mean molecular weight (Mw) of it is 74,800 and degree of saponification is 99%.

b) Polyacrylamide used was a product of American Cyanamide Company “PAM-50”, mean Mw. of it is 490,000, which is measured by Scholton’s method.

c) Polyvinyl pyrrolidone used was a product of General Aniline and Film corporation “PVP” K-30 and K-90, mean Mw. of them is 10,000, 40,000 and 360,000 respectively.
d) Poly (sodium acrylate) used was a product of TOWA GOHSEI Co., Ltd., “Alone-20.”
e) Gelatin used was derived from limed ossein, photographic inert gelatin. This material is manufactured in NIHON Leather Co., Ltd.
f) Soluble starch used was 1st grade of JIS.
g) Acrylamide-acrylic acid copolymers (AM-AA).

These copolymers were prepared by the hydrolysis of PAM-50; calculated amounts of NaOH, just necessary to hydrolyse desired amounts of acrylamide, was added to the polymer solutions, the concentration of which is about 10%. The mixture was refluxed for 1.5 hours at 70°C, and then cooled. The copolymer was precipitated adding methanol to the solution.
h) Acrylamide-1-vinyl-2-methyl imidazole copolymers.

The preparation of this copolymer was performed as follows,
(i) Monomers: The acrylamide used, was a commercial product. 1-vinyl-2-methyl imidazole was obtained from TOHO Rayon Co., Ltd.
(ii) Polymerization method (A): Following two solutions were prepared.
   Solution 1: 50% aqueous monomer solution, containing acrylamide, 1-vinyl-2-methyl imidazole and nitric acid, the latter is equivalent to vinyl imidazole.
   Solution 2: Water containing K₂S₂O₈ as catalyst; the quantity of K₂S₂O₈ corresponds 0.5-1.0 weight % to the above monomers.

   The quantity of water must be so adjusted that the concentration of the resulting polymer is 10-20%.

   Solution 2 was heated to 90°C, and was added to it Solution 1 dropwise with continuous stirring in 30 minutes. After the addition, stirring and heating (90°C) were continued for further 1 h., and then cooled and precipitated with methanol for purification.

   The degree of polymerization is controlled by such conditions as the monomer concentration, temperature, the quantity of catalyst and the rate of addition of monomer etc.

(iii) Polymerization method (B): Definite amounts of acrylamide, 1-vinyl-2-methyl imidazole, nitric acid (equivalent to vinyl imidazole), catalyst, water and a small quantity of isopropanol were mixed together and then heated to 75-80°C with continuous stirring for 2.0 hours. Isopropanol was used for the control of the degree of polymerization.

1-2. The determination of the constitution of copolymers

The determination of constitution of amphoteric polymer was performed by means of pH titration of the Parke and Davis’s method: To 50 ml of sample (polymer) solution, which was deionized by anionic (amberite IRA-400) and cationic (amberite IR-120B) ion exchange resin, was added 5 ml of 2M NaCl and 4 ml of N-HCl. The former was added to maintain the constancy of ionic strength of the sample solution during the titration process. The mixture was titrated with N-NaOH, and the titration value corrected for the blank corresponds to the constitution of ionized groups in copolymer.

1-3. Supporting electrolytic solution

2M HCIO₄ solution was neutralized with NaOH to pH values of 1.5 and 7.0, and then diluted with distilled water to make 1M-perchlorate solution.

2. Apparatus

2-1. Polarograph

Tensammetric curves were obtained with a YANAGIMOTO pen-recording AC-DC polarograph model PA-102.

The dropping mercury electrode used had a rate of mercury flow m of 1.18 mg/sec and drop time t₀ of 4.54 seconds, when measured in air-free 1M sodium perchlorate solution (pH 7.0) at zero volt vs. saturated calomel electrode (S.C.E.) and at 75 cm of height of a mercury reservoir.

The potential of the dropping mercury electrode was referred to the S.C.E. The temperature of the electrolytic solution was maintained at 25°C by means of a water thermostat. The dissolved oxygen in the electrolytic solution was removed by bubbling
pure nitrogen gas through the solution about 15-30 minutes.

For the reduction of the a.c. impedance between the electrode, chemical condenser (capacity 200 μF) was inserted in parallel between S.C.E. and auxiliary electrode (Pt wire).

2-2. pH-Meter

TOA Electronics Ltd., model HM-5A.

§ 3. Results

1. Tensammetric curves of various hydrophillic polymers

The tensammetric curves of various hydrophillic polymers were shown in Fig. 1.

In a series of poly vinyl derivatives having same main chain (—CH₁—CH—)ₙ, if the R functional groups in polymers were different, tensammetric curves were also considerably different. The difference of those curves was considered to be due to the difference of the affinity or adsorption force of the functional groups in polymers on the mercury electrode.

On the other hand, in the polymer having the same functional groups, but different main chain such as polyvinyl alcohol and soluble starch, the difference of adsorption character on the mercury electrode was also observed in the tensammetric curves.

It might be attributed to the difference of the flexibility or solubility of those polymer molecules.

In the present paper, a special emphasise is made on the study of the effect of the functional groups in water soluble vinyl polymer and the effect of main chain on the adsorption character is not reported.

2. The influence of the degree of polymerization of polymer

Figure 2 showed the influence of the degree of polymerization of polyvinyl pyrrolidone (PVP) on the tensammetric character.

