

The Relaxation Correction in the Theory of Electrophoresis of Nonconducting Solid Spherical Particles II

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The comparative analysis of the different theoretical equations for the electrophoresis of nonconducting spherical particles, as developed in an earlier publication, has been extended to some further mobility data of Mooney and Stackelberg for organic oil droplets of varying sizes in electrolyte solutions of constant concentration. The following equations in particular have been used: (i) Relaxation effect corrected equations of Overbeek and Booth; (ii) relaxation effect corrected results of computer calculations of Wiersema, Loeb, and Overbeek; (iii) surface conductivity effect corrected equations of Henry and Booth; (iv) liquid drop correction equation of Booth.

In a foregoing communication¹ a comparative evaluation has been made of the different theoretical treatments of the relaxation correction in the theory of electrophoresis of nonconducting solid spherical particles, by making use of the experimental data of Mooney^{2a} for Stanolind drops in alkali solutions. It has been mentioned^{1,3} that mobility data for particles of different sizes in electrolyte solutions of constant concentration are the most suitable for this purpose. It is the object of the present note to complete this analysis by using (i) Mooney's mobility data for droplets of (a)^{2a} Stanolind, dimethylaniline, tribromohydrin and iodobenzene in distilled water; and Stanolind in $10^{-4}N$ HCl solution; (b)^{2b} various organic liquid droplets in KCl solutions (20° and 75°); and (ii) Stackelberg *et al*'s mobility data⁴ (25°) for droplets of paraffin oil (with 1% oleic acid) in distilled water (oil weighted with (a) $C_2H_2Cl_4$ and (b) C_2Cl_4) and in $10^{-4}N$ KCl solution ($C_2H_2Cl_4$ only)*.

CALCULATIONS, RESULTS AND DISCUSSION

The details regarding the different theoretical treatments applied (including the equations), the method of obtaining the primary experimental data from the published figures**,

1. M. Sengupta and D. N. Biswas, *J. Colloid and Interface Sci.*, 1969, 29, 536; 1969, 30, 275.
- 2.a. M. Mooney, *Phys. Rev.*, 1924, 23, 396.
b. M. Mooney, *J. Phys. Chem.*, 1931, 35, 331.
3. P. H. Wiersema, Thesis, Utrecht, 1964.
P. H. Wiersema, A. L. Loeb and J. Th. G. Overbeek, *J. Colloid and Interface Sci.*, 1966, 22, 78.
4. M. v. Stackelberg, H. Heindze, F. Wilke and R. Doppelfeld, *Z. Elektrochem.*, 1957, 61, 781.

*In justification of the use of these data in the rather tedious calculations presented here it may be mentioned that the phenomenon of increase of electrophoretic mobility with particle size is rather widely observed, and is by no means confined to the present data alone. The legitimate conclusion therefore is that some general effects are involved, and it is of interest to see precisely how far the known electrical effects discussed can account for the said variation.

**Only those data have been ignored in the relaxation (ζ) calculations, the points for which fall widely off the smooth mobility vs. particle-size curves. Such data are few for Mooney's systems (two in the distilled water and one in the HCl solution systems for Stanolind; three for iodobenzene and two for dimethylaniline, both in distilled water); and rather more numerous for Stackelberg's systems (about a third of the experimental points in both the $C_2H_2Cl_4$ and C_2Cl_4 weighted paraffin oil systems in distilled water).

the procedures followed in the case of the different calculations, etc., have all been discussed previously¹. This allows us here to pass over directly to a straightforward presentation of the actual results*. The assumptions, as before, are that the oil droplets can be considered solid-like and non-conducting; also, that the electrolytic impurity in the systems involving distilled water (estimated from conductance measurements to be $\sim 2 \times 10^{-5}N$ in case of Mooney's first set of data^{2a}, and $\sim 1 \times 10^{-5}N$ for Stackelberg *et al.*'s data) can be taken to be KCl, since this is not critical. A temperature of 25° is assumed as before for Mooney's first set of data^{2a}. The values of the constants used are^{5,3}: $\epsilon_1 = 80.36(20^\circ)$, 78.54 (25°), 62.62(75°); $\eta_1 = 10.05(20^\circ)$, 8.95(25°), 3.79(75°) mPoise; $\lambda_{k+} = 66.56(20^\circ)$, 73.52(25°), 147.5 (75°); $\lambda_{H+} = 349.82(25^\circ)$; $\lambda_{Cl-} = 69.15(20^\circ)$, 76.34(25°), 160.0(75°) ohm⁻¹cm². The particles were all negatively charged.

