

VISCOSITY AND ELECTROVISCIOUS EFFECT OF THE AgI SOL. II. INFLUENCE OF THE CONCENTRATION OF AgI AND OF ELECTROLYTE ON THE VISCOSITY

G. J. Harmsen, J. van Schooten and J. Th. G. Overbeek

van't Hoff Laboratory, University of Utrecht, Utrecht, Netherlands

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INTRODUCTION

In our previous paper (1) we showed that the AgI sol does not entirely behave as a Newtonian liquid. In order to be able to continue the investigation of the electroviscous effect on a comparative basis, observations were made in viscometers of nearly identical construction, with an average velocity gradient of about 1000/sec. for water of 25°.

It was also shown that the AgI sol, when aging, exhibits a decrease in viscosity, which can be explained for the greater part by liberation of electrolyte.

In this paper the electroviscous effect will be further investigated. On theoretical grounds it is expected to be dependent on the structure of the electrical double layer. This structure is determined by the concentration of the potential-determining ions, i.e. the I⁻ ions, and by the concentrations of the neutral electrolyte determining the quantity $1/\kappa$, thus, the dimensions of the double layer.

The influence of the latter being our main point of interest, we always took care to have one and the same p_I in our sols.

EXPERIMENTAL

Preparation of the Sols

The AgI sol was prepared in portions of 800 ml. by adding a solution of 50 mmoles of AgNO₃ in 400 ml. water to a solution of 55 mmoles KI in 400 ml. water under continuous agitation. By electro dialysis the KNO₃ formed and the excess KI were removed (2). At the same time the K⁺ *gegenions* are exchanged against H⁺ ions, so that finally a so-called acid sol remains that can be represented schematically as [AgI] I⁻ H⁺. This sol is concentrated by electrodecantation, after which it is aged by heating it for 24 hr. at 85°C. After the aging the liberated electrolytes are removed by electro dialysis and electrodecantation. In this way an aged AgI sol was obtained with a concentration of ca. 1800 mmoles AgI/l., which showed no more change in viscosity with time.

From this sol eight series of 7 to 8 sol-concentrations, varying from 5 to 1800 mmoles AgI/l. were prepared. Each series was dialyzed against an HNO₃ solution of a certain concentration. Moreover, care was taken, by adding HI, that all these electrolyte solutions at the termination of the dialysis had a $p_I = 4.6$. By this method we obtained that

TABLE I

Composition of Equilibrium Solution

No.	C_{H^+} mg. ion/l.	Thick- ness of double layer, $1/\kappa$ A.	Conduc- tivity, σ $\times 10^6$ mho/cm.	Viscosity, η_0 centipoise
1	0.035	500	19	0.8937
2	0.12	278	55	0.8937
3	0.49	138	200	0.8937
4	2.3	64	1200	0.8938
5	8.2	34	3200	0.8942
6	15.0	25	5700	0.8943
7	25.6	19	9500	0.8949
8	39.0	16	14400	0.8954

each series consisted of a number of perfectly comparable sols of different sol concentrations, while moreover the properties of the dispersion medium like electrolyte concentrations, conductivity and p_I could be measured without running the risk of complications caused by the presence of sol particles (3).

Next, the kinematic viscosity of each of the sols was measured in viscometers (1) III, IV, and V at 25°C., and from these results the average was taken. The AgI content was determined by evaporation and weighing. The density of the sol, necessary in the

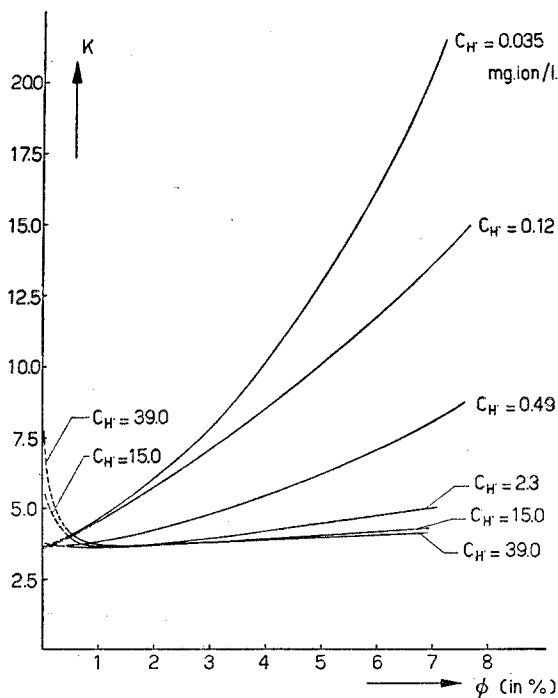


FIG. 1. The value of $K = \eta_{\text{spec}}/\phi$ for the AgI sol with different HNO_3 concentrations as a function of the volume fraction ϕ .

calculation of the dynamic viscosity, η , was calculated from the AgI content and the densities of the equilibrium liquid and of the solid AgI. The correctness of the density thus found was confirmed by some pycnometric determinations.

