BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2604—2608 (1970)

The Adsorption of Polyvinyl Pyrrolidone on Silver Iodide Surfaces

Masaaki SUGIURA

7th Division, Government Chemical Industrial Research Institute, Tokyo, 85 Shinshuku, Hiratsuka-shi, Kanagawa

(Received March 7, 1970)

Adsorption isotherms for four kinds of polyvinyl pyrrolidone (PVP), having different molecular weights, on the sol particles and the powder of silver iodide at 25°C were obtained. Further, the adsorption of PVP on the sol particles was investigated by means of the electrophoresis method. All of the PVP materials give approximate adsorption isotherms of the Langmuir type, at least up to the PVP concentration of 0.4 g/*l*. At higher concentrations, the amounts of PVP adsorbed gradually increase with the increase in the PVP concentration. The effect of the molecular weight on the PVP adsorption is not observed except for the lowest-molecular-weight material, which displays a lower adsorption. The tendency for the ζ-potential of the sol particles to increase with an increase in the PVP concentration almost coincides with that of the amount of PVP adsorbed.

In previous works, the present author and coworker have studied the adsorption of several lyophilic polymers (gelatin,[1] polyvinyl alcohol[2] and polyacrylamide[3]) on the sol particles of silver iodide as part of an investigation of the photographic emulsion of synthetic polymers. The adsorption isotherms of these polymer materials at low concentrations are roughly of the Langmuir type. However, considerable differences among the polymer materials in the limiting adsorption or in the ζ-potential for the sol particles are observed, as will be described later.

In this work, polyvinyl pyrrolidone (PVP), as a markedly water-soluble, nonionic polymer, was taken as the adsorbate to silver iodide. By measuring the amounts of PVP adsorbed on the sol particles and the powder of silver iodide and the ζ-potential of the sol particles, the adsorption behavior of PVP on the silver iodide surface could be discussed, and the values obtained were compared with those obtained for the polymers in previous works.[1–3]

Experimental

Materials. As PVP materials, PVP K-90, K-30 and K-15 obtained in the form of powder from the General Aniline & Film Co. and PVP K-60 obtained as a 45% aqueous solution from the Tokyo Kasei Kogyo Co. were used. The PVP materials were purified as follows: PVP was precipitated at room temperature (20—25°C) by the addition of freshly-distilled acetone to a concentrated solution obtained by dissolving PVP in water. The precipitate was again dissolved in small quantities of water, and then this procedure was repeated. The precipitate thus obtained was repeatedly washed with acetone and then vacuum-dried to free it from acetone and water at temperatures up to 100°C. The PVP solutions used for adsorption and electrophoretic experiments were prepared by dissolving the dry polymers in water. The concentrations of the PVP K-90 and K-60 solutions were determined by weighing the polymer films, prepared from 5-m*l* portions of the solutions cast on a stainless steel plate, after they had been vacuum-dried at 100°C for one hour. Those of the PVP K-30 and K-15 solutions were estimated from the weights of the dry polymers added to the water. The molecular weights of the PVP materials after purification were calculated from their intrinsic viscosities by the relationship;[4]

$$[\eta]=6.76\times10^{-2}M^{0.55},$$

where $[\eta]$ is the intrinsic viscosity in m*l*/g, and M, the viscosity-average molecular weight. The molecular weights of PVP K-90, K-60, K-30, and K-15 were 9.3×10^5, 3.0×10^5, 4.0×10^4, and 7.6×10^3 respectively.

Preparation of Silver Iodide Sol. Into the solution obtained by mixing 11 m*l* of a 0.1 M potassium iodide solution and 69 m*l* of water, we vigorously stirred 10 m*l* of a 0.1 M silver nitrate solution. This procedure was repeated six to ten times. All the silver iodide sols prepared in this manner were then combined and transferred into a flask with a 1-*l* capacity. After aging at room temperature for 18—24 hr, the silver iodide sol whose turbidity was in a range to be given below was used for the adsorption or electrophoretic experiments; when the sol was diluted by the addition of water to make the concentration of silver iodide 0.01 mol/*l*, the turbidity of the diluted sol was in the 0.89—1.02 cm^{-1} range. The surface area of the sol particles at a turbidity of 0.94 cm^{-1} was 1.7×10^5 cm^2/g, based on the adsorption of 1,1′-diethyl-2,2′-cyanine iodide with an assumed

---

1) M. Sugiura, *Kogyo Kagaku Zasshi*, **73**, 92 (1970).