The results of ζ potential calculations using the analytical approximations of Overbeek⁶ and Booth⁷ ($\zeta_{Overbeek}$ and ζ_{Booth} respectively, using in each case the respective *inverted* series^{8,9}), as also by means of the 'computer calculation method' of Wiersema, Loeb and Overbeek³ ($\zeta_{W.L.O.}$) are shown in figs. 1 (Stackelberg's data) and 2,3 (Mooney's data).

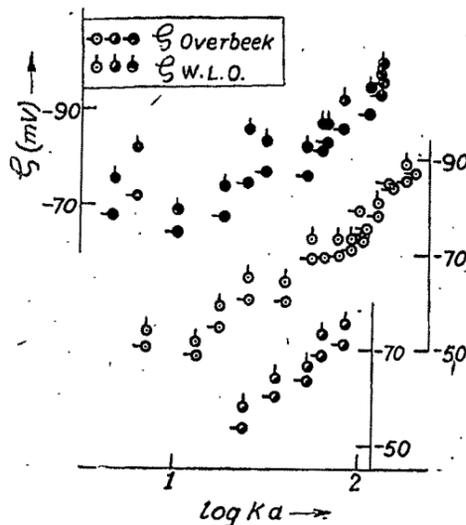


Fig. 1. ζ potential calculation from Stackelberg *et al.*'s data⁴ for paraffin oil droplets of varying sizes at 25° in distilled water (● : oil weighted with C₂Cl₄; ○ : oil with C₂H₂Cl₄), and in 10⁻⁴N KCl (◐ : oil with C₂H₂Cl₄).

* All symbols used, and the different theoretical equations etc. referred to in this paper have already been defined earlier¹.

5. R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Butterworths, London, 1959, p. 12, 465.
6. J. Th. G. Overbeek, *Koll. Beihefte*, 1943, 54, 287. "Advances in Colloid Science," Vol. III, ed. E. J. W. Verwey and H. Mark, Interscience Publishers Inc. New, York, 1950.
7. F. Booth, *Proc. Roy. Soc. London*, 1950, A203, 514.
8. D. Stigter and K. J. Mysela, *J. Phys. Chem.* 1955, 59, 45.
9. R. J. Hunter, *J. Phys. Chem.*, 1962, 66, 1367.

The *W.L.O. method* could not be applied³, because of the high ζ values involved, to iodo-benzene in distilled water; also, it has not been applied, because of low ζ at high κa , to Stanolind in distilled water and $10^{-4}N$ HCl. The ion conductance value of neither the positive nor the negative ion in the KCl solutions at 25° being significantly different from $70 \text{ ohm}^{-1} \text{ cm}^2$, the 'ionic mobility correction' to E' ($= 6\pi\eta_1 eU/Ec_1 kT$) was deemed insignificant and hence neglected in the W.L.O. calculations at 25° , though it has been applied nevertheless in the calculations for 20° and 75° , in the manner appropriate for negatively charged particles.* The extent of agreement between the results from the two different *analytical approximations* being already more or less well known (see for example, Mooney's Stanolind and ois systems, figs. 2 and 3 respectively), the results of calculations with only one approximation (namely ζ_{Overbeek}) are shown, besides $\zeta_{\text{W.L.O.}}$, for the Stackelberg systems. In the case of Mooney's first set of system^{2a}, only the best available estimate of ζ being of interest, only $\zeta_{\text{W.L.O.}}$ (or failing, ζ_{Overbeek}) values are given for the three oils.