From the viscosity determinations and the volume fraction φ , the value of $K = (\eta_{rel} - 1)/\varphi$ was calculated.

RESULTS

Measurements

The data obtained have been collected in Tables I and II and are represented graphically in Figs. 1 and 2. Table I gives the composition of the eight equilibrium liquids. Tables II-1 to II-8 give, each for a different equilibrium liquid, the corresponding values of the volume fraction φ , the viscosity η , and the value of K .

Figure 1 shows how K changes as a function of sol concentration and Fig. 2 how it depends on the thickness of the double layer $1/\kappa$.

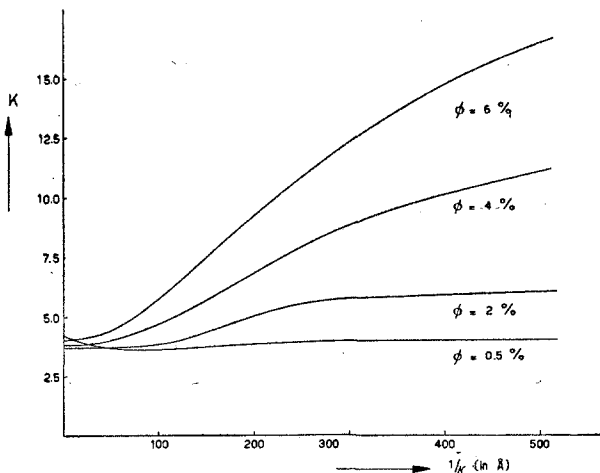


FIG. 2. Relation between $K = \eta_{spec}/\varphi$ and thickness of double layer, $1/\kappa$.

Accuracy of the Measurements

It appeared that for the lower sol concentrations ($\varphi < 1\%$) the standard deviation of the value of η , averaged from three measurements was about 0.05%. The accuracy of K was of course much smaller. The standard deviation was 20% and higher for $\varphi \leq 0.1\%$, 5–10% for $\varphi \sim 0.2\%$, and reached only 1–2% when $\varphi > 1\%$. For the greater values of φ somewhat larger deviations in η occurred owing probably to deposition of AgI in the viscometers. But even the largest errors in η , which are of the order of 0.2%, do not give rise to deviations in K of more than 1%.

As for the effect of the non-Newtonian behavior of the sols on the systematic error in the measurements we refer to our first paper (1).

TABLE II

Relation between Volume Fraction φ ,^a Viscosity η ,^b and K

II-1			II-2			II-3		
$C_{H^+}=0.035$			$C_{H^+}=0.12$			$C_{H^+}=0.49$		
φ	η	K	φ	η	K	φ	η	K
0.107	0.896 ₂	2. ₆	0.111	0.896 ₃	2. ₇	0.095	0.897 ₁	4. ₀
0.209	0.901 ₀	3. ₉	0.215	0.901 ₄	4. ₀	0.198	0.899 ₀	3. ₀
0.411	0.907 ₀	3.6 ₃	0.418	0.908 ₄	3. ₉	0.403	0.906 ₉	3. ₇
0.797	0.925 ₀	4.3 ₉	0.830	0.926 ₃	4.4 ₄	0.831	0.92 ₁	3. ₇
1.58	0.966 ₃	5.1 ₄	1.61	0.96 ₃	5.1 ₃	1.68	0.95 ₆	4.1 ₇
2.99	1.10 ₁	7.7 ₄	4.85	1.31 ₉	9.8 ₂	3.34	1.034 ₅	4.7 ₂
6.37	1.88 ₉	17.4 ₇	7.08	1.76 ₁	13.7 ₀	4.82	1.152 ₇	6.0 ₁
						7.38	1.45 ₃	8.4 ₇
II-4			II-5			II-6		
$C_{H^+}=2.3$			$C_{H^+}=8.2$			$C_{H^+}=15.0$		
φ	η	K	φ	η	K	φ	η	K
0.101	0.897 ₅	4. ₁	0.160	0.899 ₁	3. ₄	0.075	0.898 ₁	5. ₆
0.206	0.899 ₉	3. ₃	0.324	0.904 ₇	3. ₆	0.162	0.901 ₅	5. ₀
0.382	0.906 ₃	3. ₇	0.635	0.914 ₄	3. ₆	0.312	0.905 ₉	4. ₄
0.773	0.918 ₃	3.6 ₂	1.50	0.943 ₅	3.6 ₈	0.678	0.917 ₀	3.7 ₅
1.59	0.946 ₀	3.6 ₇	2.74	0.987 ₄	3.8 ₁	1.34	0.938 ₀	3.6 ₃
3.04	1.002 ₃	4.0 ₂	4.29	1.049 ₈	4.0 ₆	2.69	0.985 ₅	3.7 ₉
4.54	1.069 ₃	4.3 ₃	6.60	1.15 ₇	4.4 ₅	4.27	1.04 ₅	3.9 ₅
6.53	1.179 ₂	4.8 ₉				6.35	1.13 ₆	4.2 ₆
II-7			II-8					
$C_{H^+}=25.6$			$C_{H^+}=39.0$					
φ	η	K	φ	η	K			
0.021	0.896 ₃	7 ± 3	0.037	0.898 ₂	8 ± 2			
0.049	0.897 ₂	5 ± 1	0.103	0.901 ₂	6. ₃			
0.113	0.899 ₇	4. ₇	0.225	0.905 ₄	5. ₀			
0.384	0.907 ₄	3. ₆	0.476	0.913 ₀	4. ₁			
1.14	0.932 ₆	3.6 ₉	1.09	0.93 ₃	3. ₃			
1.82	0.955 ₃	3.7 ₃	2.11	0.965 ₄	3.7 ₀			
2.68	0.985 ₅	3.7 ₃	2.95	0.99 ₆	3.8 ₀			
			4.87	1.06 ₃	3.9 ₆			

