

LETTERS TO THE EDITORS

ERRATA TO "VISCOSITY AND ELECTROVISCOUS EFFECT OF THE AgI SOL. II. INFLUENCE OF THE CONCENTRATION OF AgI AND OF ELECTROLYTE ON THE VISCOSITY" (1)

Mr. P. Mukerjee of the University of Southern California has drawn our attention to an error in Table III (p. 76) of the above-mentioned paper (1). The calculated values of the correction factor  $f$  from the modified Einstein equation

$$\eta_{rel} = 1 + 2.5 \varphi (1 + f) \quad [1]$$

as given in columns 4-7 of Table III should be multiplied by about 100. The correct values are given below, calculated for an average particle radius of 170 Å, other data being those mentioned in the paper (1).

TABLE III (CORRECTED)

Equilibrium solution no.	$1/\kappa$ A.	Electrolyte content, millimoles/l.	Correction factor		Correction factor	
			$f$ according to Smoluchowski (2)	$\zeta = 200$ mv. $\zeta = 100$ mv.	$f$ according to Booth (3)	$\zeta = 200$ mv. $\zeta = 100$ mv.
1	500	0.035	158	39	1.04	0.26
2	278	0.12	54	13.6	0.78	0.20
3	138	0.49	16	4.0	0.57	0.14
4	64	2.3	2.5	0.62	0.42	0.11
6	25	15.0	0.53	0.13	0.24	0.06

Our experimental results when extrapolated to infinite dilution of the colloidal particles can be expressed by

$$\eta_{rel} = 1 + K \varphi \quad [2]$$

in which  $K$  has the value 3.55, with an uncertainty of about 3 %. The difference between 3.55 and the Einstein value 2.5 is considered not to be an electroviscous effect in the sense of Smoluchowski and Booth, because it is independent of the electrolyte content. It is ascribed to the fact that silver iodide particles are not truly spherical (4). The experimental electroviscous effect at infinite dilution is thus smaller than the uncertainty in  $K$ , say smaller than 0.1, which is below the calculated values, considering that the  $\zeta$ -potentials of the silver iodide sols are certainly above 75 mv. and probably above 100 mv.

We are inclined to ascribe the difference between the experiments and Booth's theory to the fact that Booth gives only the first term of a series

expansion in  $\zeta$  and that for a  $\zeta$ -potential of about 100 mv. more terms of the series should be considered. The range of applicability of Smoluchowski's theory (very thin double layers) has probably not yet been reached even at the highest electrolyte content.

## REFERENCES

1. HARMSEN, G. J., VAN SCHOOTEN, J., AND OVERBEEK, J. TH. G., *J. Colloid Sci.* **8**, 72 (1953).
2. SMOLUCHOWSKI, M. VON, *Kolloid-Z.* **18**, 194 (1916).
3. BOOTH, F., *Proc. Roy. Soc. (London)* **A203**, 533 (1950).
4. Another possible explanation has been proposed by HARMSEN, G. J., VAN SCHOOTEN, J., AND VAN DER WAARDEN, M., *J. Colloid Sci.*

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### EFFECT OF SWELLING OR OF AN ADSORBED LAYER ON THE VISCOSITY OF A SUSPENSION OF SPHERICAL PARTICLES

In an article, "Flow of Concentrated Suspensions," by P. S. Williams (1), some data are reported on the relative viscosity of some suspensions of small glass spheres in glycerol-water solutions. One interpretation of the results was given in terms of a theoretical equation published by one of the present writers (2), the equation being

$$\ln \eta_r = 2.5\varphi/(1 - \lambda\varphi) \quad [1]$$

where  $\eta_r$  is the relative viscosity,  $\varphi$  is the volume fraction of the suspended spheres, and  $\lambda$  is a parameter which measures the crowding interaction of the spheres with each other. The systems were not precisely monodisperse; and  $\lambda$  must therefore be interpreted as an average value, since the crowding effect varies with the ratio of the sphere diameters.

The values of  $\lambda$  computed by Williams vary with  $\varphi$ , the range in  $\lambda$  being roughly from 1.5 to 3.5. Such a wide variation casts doubt on the theory. However, suspended particles of colloidal dimensions may carry rigidly adsorbed layers of the liquid which are commensurable with the particle diameter. If allowance is made for such an adsorbed layer, the effective hydrodynamic volume being thereby increased by a factor  $f$ , the theoretical equation then becomes

$$\ln \eta_r = 2.5f\varphi/(1 - \lambda f\varphi). \quad [2]$$

To test this equation it is convenient to write it in the form

$$1/\varphi = f\lambda + 2.5f/\ln \eta_r. \quad [3]$$