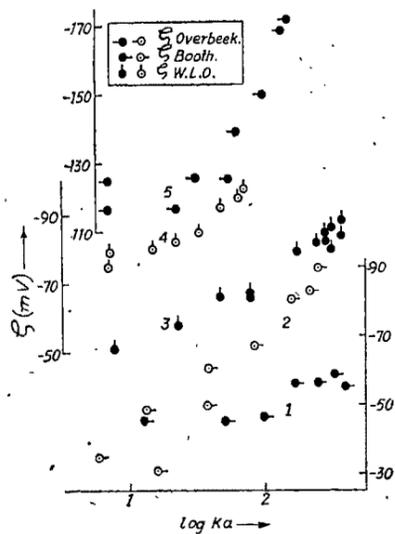


Fig. 2. Same as in Fig. 1 for Mooney's data^{2a} for Stanolind droplets in $10^{-4}N$ HCl and distilled water (systems 1, 2 respectively, with right ordinate), and dimethylaniline, tribromohydrin and iodo-benzene droplets all in distilled water (systems 3, 4 and 5 respectively with left ordinates).

The expected relative magnitudes of ζ_{Booth} and ζ_{Overbeek} calculated from the respective inverted series (the following general equation 1) are interesting to consider. Since C_1 is always positive and C_3 negative (always in the case of Overbeek expression, and at least for

*The net corrections ($\Delta E'$) are insignificantly small ($< 1\%$ of E') in all cases, because the counterion-conductance-factor (m_{k+}) is not greatly different from the reference value 0.184 in spite of λ_{k+} being large at 75° . Here, for KCl 20° , $m_{\pm} < 0.184$, and the corrections for the two ions have the same (negative) sign; while for KCl 75° (cf. NaOH at 25° , ref. 1), $m_+ > 0.184$ and $m_- < 0.184$, so the corrections are opposite in sign, though E' is still negative. (In ref. 1, $\Delta E'$ was always positive because the correction due to the slower counterion Na^+ was more significant).

1-1 electrolytes ($q_3 = 1$ and q_3^* positive) in the case of the Booth expression), therefore, in the inverted equation for ζ namely⁹

$$\zeta = \frac{U}{C_1} - \frac{C_3}{C_1} \left(\frac{U}{C_1}\right)^3 - \frac{C_4}{C_1} \left(\frac{U}{C_1}\right)^4 \quad (1)$$

the consideration of relaxation correction upto the cubic term (i.e. $\zeta_{Overbeek}$) always leads to a (numerically) larger calculated value, irrespective of the sign of the particle charge, as compared to the calculation when relaxation correction is neglected (upto the linear term in eqn. 1 i.e. ζ_{Henry}). In calculations inclusive upto the quartic term in the above equation

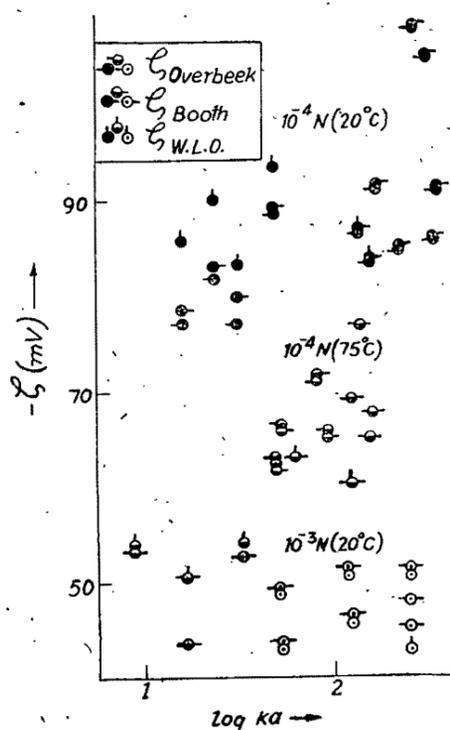


Fig. 3. Same as in Fig. 1 for Mooney's data² for various organic oil droplets in KCl solutions (O : $10^{-3}N$ (20°); ◐ : $10^{-4}N$ (75°); ● : $10^{-4}N$ (20°).

