

VISCOSITY AND ELECTROVISCIOUS EFFECT OF THE AgI SOL. I. INFLUENCE OF THE VELOCITY GRADIENT AND OF AGING OF THE SOL.

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INTRODUCTION

Although the relation between viscosity and the concentration of macromolecular solutions has already been investigated extensively and successfully, this subject causes greater difficulties with hydrophobic sols, and the small amount of experimental material can only very partly be fitted into the picture (1).

The Einstein (2) relation

$$\eta_{\text{rel}} = 1 + 2.5 \varphi \quad [1]$$

was derived for very dilute suspensions of rigid, spherical uncharged particles. It has been extended to higher concentrations by different investigators, usually by adding a term in φ^2 , the coefficient of which, unfortunately, is given differently by every investigator, varying between 2.5 and 75.

As our investigation is carried out with roughly spherical particles, the influence of deviating shapes of the particles will not be considered here.

The influence of the charge of the particles was considered by Smoluchowski (3) who published in 1916 his equation on the so-called electroviscous effect:

$$\eta_{\text{rel}} = 1 + 2.5 \varphi \left[1 + \frac{1}{\sigma \eta_0 a^2} \left(\frac{\epsilon \zeta}{2\pi} \right)^2 \right] \quad [2]$$

In Eqs. [1] and [2] η_{rel} is the relative viscosity of the suspension; φ , the volume fraction of suspended particles; σ , the specific conductance; η_0 , the viscosity; ϵ , the dielectric constant of the dispersion medium; a , the radius of the particles, and ζ , the potential of the double layer at the slipping plane between particles and liquid. A derivation of this equation was given by Krasny-Ergen (4), who found a slightly deviating numerical factor.

Booth (5) recently published a theory about the electroviscous effect, arriving at a much smaller correction term

$$\eta_{\text{rel}} = 1 + 2.5 \varphi \left[1 + q^* \left(\frac{e\xi}{kT} \right)^2 (1 + \kappa a)^2 Z(\kappa a) + \dots \right] \quad [3]$$

with

$$q^* = \frac{\epsilon k T \sum n_i z_i^2 \rho_i}{\eta_0 e^2 \sum n_i z_i^2} \quad \text{and} \quad \kappa^2 = \frac{4\pi e^2 \sum n_i z_i^2}{\epsilon k T}$$

in which equation e is the elementary charge; n_i the number of ions, i , per unit volume; z_i the valency, and ρ_i the frictional constant of the ion i ; k Boltzmann's constant; and Z a certain function of κa .

The equations of both Smoluchowski and Booth are restricted to very dilute suspensions. Smoluchowski's equation is moreover restricted to thin double layers, that is to relatively high concentrations of electrolytes, whereas Booth's equation applies to any thickness of the double layer.

The equations for the electroviscous effect were only tested in a few cases, from which it appeared that the effect found was much smaller than that predicted by the equation of Smoluchowski (5,6).

The object of the present investigation was to examine experimentally the electroviscous effect at different sol concentrations with a well-defined hydrophobic sol. The AgI sol was chosen, which has been extensively studied by Kruyt and his co-workers.

AGING OF THE AgI SOL

A fresh silver iodide sol, prepared (7,8) by mixing solutions of AgNO_3 and KI (with a slight excess of KI), followed by electro dialysis and elec-