2) M. Sugiura and A. Yabe, *ibid.*, in press.

3) A. Yabe and M. Sugiura, *ibid.*, **72**, 2356 (1969).

4) G. B. Levy and H. P. Frank, *J. Polym. Sci.*, **17**, 247 (1955).

molecular area of 43 Å^2.[5] On the basis of this particle size, assuming that the sol particles were spherical, the surface areas for other silver iodide sols were estimated from their turbidities by applying Rayleigh's law. The turbidity measurements were carried out using a Tokyo Koden nephelometer, and the dye-adsorption experiment was done by the method of Suzuki and Ishida.[6]

Preparation of Silver Iodide Powder. A silver iodide powder was prepared in the manner described by Mathai and Ottewill.[7] The surface area determined by the adsorption of the cyanine dye mentioned above was 6.7×10^3 cm^2/g. This dye-adsorption experiment, considering that the dye adsorption was affected by cosolutes, was carried out by suspending the powder in a solution which had the same composition as the solvent of the sol described above. The particle size of this powder, obtained by the dye adsorption, roughly agreed with the results of observation using an electron micrograph.

Adsorption of PVP on Silver Iodide Sol Particles. 45 m*l* of the silver iodide sol were added to 5 m*l* of the PVP solution at 25±0.1°C. The mixture was maintained at this temperature for 1 hr, with occasionally shaking, and then centrifuged at room temperature for 30 min at 15000 g. The PVP concentration of the supernatant solution was determined interferometrically. For this we used a Zeiss interferometer with a 4- or 8-cm cell. The standard solutions used in constructing the calibration curves were prepared by mixing 5-m*l* portions of PVP solutions of known concentrations and a 45-m*l* portion of the supernatant solution obtained by centrifuging the silver iodide sol used for PVP adsorption.

The time dependence of the PVP adsorption was not recognized at times longer than 15 min, as is shown by the four examples in Fig. 1. The silver iodide particles dispersed in the sols were not precipitated in the presence of PVP during the adsorption process. However, since the particles were aggregated in the presence of PVP in the low concentration range, the aggregation was confirmed by the turbidity measurements.

Adsorption of PVP on Silver Iodide Powder. A 5-g portion of silver iodide powder was added to 50 m*l* of the PVP solution in a conical flask with a 100-m*l* capacity. After sealing, the contents were agitated with a magnetic stirrer for 1 hr in a thermostatted chamber at 25±1°C, and then centrifuged at room temperature for 15 min at 9000 g. The PVP concentration of the supernatant solution was determined interferometrically, as has been described above. In these measurements, since the adsorption equilibrium was almost established for 30 min, as is shown in Fig. 1, one hour was chosen as the time for the equilibration of PVP with the powder.

Electrophoretic Measurements. The electrophoretic measurements of the sol particles were carried out at 25±1°C using an ultramicroelectrophoresis apparatus described previously.[1] The sols used for these measurements were prepared as follows: a silver iodide sol having the same composition as the sol used for the adsorption experiment was diluted five-fold by a supernatant solution obtained by centrifuging the same sol, and then 45 m*l* of the diluted sol were added to 5 m*l* of the PVP solution. The ζ-potential of the sol particles was calculated using Henry's equation:[8]

$$\zeta=4\pi\eta u/Df(\kappa a), \qquad (2)$$

where η is the solvent viscosity; u, the mobility of the particle; D, the dielectric constant of the medium, and $f(\kappa a)$, the Henry factor, in which κ is the Debye-Hückel function, and a, the particle radius; the η values were obtained from the viscosity measurements of solutions with the same compositions as the solvents.