^a In volume per cent.^b In centipoises.

DISCUSSION OF RESULTS

(a) *Very Low Sol Concentrations*

If, for the present, we forego the deviating behavior at higher electrolyte concentrations, extrapolation to $\varphi = 0$, gives a value for K lying between 3.4 and 3.6. The deviation of the value 2.5 from the Einstein equation is probably caused by a slight deviation of the spherical form, which is not visible on the electron microscope picture, but which is in accord with the crystalline character of AgI.

The extrapolated value of K is evidently not noticeably dependent on the electrolyte concentration. It is of interest to compare this result with the theories of Smoluchowski and Booth, which hold only for very dilute sols [see our first paper (1)].

For this purpose the value of the ζ -potential has to be known. From the work of Mackor (4) on the structure of the double layer of AgI it can

TABLE III

Equilibrium solution no.	$1/\kappa$	Electrolyte content	Correction factor f according to Smoluchowski		Correction factor f according to Booth	
			$\zeta = 200$ mv.	$\zeta = 100$ mv.	$\zeta = 200$ mv.	$\zeta = 100$ mv.
	<i>A.</i>	<i>mmoles/l.</i>				
1	500	0.035	1.70	0.43	0.010	0.003
2	278	0.12	0.59	0.15	0.008	0.002
3	138	0.49	0.16	0.04	0.006	0.001
4	64	2.3	0.03	0.01	0.004	0.001
6	25	15.0	0.006	0.001	0.003	0.001

be inferred, that at $p_I = 4.6$ the total double layer potential is about 350 mv., from which at the electrolyte contents used by us, 100–200 mv. is located in the diffuse layer.

The equations of Smoluchowski and Booth both have the form $K = 2.5(1 + f)$, whereby, in our case, the numerical value 2.5 will have to be replaced by 3.6. Calculating now f for ζ -potentials of 100 and 200 mv., we find the values shown in Table III.

Taking into account that the equation of Smoluchowski may only be applied when the dimension of the double layer is small in respect to the particle diameter, only the equilibrium solutions 4 and 6 may be used for testing the equation of Smoluchowski in this table.

It then appears that in these cases the correction term according to Smoluchowski is smaller than 0.03. Thus, Smoluchowski's equation is not in conflict with our observations, provided that the conditions under which the equation is valid are not disregarded. The equation of Booth

gives for all electrolytic liquids very small correction terms, which come entirely within the error of our observation. It may therefore be concluded that the theory of Booth is not contradicted by our experiments either.

When looking at Fig. 1, one is struck by the anomalous behavior at higher electrolyte concentrations. Here the question arises as to whether this anomaly is characteristic for the sol, or whether it is due to a systematic error in calculation or measurement.

Since an abnormally high viscosity of the sol with higher electrolyte concentrations does not seem probable, we are inclined to look for the cause in an incipient orthokinetic flocculation in the sol or perhaps more in the slight flocculation on the wall of the capillary that is practically independent of the sol concentration. Considering that the times of efflux are proportional to the fourth power of the capillary diameter and assuming that without flocculation phenomena the value of $K = 3.6$ would have been found, then this would signify, with solution 8, a narrowing of the capillary of about 0.07%. The radius of the capillary being 0.25 mm. this would turn out to be an AgI layer of about 1500 Å., thickness. As this is only a few times the particle diameter, our supposition seems quite reasonable. That this flocculation is not noticeable with higher sol concentration is for the simple reason that the small increase in the time of efflux then causes only a very slight error in η_{spec} . In our further considerations, this increase has therefore been left out of account.