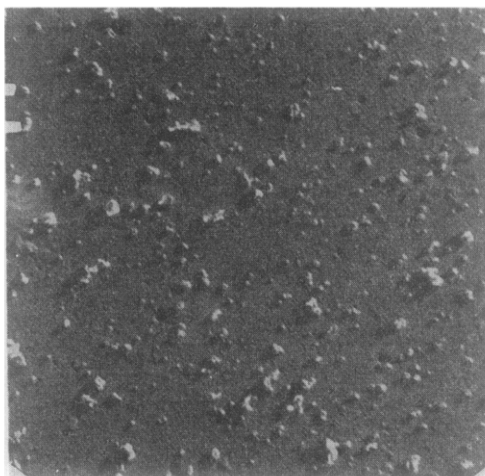
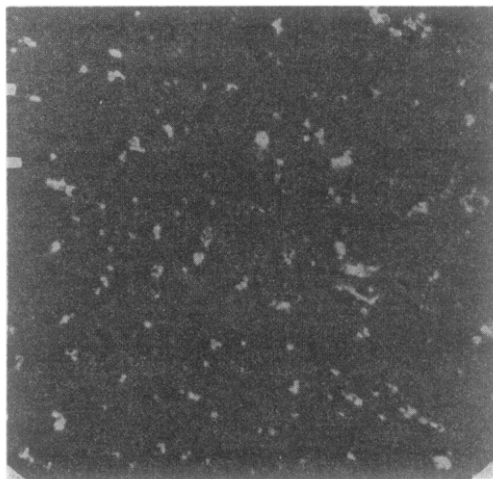


FIG. 1. (a) Fresh AgI sol. Pt-shadowed. 1:10,000.



(b) Aged AgI sol. Pt-shadowed. 1:10,000.

trodecantation, shows aging phenomena as, e.g., an increase in conductivity and in the activity of I^- ions (9). The viscosity also changes by this aging. This decrease in viscosity may, in principle, have several causes: (a) change in form of the particles; (b) change in size of the particles owing to recrystallization or slow flocculation; and (c) liberation of electrolyte.

The increase in the conductivity and increase in the concentration of I^- ions indicate that case (c) actually occurs.

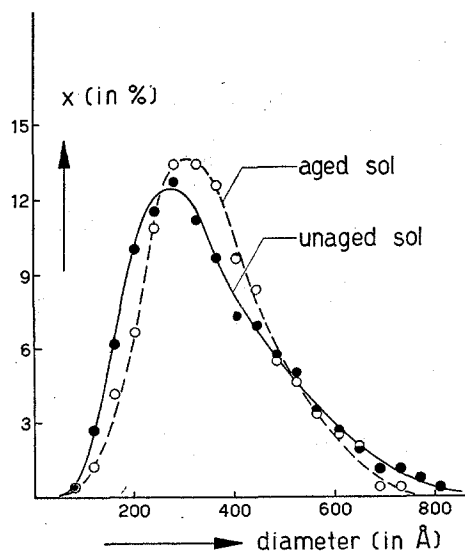


FIG. 2. Distribution of diameters of particles of a fresh and an aged AgI sol.

Taking into account the preparation of the sol in which the *gegenions* have been exchanged against H^+ ions by the electro dialysis, liberation of occluded KNO_3 and of adsorbed HI can be expected.

In order to test how far one or the other of the above-mentioned factors plays a part, an electron micrograph of an unaged sol was compared with one of the same sol that had been aged by heating for 24 hr. at $85^\circ C$. (see Figs. 1a and b, respectively).

On the basis of some pictures made at smaller magnifications, the distribution curves of the diameters for the two sols were determined (see Fig. 2). It is clear that from these pictures hardly any difference can

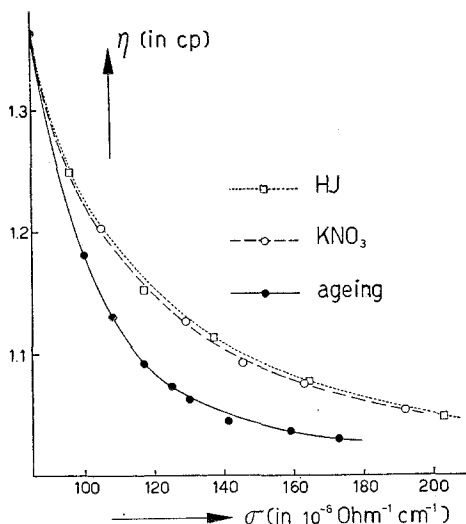


FIG. 3. Relation between viscosity and specific conductivity of an AgI sol. $\varphi = 2.33\%$.

be found between the aged and the unaged sol. Moreover, it appears from the length of the shadows (the particles have been shadowed with platinum at an angle $\tan^{-1} 4$) that the particles are nearly spherical.