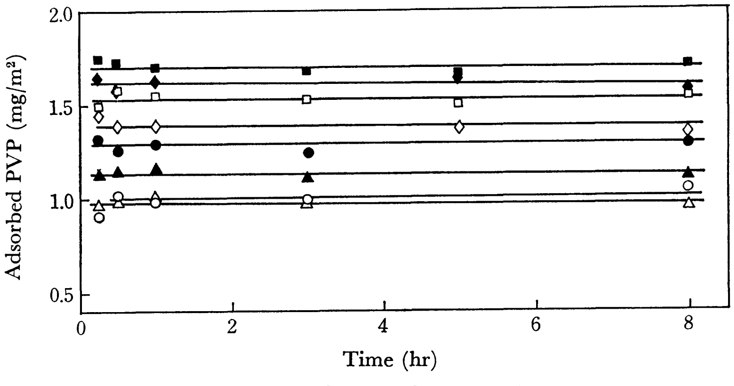

Fig. 1. Time dependence of PVP adsorption. Adsorption of PVP on silver iodide sol particles from the solutions of added concentration.
□ K-90 8.73×10^{-2} g/*l*, ■ K-90 4.37×10^{-1} g/*l*,
◇ K-15 1.73×10^{-1} g/*l*, ◆ K-15 8.64×10^{-1} g/*l*
Adsorption of PVP on silver iodide powder from the solutions of added concentration.
○ K-90 8.73×10^{-2} g/*l*, ● K-90 4.37×10^{-1} g/*l*,
△ K-15 1.73×10^{-1} g/*l*, ▲ K-15 8.64×10^{-1} g/*l*

---

5) R. Peacock and A. M. Kragh, *J. Photogr. Sci.*, **16**, 229 (1968).

6) S. Suzuki and T. Ishida, *J. Soc. Sci. Phot. Jap*, **25**, 30 (1962).

7) K. G. Mathai and R. H. Ottewill, *Trans. Faraday Soc.*, **62**, 750 (1966).

8) D. C. Henry, *Proc. Roy. Soc., Ser. A*, **133**, 106 (1931).

Results

Adsorption of PVP on Silver Iodide Sol Particles. The adsorption isotherms for PVP K-90, K-60, K-30, and K-15 on the sol particles are given in Fig. 2, plotted as mg PVP adsorbed per m^2 of the surface against the PVP concentration. There is no significant difference in the amounts adsorbed among PVP K-90, K-60, and K-30; PVP K-15, which has the lowest molecular weight, alone gives a lower adsorption.

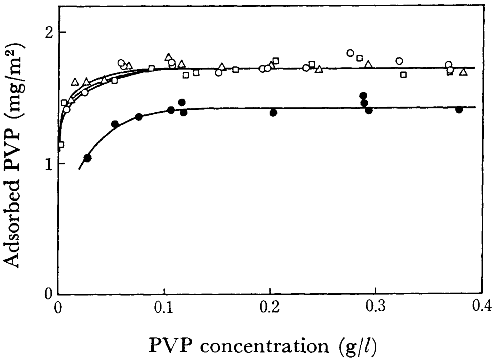

Fig. 2. Adsorption isotherms for PVP on silver iodide particles.
○ K-90, △ K-60, □ K-30, ● K-15

The turbidity-*versus*-PVP-concentration curves for silver iodide sols in the presence of PVP K-90, K-60, K-30, and K-15 are given in Fig. 3; the sols used for these measurements were prepared by adding the silver iodide sols, which gave a turbidity of 0.94 cm^{-1} in the absence of PVP, to various PVP solutions; then, after an hour, the turbidities were measured. The sol particles were aggregated in the presence of a PVP of a high molecular weight, such as PVP K-90 or K-60.