(b) Higher Sol Concentrations

For the highest two electrolyte concentrations (25.6 and 39.0 mmoles/l.) the relation between K and φ is given by two fairly coinciding straight lines. For these cases the relative viscosity may be written

$$\eta_{\text{rel}} = 1 + k_1\varphi + k_2\varphi^2 \quad [1]$$

in which $k_1 = ca. 3.55$ and $k_2 = ca. 8$.

For lower electrolyte concentrations the relation between K and φ is at least of the second degree; that between η and φ is therefore at least of the third degree.

$$\eta_{\text{rel}} = 1 + k_1\varphi + k_2\varphi^2 + k_3\varphi^3 + \dots \quad [2]$$

Here also k_1 can be put at *ca.* 3.55, while the best-fitting values of k_2 and k_3 greatly increase with decreasing electrolyte concentration, as is presented by Table IV.

As the different points of one curve are mutually not entirely comparable, because of unequal deviations from Newtonian behavior (cf. our previous paper), too much importance should not be attached to the exact value of the constants k_2 and k_3 . Table IV is merely intended to illustrate the trend in these constants.

Theoretical Interpretation of the New, Higher Order, Electroviscous Effect

That the rapid increase in viscosity with decreasing electrolyte concentration finds expression only in the constants k_2 and k_3 , and not in k_1 ,

shows that, at least in this case, the electroviscous effect is based on an interaction between the sol particles.

The particles which are carried away in the laminar flow have to pass each other. This passing is only possible if the particles are also displaced perpendicularly on the streamlines of the liquid. This displacement is the source of an extra dissipation of energy and consequently manifests itself in an extra contribution to the viscosity proportional to the number of meetings between particles, that is to the second and higher powers of the concentration. For uncharged particles, the displacement will be over a distance of the order of the radius of the particles; when the particles are charged the displacement is expected to cover distances of the order of the thickness of the double layer. An important electroviscous effect is therefore only expected when the thickness of the double layer is of the same order of, or larger than, the particle radius. Figure 2 shows that this is in good agreement with our results, the particle radius being of the

TABLE IV
Constants from Equation [2]

No.	Electrolyte concentration mmoles/l.	k_1	k_2	k_3
1	0.035	3.40	80	2200
2	0.12	3.60	100	600
3	0.49	3.40	30	525
4	2.3	3.55	10	160
5	8.2	3.55	10	50
6	15.0	3.55	8	50
7	25.6	3.55	8	—
8	39.0	3.55	8	—

order of 150 Å. (see previous paper). With larger particles the effect will be quite difficult to detect owing to the difficulty of having a value of $1/\kappa$ larger than 1000 Å.

The non-Newtonian behavior of sols showing this higher order electroviscous effect is also easily explained. The displacement of the particles in passing is caused by the repulsive force, and the total displacement will be smaller the more rapid the passing. Consequently at high rates of shear the extra dissipation of energy and its influence on the viscosity will be smaller.

As the viscosities in solutions 7 and 8 (25.6 and 39.0 mmoles/l.) do not differ mutually and are only slightly smaller than the solution 6 (15 mmoles/l.) it may be assumed that in these cases the interaction has been reduced to a merely hydrodynamic one. Theories for that case have been developed by Guth (5) and Vand (6) among others, who found for k_1 2.5 and for k_2 14.1 and 7.349, respectively. So the order of magnitude of k_2 is the same as in our Eq. [1]. Further conclusions cannot be made as

long as we do not know how to account exactly for the greater hydrodynamic volume which is reflected in $k_1 = 3.55$.

SUMMARY

Viscosity measurements were carried out on silver iodide sols with different sol concentrations and electrolyte concentrations. Independent of the electrolyte concentration the measurements extrapolated to a value of $K = \eta_{rel}/\varphi$ of 3.55 for a volume concentration $\varphi = 0$.

At higher sol concentration and with low electrolyte concentration, the interaction of the double layers gave rise to an increased viscosity (electroviscous effect). With electrolyte concentrations above 25 mmoles/l. the electroviscous effect has practically disappeared. The remaining excess viscosity can be explained by hydrodynamic interaction. So, an electroviscous effect is not measurable at $\varphi = 0$. This is in accord with Booth's theory but does not conflict either with the theory of Smoluchowski, within the range of application of the latter (thin double layer).

A theoretical explanation of the electroviscous effect at high concentrations is given, based upon the repulsive forces between particles passing each other in the laminar flow.

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