

## The Primary Electroviscous Effect Some Numerical Estimates from Booth's Theory

M. SENGUPTA and S. A. ALI

Department of Chemistry, Science College, Calcutta-9

Manuscript received 6 January 1973; revised 4 August 1973; accepted 20 September 1973

The theoretical expressions of Smoluchowski and Booth for the primary electroviscous effect in suspensions of charged particles have been considered. The range of  $ka$  values over which the computed numerical values of the Booth function  $Z(ka)$  were hitherto available from the plots given by Booth, has been considerably expanded by use of the limiting forms of the function  $Z(ka)$  for large and small values of  $ka$ ; and it has been shown that  $\log[\pi b^2(1+b)^2 Z(b)]$  is very nearly linear over a limited range of moderate values of  $ka$ . The electrostatic contribution to viscosity in suspensions of non-conducting charged spherical particles has been calculated as function of  $ka$  for two systems of limiting simplicity, viz., (i) constant  $\zeta$  potential, and (ii) constant  $\zeta$  and particle radius  $a$ .

THE primary electroviscous effect, i.e., the electrostatic contribution to viscosity in suspensions, arising from the distortion of the diffuse counter-charge distribution around an isolated charged particle due to the ions being dragged along by the shearing flow of the moving fluid, has been considered theoretically by Smoluchowski<sup>1</sup>, Krasny-Ergen<sup>2</sup>, Finkelstein and Chursin<sup>3</sup>, and particularly rigorously by Booth<sup>4</sup>. The predicted effect is extremely minute, and is complicated by the simultaneously occurring secondary (also electrostatic) effect<sup>5</sup> which arises from the charge and flow interactions of the diffuse charge atmospheres round the neighbouring particles. For the separation and identification of the primary effect the intrinsic viscosity must be obtained by extrapolation of  $\eta_{sp}/\phi$  to zero particle concentration ( $\phi$ ) using appropriate methods of dilution; the  $K$  value thus obtained ( $K = \lim_{\phi \rightarrow 0} \eta_{sp}/\phi$ ) may then be compared with the estimates of the same quantity as predicted by the different theoretical treatments of the primary electroviscous effect, viz.,

$$K_{Smol} = 2.5 \left[ 1 + \frac{1}{\sigma \eta_0 a^2} \left( \frac{e\zeta}{2\pi} \right)^2 \right] \quad \dots (1)$$

$$K_{Booth} = 2.5 \left[ 1 + q^* \left( \frac{ze^2}{\epsilon a k T} \right)^2 Z(ka) \right] \quad \dots (2)$$

where  $\sigma$ ,  $\eta_0$  and  $\epsilon$  are respectively the specific conductivity, viscosity and dielectric constant of the suspension medium and  $a$  is the radius of the particle which carries at its surface  $ze$  units of charge and a potential difference  $\zeta$  with respect to the bulk medium.  $q^*$  is a quantity whose numerical value depends only on the mobilities of the ions present in the solution, and  $Z(ka)$  is a complicated but known function<sup>4</sup> of  $ka$  (the ratio of the particle radius  $a$  to the Debye-

Huckel thickness of the charge atmosphere round the particle  $1/k$ ). The Smoluchowski equation is limited to the range of large values of  $ka$ . Further, by introduction of the relation between the particle charge and its potential, viz.,

$$ze = \epsilon a \zeta (1 + ka) \quad \dots (3)$$

valid for small values of  $\zeta$  ( $< 25$  mV), the Booth equation (2) can be expressed in terms of  $\zeta$ :

$$K_{Booth} = 2.5 \left[ 1 + q^* \left( \frac{e\zeta}{kT} \right)^2 (1 + ka)^2 Z(ka) \right] \quad \dots (4)$$

A further simplification can be made by assuming the mobilities of all ions present in the solution to be identical, when equation (4) becomes:

$$K_{Booth} = 2.5 \left[ 1 + \frac{1}{\sigma \eta_0 a^2} \left( \frac{e\zeta}{2\pi} \right)^2 \pi (ka)^2 (1 + ka)^2 Z(ka) \right] \quad \dots (5)$$

A number of attempts have been made to measure experimentally the magnitude of the electroviscous effect. The results have however generally been inconclusive, mostly because of the minuteness of the effect to be detected, calling for elaborate precautions to avoid other possible simultaneously occurring spurious effects. Only in a very recent critical experimental investigation of the problem<sup>6</sup> has the Booth estimate of the primary electroviscous effect been successfully confirmed in synthetic latex dispersions.