Adsorption of PVP on Silver Iodide Powder. The adsorption isotherms for PVP K-90, K-60, K-30, and K-15 on the silver iodide powder up to the PVP concentrations of 0.4 g/*l* and 4.5 g/*l* are given in Fig. 4 and Fig. 5 respectively. These isotherms in low PVP concentrations show tendencies similar to those shown in Fig. 2. At higher

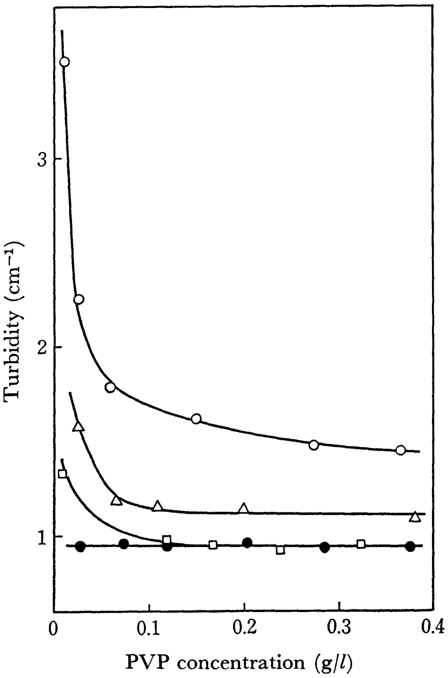

Fig. 3. Turbidity *vs.* PVP concentration curves for silver iodide sols in the presence of PVP.
○ K-90, △ K-60, □ K-30, ● K-15

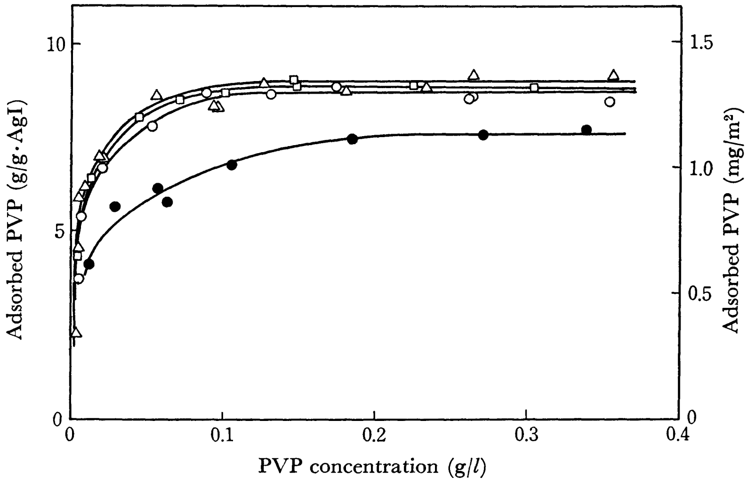

Fig. 4. Adsorption isotherms for PVP on silver iodide powder up to PVP concentration of 0.4 g/*l*.
○ K-90, △ K-60, □ K-30, ● K-15

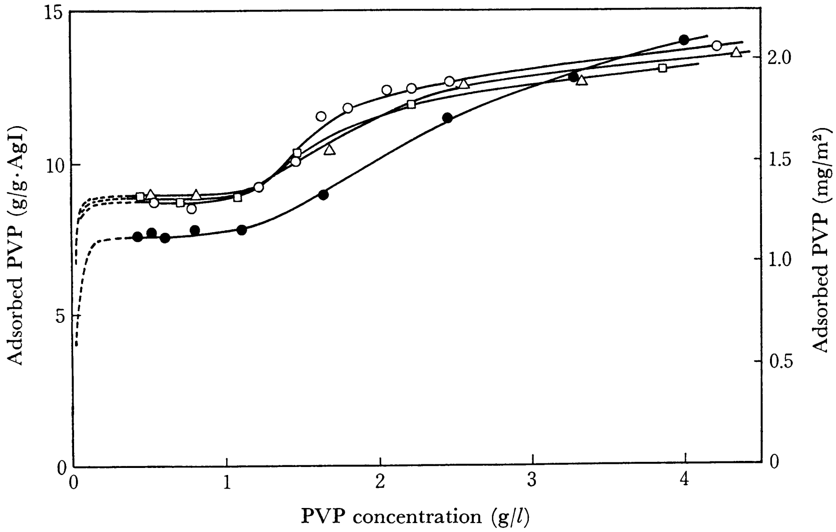

Fig. 5. Adsorption isotherms for PVP on silver iodide powder up to PVP concentration of 4.5 g/*l*.
○ K-90, △ K-60, □ K-30, ● K-15

PVP concentrations, the amounts of PVP adsorbed gradually increase with an increase in the PVP concentration.