In order to examine how far the liberated electrolyte may explain the change in viscosity, a $0.06 N KNO_3$ solution was added dropwise to a portion of an unaged sol ($\varphi = 2.33\%$) and the viscosity and the specific conductance were measured. The same was done with another part of this sol and a $0.015 N HI$ solution. The influence of those additions on the sol concentration φ was negligible.

Figure 3 shows the viscosity as a function of the conductivity. These curves were compared with a similar curve of the aging AgI sol. The aging was performed at $45^\circ C$.; the measurements were made, however, at 25° . The last point was measured 500 hr. after the starting point. The specific resistance as well as the viscosity decreased regularly.

TABLE I
Data for Ostwald Viscometers Used

No.	Viscometer constant, k	Mean gradient of velocity for water of 25°C.	Diameter of the capillary, $\frac{HdgR}{2R}$	Time of efflux for water of 25°C.
		$\left(\frac{dv}{dr}\right)_{av} = \frac{HdgR}{3\eta l}$		
		sec. ⁻¹	cm.	sec.
I	0.002656	700	0.038	338.2
II	0.01176	1000	0.055	76.9
III ^a	ca. 0.00665	ca. 900	0.050	ca. 135
IV	0.00775	900	0.050	116.3
V ^a	ca. 0.00692	ca. 900	0.050	ca. 130

^a No exact values are given for viscometers III and V, as the latter had to be repaired between times. They were fairly equal to viscometer IV. After each reparation the viscometer was calibrated anew.

If we compare the three curves we see that the viscosity decreases more rapidly than might be expected on the basis of the conductivity and the KNO₃ and HI curves. So our conclusion must be that the liberation of electrolyte is, in fact, the most important, but not the only cause of the decrease in viscosity. In this case we think of a perfecting of the AgI crystals which, though not growing into larger, do grow into more compact particles and thus might cause a decrease of the viscosity.

TABLE II
(a) Electrolyte: HNO₃ 39.0 mmoles/l. + HI 0.035 mmole/l.

vol. %	Viscometer									
	I		II		III		IV		V	
	η	K	η	K	η	K	η	K	η	K
0.476	0.9142	4.41	0.9120	3.89	0.9130	4.14	0.9126	4.05	0.9135	4.23
1.09	0.9340	3.95	0.9310	3.64	0.9338	3.94	0.9311	3.65	0.9331	3.86
2.11	0.9672	3.80	0.9648	3.67	0.9651	3.68	0.9650	3.68	0.9658	3.73
2.95	1.0038	4.10	0.9953	3.78	0.9965	3.83	0.9934	3.71	0.9973	3.87
4.87	1.0743	4.10	1.0676	3.95	1.0685	3.97	1.0667	3.94	1.0686	3.97

(b) Electrolyte: HI 0.035 mmole/l.

0.411	0.9099	4.41	0.9088	4.11	0.9069	3.60	0.9071	3.66	—	—
0.797	0.9270	4.68	0.9245	4.33	0.9248	4.37	0.9256	4.46	0.9245	4.33
1.58	0.9668	5.18	0.9615	4.80	0.9665	5.16	0.9661	5.12	0.9664	5.15
2.99	1.1089	8.05	1.0915	7.40	1.1016	7.78	1.1007	7.74	1.0994	7.70
6.37	1.9330	18.26	1.8516	16.82	—	—	1.8834	17.40	1.8934	17.54

INFLUENCE OF THE RATE OF SHEAR ON THE VISCOSITY OF AgI SOLS

The viscosity measurements were carried out in a number of Ostwald viscometers all having the same outward dimensions but different capillary diameters. The data for the viscometers used have been collected in Table I.

All viscosities have been determined at $25 \pm 0.01^\circ\text{C}$.

The kinematic viscosity, ν , was calculated in centistokes, according to

$$\nu = \frac{\eta}{d} = kt - \frac{0.6}{t},$$

in which t is the time of efflux, and d the density. The factor 0.6 has been derived from Sporkel's work (10).