Now, it has recently been shown that the complicated second order electrical effects associated with the distortion of the double layers round charged particles, as in electrophoresis<sup>7</sup> or sedimentation<sup>8</sup>, can be considerably simplified under certain

simplifying conditions, such as the constancy of the  $\zeta$  potential, which can also be easily realised experimentally. The merit of such treatments is that the complications due to the possible variation of such quantities as  $\zeta$  etc., which are critically dependent on the ionic condition etc. of the solution, are excluded, so that the relaxation effects mentioned can then be conveniently studied. The significance of this in testing elaborate theories, e.g., of electrophoresis, has been mentioned by Overbeek also. In the present paper the results of imposition of two such simplifying conditions namely [(a)  $\zeta$  constant; and (b)  $\zeta$  and  $a$  both constants] on the primary electroviscous effect are considered separately.

### Calculations and Results

The explicit functional form of the function  $Z(b)$  (eqns. 2, 4, 5) has been given by Booth; also, its computed value has been shown graphically in the form of two plots [ $Z(b)$ , and  $Z(b)(1+b)^2$ ] over a certain range of values of  $b (=ka)$ . The first of these plots can be extrapolated confidently to smaller values of  $ka$  (upto  $ka = 0.1$ ), and the second plot to larger values of  $ka (= 14.25)$ . Also, the limiting forms of the function  $Z(b)$  for both small and large values of  $ka$  have been given by Booth; using these forms the range of computation can be extended to

It is seen that  $\log[\pi b^2(1+b)^2 Z(b)]$  is very nearly linear over a rather large range of values of  $\log ka$  (from  $\log ka = -1.0$  to  $1.0$ ).

The computed numerical values of the electrical contribution to the viscosity of a homodisperse suspension of spherical particles (particle vol. fraction  $\phi$ ), calculated by Smoluchowski's and Booth's equations (equations 1 and 5 respectively) for some constant  $\zeta$  potential values ( $\zeta = 50, 75, 100$  and  $125$  mV) are shown as function of  $ka$  in Fig. 2. Here  $\phi = 0.006$ ;  $\eta_0 = 89.3 \times 10^{-4}$  poise,  $\epsilon = 78.54$ ; also  $k = 0.2222 \times 10^6$  cm $^{-1}$  and  $\sigma = 1 \times 10^{-5}$  ohm $^{-1}$  cm $^{-1}$ , which would signify an ordinary distilled water specimen (or, an extremely dilute ( $5 \times 10^{-5}N$ ) KCl solution, say) at  $25^\circ$ . The electrolyte concentration being constant along any particular curve,  $\zeta$  may plausibly be assumed to remain constant also; hence the curves in Fig. 2 are best interpreted as giving the variation on  $\eta_{el}/\eta_0$  with particle size (over the range  $a = 2.25-0.012\mu$ ) in the above medium.

It is seen that  $\eta_{el}/\eta_0$  is quite small ( $\sim 10^{-3}$ ), and decreases steadily with increasing  $ka$ . Also, the Smoluchowski estimates are generally much larger than those from Booth's theory, specially when  $\zeta$  is large; with increasing  $ka$  however, the former rapidly approach the latter estimates, and at about  $ka = 30$

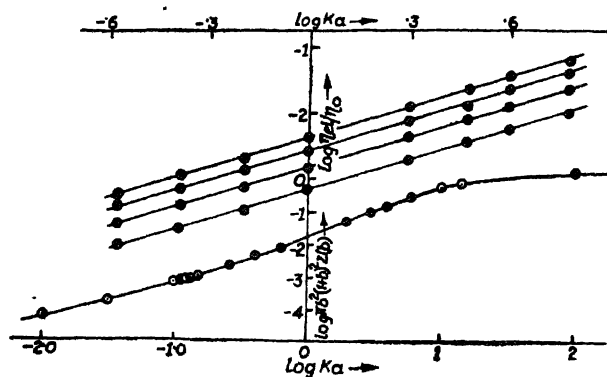


Fig. 1.

Fig. 1. Plot of  $\log[\pi b^2(1+b)^2 Z(b)]$  as function of  $b (=ka)$  (lower ordinate and abscissa). Also (upper ordinate and abscissa),  $\log \eta_{el}/\eta_0$  as function of  $\log ka$ , according to the Booth theory, for homodisperse aqueous suspensions in different electrolyte concentrations at  $25^\circ$  ( $\phi = 0.006$ ,  $\sigma = 1 \times 10^{-5}$  ohm $^{-1}$  cm $^{-1}$ ,  $\eta_0 = 89.3 \times 10^{-4}$  poise,  $a = 4.5 \times 10^{-6}$ ,  $\epsilon = 78.54$ ), for four different constant values of  $\zeta$  ( $= 50, 75, 100$  and  $125$  mV respectively, from the lowest upwards).

still smaller (0.01) and larger (100) values of  $ka^*$ . In this manner an extended plot of  $\log [\pi b^2(1+b)^2 Z(b)]$  has been constructed, and is shown in Fig. 1.