ζ-potential of Sol Particles. The ζ-potential-*versus*-PVP-concentration curves for silver iodide sols in the presence of PVP K-90, K-60, K-30, and K-15 are given in Fig. 6; the free PVP concentrations were estimated from the relation between the added element and the equilibrium concentration of the PVP obtained from the measurements of the PVP adsorption on the sol particles, assuming that the amounts of PVP adsorbed per unit of the surface area of the particles in the diluted sols were equal to those in the concentrated sols. The ζ-potential of the sol particles in the absence of PVP was -75.6 mV. The tendency for the ζ-potentials to increase with an increase in the PVP concentration coincides with that of the amounts of PVP adsorbed.

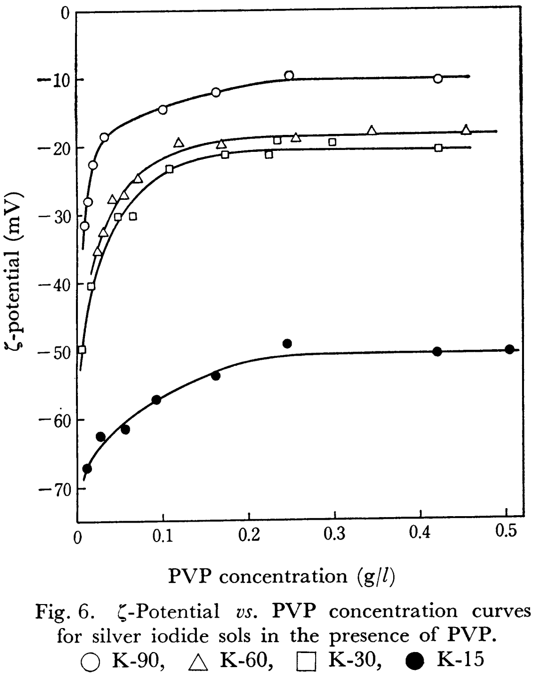

Fig. 6. ζ-Potential *vs*. PVP concentration curves for silver iodide sols in the presence of PVP.
○ K-90, △ K-60, □ K-30, ● K-15

Discussion

The adsorption isotherms and the turbidity curves for PVP in the low-concentration region are similar to those for polyvinyl alcohol and polyacrylamide, both nonionic, lyophilic polymers, obtained in previous works.[2,3] It can be considered that the plateaux of the isotherms in Fig. 2 or Fig. 4 are suitable for the monolayer saturation of PVP, since the ζ-potential curves, suggesting the coverages of the silver-iodide surfaces, approach constant values at the PVP concentrations reaching the plateaux. At higher concentrations of PVP, the increase in the isotherms, therefore, intimates that the adsorption extends to two or more molecular layers. In fact, in all cases considerable amounts of PVP were confirmed to be adsorbed at high PVP concentrations, up to about 30 g/*l*, though their exact values could not be obtained because of the difficulty of measuring the slight difference between the added element and the equilibrium concentration of PVP.

The difference in the amount of PVP adsorbed per unit of surface area between the sol particles and the powder, presented in Fig. 2 and Fig. 4, is mainly caused by a disagreement between the surface

TABLE 1. LIMITING ADSORPTION AND ζ-POTENTIAL FOR VARIOUS POLYMER MATERIALS ON SILVER IODIDE SOL PARTICLES, AND VALUES OF ν