It is clearly seen that the adsorption of polymer on mercury electrode becomes weaker with the increase of the degree of of polymerization in the case of PVP, which has strongly adsorbable functional groups, but in the case of polymers having weakly adsorbable functional group, such as poly acrylamide, the degree of polymerization had little or no influence on the adsorption property.

For the explanation of the effect, it is considered that the mobility of polymer molecule will be decreased and steric hindrance of functional groups in polymer molecule at mercury electrode will be increased, when the degree of polymerization of polymer in-
creases. Therefore, the adsorption force of polymer on the mercury electrode will be weakened.

3. The influence of the blending of polymer

A polymer, which is adsorbed strongly to mercury electrode was blended with another polymer, which adsorbed weakly. For example, when poly acrylic acid and poly acryl amide are mixed in the media of pH 1.5, the resulting solution shows the tensammetric curves, very close to that of the strongly adsorbing one (PAA), and the presence of weak one (PAM) had little or no influence. (cf. Fig. 3)

4. The influence of the constitution of copolymer and pH

With electrolytic polymer, the adsorption character is largely dependent on the pH of media, so that most of the measurements were done at pH 1.5 and 7.0.

The influence of pH and constitution of copolymer on the tensammetric curves, which obtained with acryl amide and acrylic acid copolymer, was shown in Figs. 4 and 5.

Figures 4 and 5 show clearly that the adsorption of copolymer on mercury electrode become stronger with the increase of the contents of carboxyl groups in copolymer at pH 1.5 (at the pH, carboxyl group do not almost dissociate, because pKa of carboxyl group in the copolymer is 4.5).

On the contrary, in the case of pH=7, adsorption force to mercury electrode was weakened with the increase of the contents of carboxyl groups in copolymer (in the case, carboxyl groups completely dissociate).

The homopolymer of 1-vinyl-2-methyl imi-
dazole has a little solubility in supporting electrolyte solution, therefore tensammetric curves can not be measured, but if vinylimidazole is copolymerized with acrylamide, the solubility of copolymer for supporting electrolytic solution increases; because acrylamide has a strong hydrophilic property, so that, adsorption measurement by tensammetry become possible.

In the case of copolymer of acrylamide-vinyl imidazole, the dependence of the constitution of copolymer is same to the copolymer of acrylamide and acrylic acid—the adsorption force on mercury electrode become stronger with the increase of the contents of 2-methyl imidazole groups in copolymer—, but the dependence of pH of supporting electrolytic solution on the adsorption character almost disappears.

It may be considered that vinyl imidazole groups adsorb very strongly to mercury electrode, even if, it is ionized form. This can be supposed from that the homopolymer of vinyl imidazole has little solubility for supporting electrolytic solution. Therefore the adsorption force of imidazole groups on mercury electrode would be caused by the Van der waals force.

From the experimental results obtained, it may be considered that the adsorption of polymer on mercury electrode is not caused by the coulomb force between ionized functional groups (dissociated group) and charge of mercury electrode, but by other chemical or physical force (ex, van der waals force etc.).

5. The influence of the preparation methods of copolymers

The polymers, which have same composition, do not always give same adsorption character on mercury electrode or tensammetric curve. Fig. 6 shows the tensammetric curves of copolymers, the composition of which is the same but the method of preparation was different.

Figure 6 shows clearly that the adsorption force on the mercury electrode of the copolymer prepared by the method B was stronger than that by the method A.

This difference is considered to be caused by the variation of distribution or mutual position of functional groups in polymer molecule.

The difference between method A and B can be explained by the variety of the products of monomer reactivity ratio $(r_1r_2)$. The values of $(r_1r_2)$ for the method of A and B were 0.54 and 0.22 respectively, these values were not determined by the usual method, but were calculated from analytical
data of polymers, the polymerization degree were both about 90%. Increase of $r_1r_2$, increases the probability of two imidazole groups occupying adjacent position in polymer having large $r_1r_2$ value, is considered little adsorption efficiency per unit imidazole groupe.

And by the method B, it is supposed that the composition of all polymer molecule are not the same, and some molecules contain relatively high percentage of imidazole groups, and these imidazole rich molecules adsorb strongly to mercury electrode.

§ 4. Discussion

By the comparison of the tensammetric data described above, with the results from the turbidity measurement on silver chloride crystals (2, 6, 7, 8, 9), it may be concluded as follows.

1. Similar characters in the results of both measurements

a) When a polymer, which adsorbs strongly to adsorbate (substrate) is blended with another polymer which adsorbs weakly, the resulting mixture gives adsorption character very close to the former and the presence of the latter shows little or no influence.

b) Copolymer containing strongly adsorbable functional groups and weakly adsorbable one, shows intermediate property between individual homopolymers.

c) When the pH of media is changed, adsorption force on the adsorbate (substrate) of dissociated functional group is weaker than that of the undissociated one.

d) When the copolymers are prepared by the different method of polymerization, their behavior of adsorption on adsorbate is different.

2. Different character in the results of both measurements

a) The order of the strength of adsorption force of several polymers to silver chloride is different to that to the mercury electrode.

b) In the turbidity measurements, the effect of cationic groups in copolymer appears more clearly than that of anionic groups, on the contrary, in the tensammetry the effect of anionic groups predominates.

c) The influence of the degree of polymerization appears more distinctly in tensammetry.

The difference on the method of measurement will mainly be caused by the difference of adsorbate (Hg and AgX) but in the principal parts, the results from the both measurements agree well for adsorption character.

In other words, this facts suggest that the turbidity measurement mainly indicates the adsorption character of water soluble polymer on silver chloride crystals.

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