(i.e. ζ_{Booth}), on the other hand, C_4 (like q_4^*) is positive or negative according as $\lambda_- > \lambda_+$ or $\lambda_- < \lambda_+$; hence, were the coefficient C_3 exactly identical in the two treatments, $\zeta_{Booth} > \zeta_{Overbeek}$ (numerically) for negative particles (U negative) in the first case, and for positive particles (U positive) in the second. This would be natural, because only for counter-ions slower than the coions can a larger relaxation effect (described more adequately by the Booth equation) be expected. As it is, the actual results may sometimes be confounded because of the slight difference between the numerical values of the common coefficient C_3 in the two treatments.

The results of actual numerical calculations of ζ_{Overbeek} , ζ_{Booth} and $\zeta_{\text{W.L.O.}}$ are in general as expected³, and similar to those reported earlier^{11,10}. The more important results are: (i) None of the calculated ζ values (not even $\zeta_{\text{W.L.O.}}$) remain constant* over the range of κa values studied. (a) In *low ζ systems* (≤ 75 mV: Stanolind in $10^{-4}N$ HCl, oils in $10^{-4}N(75^\circ)$ HCl), $\zeta_{\text{W.L.O.}}$, ζ_{Overbeek} and ζ_{Booth} are nearly equal at all κa (~ 10 -200); (b) In *intermediate ζ systems* (~ 75 -110 mV: oils in $10^{-4}N$ KCl(20°), Stanolind, tribromohydrin, dimethylaniline and paraffin oil (both C_2Cl_4 and $C_2H_2Cl_4$ weighted) all in distilled water), $\zeta_{\text{W.L.O.}} > \zeta_{\text{Booth}}$ and $\zeta_{\text{Booth}} > \zeta_{\text{Overbeek}}$ (difference at $\kappa a \sim 15$, about 8% of $\zeta_{\text{W.L.O.}}$ for the former and 4% of ζ_{Booth} for the latter), but the differences decrease steadily with increasing κa to about 2% and 0% respectively at $\kappa a \sim 100$; (c) In *high ζ systems* (≥ 150 mV: iodobenzene in distilled water) where the difference $\zeta_{\text{Booth}} \sim \zeta_{\text{Overbeek}}$ is known¹⁰ to be quite large even at moderately large values of κa , the calculated ζ_{Overbeek} values may thus be substantially different from the correct ζ potentials involved, because of the extent of uncertainty in the calculated ζ_{Overbeek} values.

(ii) The counterion (K^+) being slightly slower than the coion (Cl^-), and the particles being negatively charged, $\zeta_{\text{Booth}} > \zeta_{\text{Overbeek}}$ (though only very slightly)** in most of the systems.

The final mobility vs. κa curves (figs. 4 and 5) have been calculated as before¹, using in the case of the orthodox method of relaxation correction (W.L.O. or Overbeek (*direct* series) method) a suitable average value from among the calculated individual ζ values for each system, and in the case of the approximate method of relaxation correction by way of surface conductivity correction^{11,12} the values of ζ and σ_s/σ_1 as determined for each system from the limiting slope of the $1/U$ vs. $1/a$ plot. On comparison with the theoretical mobility vs. κa curves over the entire range of κa values following from the rigorous (W.L.O.) relaxation theory³, it would be seen that:

(1) The experimental points in the systems shown lie mostly on the right ascending portion ($\kappa a = 20$ -200) of the complete mobility vs κa curves. For systems showing a rather sustained steep increase of mobility with particle size over this range of κa values, (iodobenzene, tribromohydrin, Stanolind all in distilled water, and oils in $10^{-4}N$ KCl(75°)), the surface conductivity correction method is seen to lead to better agreement with experimental results, while for systems showing mobility variation only over range of small κa values and little variation thereafter (dimethylaniline in distilled water) the orthodox relaxation correction method is more successful. The same is generally also true in case of other data analysed¹⁰:

10. M. Sengupta, and S. S. Jana, unpublished results.

11. F. Booth, *Trans. Faraday Soc.*, 1948, 44, 955.

12. D. C. Henry, *Trans. Faraday Soc.*, 1948, 44, 1021.

* The other possible assumption, namely that the surface charge density should remain constant instead, does neither alter the relaxation calculations nor is found to be vindicated any better by the actual experimental results, because the surface charge densities calculated from the ζ potentials found, by using the computational equation³ show the same lack of constancy as do the ζ potentials themselves, because over the κa range involved, the relation between the two is nearly linear.

** The small difference in the values of the coefficient C_3 in the two treatments (as also any small errors involved in evaluating the various functions graphically, etc.) do not generally appear to be able to confound this result.

(ii) For a few smallest particles ($a \sim 10^{-4}$ cm) in almost electrolyte free (distilled water, $\kappa \sim 10^6$ cm $^{-1}$) solutions (Fig. 3), the surface conductivity corrected mobility curves show a minimum at $\kappa a \sim 10$ -20. The relaxation corrected curves do not yet do so even at the lowest κa values involved, presumably because the expected minimum³ occurs at still lower κa values. The experimental data, though somewhat uncertain in this region of extremely fine particles, also do not yet show any evidence of the occurrence of a minimum.

(iii) The ζ values obtained in case of the relaxation and surface conductivity corrections for the different systems* are unfortunately not in such good agreement with one another as found earlier. Since $\zeta_{relax.av.}$ is generally obtained from the data for the

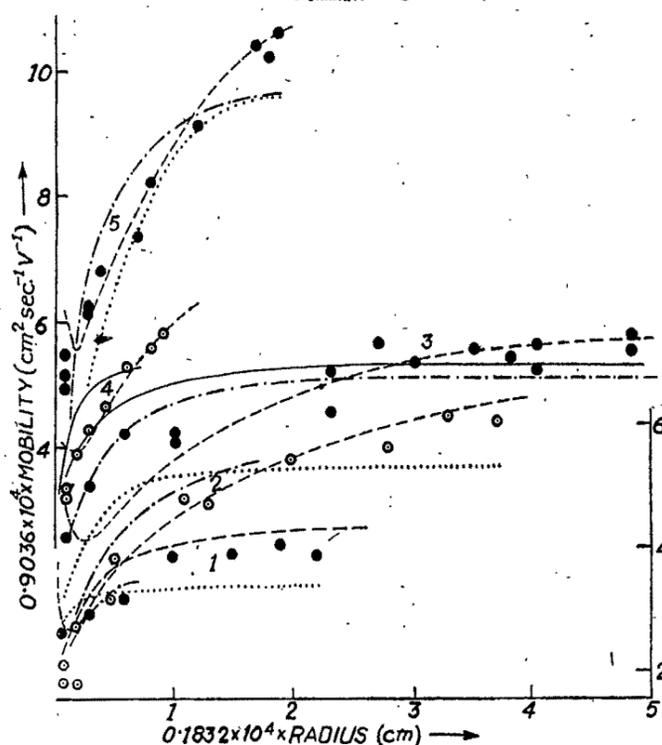


Fig. 4. Theoretically calculated electrophoretic mobilities ($U_{W.L.O.}$, ... $U_{Overbeck}$, $U_{surface\ cond.}$, $U_{Hg\ drop\ (Booth)}$) compared with Mooney's data² (see Fig. 2 legend for details of systems).