\* The computed numerical values of  $\log[\pi b^2(1+b)^2 Z(b)]$  for one particular small  $ka$  value ( $ka = 0.10$ ) are respectively  $-3.213$  and  $-3.189$  according as the value of  $Z(b)$  is derived from its limiting functional form or the extrapolated  $Z(b)$  curve. For large  $ka$ , however, the mutual agreement is a trifle less good. The computed values for  $ka = 16, 25, 35, 50$  using the limiting functional form of  $Z(b)$  fall just a little above the smooth curve corresponding to two computed values (for  $ka = 10$  and  $14.25$ ) using the extrapolated  $Z(b)(1+b)^2$  curve, and one (for  $ka = 100$ ) using the limiting functional form of  $Z(b)$ .

the two are nearly equal in magnitude, for all the different  $\zeta$  considered.

The nature of variation of  $\eta_{el}/\eta_0$  with  $\zeta$  when both  $k$  and  $a$  are separately constant, is, in case of both theories, quite obvious (equations 1 and 5), and need not be further discussed. Of some greater interest is the case when, instead, the product  $ka$  is the only significant variable involved; the variation of  $\log \eta_{el}/\eta_0$  according to the Booth theory would then naturally be similar to that of the function  $\log[\pi b^2(1+b)^2 Z(b)]$  (i.e., linear over a certain range of  $ka$ ). In Fig. 1, this variation with  $\log ka$ , of

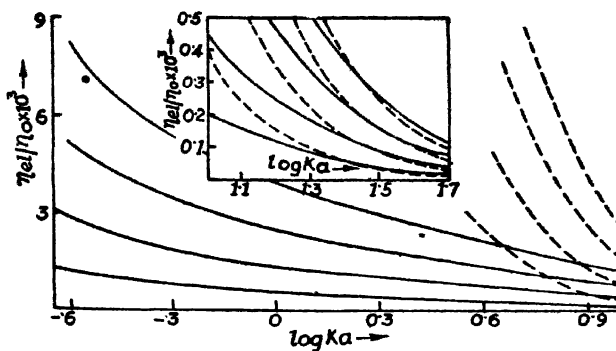


Fig. 2.

Fig. 2. Plot of  $\eta_{e1}/\eta_0$  as function of  $ka$ , according to Booth (—) and Smoluchowski (---) theories, for homodisperse aqueous suspensions ( $\phi$ ,  $\eta_0$ ,  $\epsilon$ ,  $\sigma$  as above;  $k = 0.222 \times 10^6$   $\text{cm}^{-1}$ ) of different particle sizes at  $25^\circ$  for four different constant values of  $\zeta$  ( $= 50, 75, 100$  and  $125$  mV respectively, from the lowest upwards).

$\log \eta_{e1}/\eta_0$  (for four different values of  $\zeta$ ) is shown alongside the variation of the function mentioned.

Here, the variation of  $ka$  implies the variation of  $k$  alone, since  $a$  in equation 5 is assumed not to vary; each linear curve thus gives in effect the variation according to the Booth theory, of  $\log \eta_{e1}/\eta_0$  with  $\log ka$ , at a particular  $\zeta$  value; i.e., for different homodisperse suspensions each containing similar size particles suspended in different ionic strength media,  $\zeta$  remaining constant notwithstanding. This condition may well be difficult to realise in practice as  $\zeta$  is known to depend upon the ionic conditions in solution.

### References

1. M. SMOLUCHOWSKI, *Kolloid Z.*, 1916, 18, 190.
2. W. KRASNY-ERGEN, *Kolloid Z.*, 1936, 74, 172.
3. B. N. FINKELSTEIN and M. P. CHURSIN, *Acta physicochim.*, U.R.S.S., 1942, 17, 1.
4. F. BOOTH, *Proc. Roy. Soc. (London)*, 1950, A203, 533.
5. B. E. CONWAY and A. DOBRY-DUCLAUX, "Rheology", ed. F. Eirich, Vol. 3, Chapt. 3, Academic Press, New York, 1960.
6. J. STONE-MASUI and A. WATILLON, *J. Colloid and Interface Sci.*, 1968, 29, 187.
7. M. SENGUPTA and D. N. BISWAS, *J. Colloid and Interface Sci.*, 1969, 29, 536.
8. M. SENGUPTA, *J. Colloid and Interface Sci.*, 1968, 26, 240.
9. P. H. WIERSEMA, A. L. LOEB and J. TH. G. OVERBEEK, *J. Colloid Sci.*, 1966, 22, 78.