In order to test whether the AgI sol behaves as a Newtonian liquid, viscosity measurements were carried out on two series of sol concentrations in all five viscometers, the one series containing considerable electrolyte, the other one only a small amount. The aqueous solutions in which the AgI was suspended contained only HNO_3 and HI, while in both cases the p_1 ¹ amounted to 4.6. The viscosity of each sol was calculated in centipoises and from it the value of $K = (\eta_{\text{rel}} - 1)/\phi$. The results have been recapitulated in Tables IIa and b. They show that with a higher electrolyte concentration (Table IIa) the effect of the time of efflux on viscosity is very slight. For the low electrolyte concentration, on the other hand, and with the higher sol concentrations, the viscosity is clearly dependent on the time of efflux. Evidently, the deviation from Newtonian behavior increases with increasing interaction between the double layers, and the viscosity increases with decreasing rate of shear.

The flow pattern in the capillary obeys the equation

$$\frac{1}{r} \frac{dv}{dr} = - \frac{Hdg}{2l\eta}$$

in which g is the acceleration of gravity. For all our viscometers H/l has the same value. Therefore, for one definite sol the profile of flow is given by

$$\frac{1}{r} \frac{dv}{dr} = - \frac{\text{const.}}{\eta}$$

where the constant is independent of the viscometer used.

If, as a first approximation, η is also taken as constant, then the mean gradient will be proportional to the radius of the capillary. Extrapolation to a velocity gradient $\frac{dv_{\text{av}}}{dr} = \text{zero}$, is consequently obtained by extrapolating to a capillary radius $R = 0$. In Fig. 4 the values of K obtained for

¹ p_1 = negative logarithm of concentration of I^- ions.

the viscometers I, II, and IV in the last three rows of Table IIb have therefore been plotted against R .

It is true that the observations do not admit accurate extrapolation to $R = 0$, but the points indicated do show that the influence of the rate of shear on the value of K is not very large. Qualitatively, the effect of the sol concentration and the electrolyte concentration will therefore not be different from the extrapolated value, if measured at a finite rate of shear.

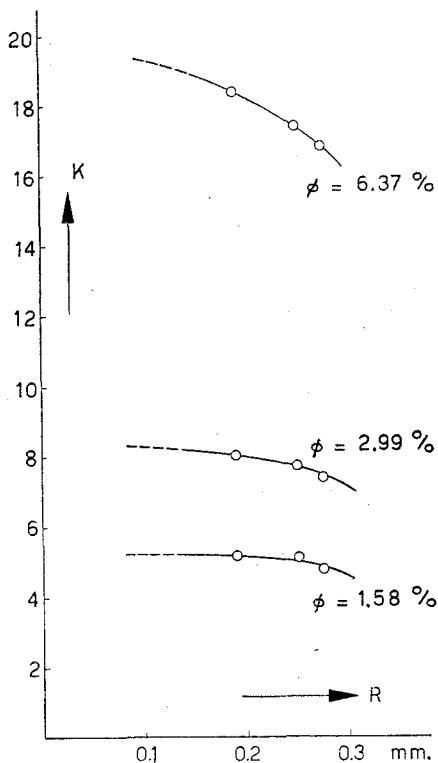


Fig. 4. Dependence of K on the radius of the capillary of the viscometer (\sim rate of shear).

In order to restrict the number of measurements, we continued our investigation [see next paper (11)] with viscometers III, IV, and V, thus working with an average gradient

$$\left(\frac{dv}{dr}\right)_{av} = \frac{HdgR}{3l\eta}$$

or of $8/\eta$, that is of 500–1000/sec.

For details on the preparation of the AgI sols we refer to our second paper (11).

SUMMARY

It was shown that the change of the viscosity of silver iodide sols during aging was mainly, but not exclusively, caused by the liberation of electrolytes.

The viscosity of AgI sols was shown to decrease with increasing rate of shear, the more so as the concentration of the sol was higher and that of the electrolytes lower. For the investigation of the influence of these concentrations on the viscosity, a rate of shear of 500–1000/sec. was considered sufficiently low, and extrapolation to zero rate of shear was deemed unnecessary.

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