- 1 : $\zeta_{Ov.} = 50$ mV, $\zeta_{s.c.} = 65.2$ mV, $\sigma_s = 5.71 \times 10^{-9}$ ohm $^{-1}$, $\zeta_{Hq} = 7.7$ mV, $\kappa/\kappa' = 10$;
 2 : $\zeta_{Ov.} = 80$ mV, $\zeta_{s.c.} = 121.8$ mV, $\sigma_s = 2.42 \times 10^{-9}$ ohm $^{-1}$, $\zeta_{Hq} = 11.8$ mV, $\kappa/\kappa' = 10$;
 3 : $\zeta_{W.L.O.} = 80$ mV, $\zeta_{s.c.} = 100.1$ mV, $\sigma_s = 1.67 \times 10^{-9}$ ohm $^{-1}$, $\zeta_{Hq} = 14$ mV, $\kappa/\kappa' = 6$;
 4 : $\zeta_{W.L.O.} = 82$ mV, $\zeta_{s.c.} = 120.3$ mV, $\sigma_s = 0.75 \times 10^{-9}$ ohm $^{-1}$;
 5 : $\zeta_{Ov.} = 155$ mV, $\zeta_{s.c.} = 194.6$ mV, $\sigma_s = 1.02 \times 10^{-9}$ ohm $^{-1}$, $\zeta_{Hq} = 30$ mV, $\kappa/\kappa' = 6$.

* The linear extrapolations, made for deriving the $\zeta_{s.c.}$ and σ_s/σ_1 values reported, do not involve the least square method; also, the 'averaging' represents more properly a suitable average choice over the calculated $\zeta_{W.L.O.}$ or $\zeta_{Ov.}$ values so as to ensure a good fit of the calculated mobility curves with experimental data.

smaller particles (κa small), whereas $\zeta_{s.c.}$ is obtained from those for the largest particles ($\kappa a > 70$ for distilled water, $\kappa a > 30$ for $10^{-4}N$ solution), therefore, even the limited agreement between the two as actually found may be considered encouraging. (Also significant is the fact that $\zeta_{s.c.}$ is always of larger magnitude than ζ_{relax}). Also, in spite of the scatter which the calculated ζ values show (due to experimental errors), it is still possible to discern however, with increasing κa , an increasing trend in ζ in most of the systems studied. This general increase in ζ (and the derived quantity 'surface charge density σ ') points most likely to the fact that the assumption that in systems of constant electrolyte concentration ζ or σ plausibly remain constant, is not fully justified.

(iv) The values of specific surface conductivity σ_s (see Figs. 4, 5) calculated from σ_s/σ_1 for the different systems by making use of the specific conductivity (σ_1) values of the different media, show a tendency to increase with (a) increase of electrolyte concentration of the solutions at constant temperature, as also (b) increase of temperature at constant concentration. Though the magnitudes of σ_s found, generally agree with those obtained from the theoretical equations for surface conductance at a plane double layer¹³, it remains to be seen how far the said variations of σ_s do so.

Finally, it is of some interest to see how far the observed variation of mobility with size in the systems under consideration may be attributed to factors other than the second order electrical effects considered; for example to the fact that the particles happen to be

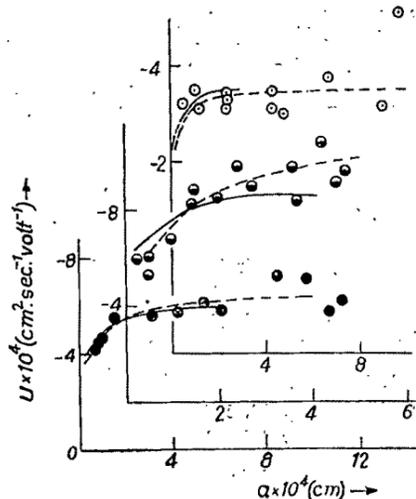


Fig. 5. Same as in fig. 4 for Mooney's data^{2b} (see fig. 3 legend for details of systems).

- : $\zeta_{W.L.O.} = 48.0\text{mV}$, $\zeta_{s.c.} = 50.0\text{mV}$, $\sigma_s = 1.68 \times 10^{-9} \text{ohm}^{-1}$;
- : $\zeta_{W.L.O.} = 60.1\text{mV}$, $\zeta_{s.c.} = 76.1\text{mV}$, $\sigma_s = 1.64 \times 10^{-9} \text{ohm}^{-1}$;
- : $\zeta_{W.L.O.} = 87.4\text{mV}$, $\zeta_{s.c.} = 94.2\text{mV}$, $\sigma_s = 0.58 \times 10^{-9} \text{ohm}^{-1}$.