Polymer	Molecular weight	Limiting adsorption (mg/m²)	Limiting ζ-potential (mV)	ν**
PVP	9.3×10^5(K-90)	1.7	−10	1.2
	3.0×10^5(K-60)	1.7	−18	1.0
	4.0×10^4(K-30)	1.7	−21	1.0
	7.6×10^3(K-15)	1.4	−51	1.0
Gelatin	1.1×10^5 (pH 6.0 —6.5)	6.0	−11	1.5
	8.8×10^4	4.8	−13	1.2
	7.3×10^4	4.3	−14	1.0
	6.1×10^4	4.0	−13	1.0
	8.8×10^4(pH 4.7)	6.0	0	1.0
	8.8×10^4(pH 3.6)	4.0	+12	3.0
Polyvinyl alcohol	1.2×10^5(99.4)*	1.95	− 6	1.5
	6.4×10^4(99.4)*	1.9	− 8	1.5
	2.9×10^4(99.4)*	1.9	− 9	1.45
	1.7×10^4(99.4)*	1.9	−12	1.3
	7.7×10^4(98.8)*	1.9	− 7	1.5
	7.7×10^4(96.5)*	1.95	− 6	1.5
	7.7×10^4(94.4)*	2.2	− 6	1.5
	7.7×10^4(92.3)*	2.75	− 7	1.5
	7.7×10^4(90.6)*	3.1	− 7	1.5
Polyacrylamide	7.1×10^5	3.6	− 3	1.0
	2.2×10^5	3.4	− 6	1.0
	8.9×10^4	2.4	−13	1.0
	5.2×10^4	1.5	−16	1.0

* % hydrolysis

** The values for PVP were calculated from the isotherms in Fig. 4 and for gelatin from those obtained for ten-fold diluted sols.

area required for PVP adsorption and that derived from the cyanine dye adsorption, except for the difference in the adsorption behaviour of PVP molecules at the surfaces; the low ionic strength in the solvent tends to decrease the adsorption. In this regard, further investigation is necessary.

The values of the limiting adsorption and the ζ-potential for PVP on the sol particles at monolayer saturation are listed in Table 1 and compared with those obtained for gelatin,[1] polyvinyl alcohol[2] and polyacrylamide[3] in previous works; the sols used all contained the same quantity of silver iodide per unit of volume, and the surface areas of the sol particles, to facilitate comparison, were recalculated from the turbidities of the sols in the absence of the polymers by applying Rayleigh's law on the basis of the particle size of the sols used for PVP. These values for PVP are smaller than those for the other polymers. This indicates that the surfaces of the silver iodide particles were more loosely covered with PVP molecules. On the other hand, as has been shown in previous paper, the power of PVP to protect gold sol against an electrolyte is stronger than that of polyvinyl alcohol and only slightly inferior to that of gelatin.[9,10] Therefore, it may be considered that PVP molecules, in consequence of their orientation, form a more stable hydration shell around silver iodide particles than those of polyvinyl alcohol.

Table 1 also includes the parameters, ν, estimated from the Frisch-Simha-Eirich[11] (FSE) equation:

$$\theta/\nu(1-\theta)^{\nu}=KC \qquad (3)$$

where θ is the surface converge; C, the equilibrium concentration of the polymer, and K, a constant; θ is replaced by a/a_∞ where a is the amount of polymer adsorbed at the concentration, C, and where a_∞ is the limiting adsorption. The ν parameter does not represent the number of anchor segments adsorbed per polymer chain, as has been described by Frisch *et al*, but only the deviation from the Langmuir form on the polymer adsorption, as has been pointed out by Curme and Natale.[12] From the values of ν, PVP also follows roughly the Langmuir-type adsorption in the low-concentration region, and the PVP molecules appear to be adsorbed from an aqueous solution on the silver-iodide surfaces without any remarkable transfiguration.

---

[9] M. Sugiura and E. Fujii, *Kogyo Kagaku Zasshi*, **67**, 268 (1964).

[10] E. Fujii and M. Sugiura, *ibid.*, **65**, 1609 (1962).

[11] H. L. Frisch, M. Y. Hellman and J. L. Lundberg, *J. Polym. Sci.*, **38**, 441 (1959).

[12] H. G. Curme and C. C. Natale, *J. Phys. Chem.*, **68**, 3009 (1964).