13. J. J. Bikerman, *Z. phys. Chem.*, 1933, A163, 378.
F. Urban, H. L. White and E. A. Strassner, *J. Phys. Chem.*, 1935, 39, 311

fluid in nature. The liquid drop electrophoresis equation of Booth¹⁴ for the particular case when the charge distribution in the fluid of the drop is of the form of a diffuse double layer (thickness $1/\kappa'$) analogous to that in the outer solution, has been shown¹⁵ to be the most successful. The velocities calculated by using this equation in the case of Mooney's systems^{2a} are also shown in fig. 4.* (The viscosity value at 25° used are: $\eta_{\text{Stanolin}} = 1.194$, $\eta_{\text{Dobenzene}} = 0.0156$ and $\eta_{\text{dimethylaniline}} = 0.013$ poise). The best values of the adjustable parameters $\zeta_{s.c.}$ and κ/κ' for the different systems are also shown.

CONCLUSION

As is well known¹⁶, the relaxation and the *normal* surface conductivity effects are fundamentally identical, being essentially the corrections to include the effect of polarisation of the electrical double layer near the charged particle surface. The relaxation correction is however more comprehensive and rigorous mathematically, and the fact that this method of correction gives by far a much fuller and detailed account of the electrophoresis phenomena need hardly be gainsaid. However, the complete treatment (computation) of the relaxation effect is as yet available only upto moderately large value of ζ (≤ 150 mV), while the analytical approximations thereto (which involve rather tedious calculations) are known¹⁰ to be incomplete at $\zeta \sim 100$ mV, and distinctly inaccurate for still higher values of ζ . The surface conductivity correction method, which is known to give equally correct results for low ζ , has thus a distinct advantage for application to high ζ systems also. This being so, the question becomes pertinent whether in the numerous instances, where the 'polarisation of the atmosphere' effect would profitably be taken into account, it is worthwhile to go in for a rigorous treatment by way of relaxation correction, or else a tolerably approximate surface conductivity correction treatment could profitably be used instead¹⁷.

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* In case of Mooney's other system^{2b}, the particular oil to which any electrophoretic mobility curve refers, is not mentioned. Also, Stackelberg's systems⁴ contained contaminants, which can legitimately be presumed to have affected the tiny motion within the droplets. Both these systems are thus unsuitable for analysis from the view-point of liquid drop electrophoresis equations.

14. F. Booth, *J. Chem Phys.*, 1951, 19, 1331.

15. M. Sengupta, *J. Electroanal. Chem.*, 1968, 19, 199.

16. J. Th. G. Overbeek, in "Colloid Science," Vol. I, ed., H. R. Kruyt, Elsevier, Amsterdam, 1952.

17. C. T. O'Konski, *J. Phys. Chem.*, 1960, 64, 605.

Relaxation Correction in the Theory of Electrophoresis*

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The relaxation and surface conductivity corrections in the theory of electrophoresis of non-conducting solid spherical particles have been considered comparatively. It has been shown that for systems of constant ζ potential the relaxation corrected mobility versus κa curves can be well simulated at least in their essential aspects, by the much more easily calculated surface conductivity corrected mobility curves. The comparative application of the two methods for calculating the mobility curves from actual experimental data has been illustrated in some typical cases, viz. those involving (a) low κa , and (b) high ζ .

IN some recent publications^{1,2} the relaxation correction in the theory of electrophoresis of non-conducting solid spherical particles has been considered in its different modifications, viz. the different analytical approximations of Overbeek³ and Booth⁴, vis-a-vis the computer calculation solution of the problem by Wiersema *et al.*⁵ (W-L-O), all in relation to some electrophoretic mobility data of Mooney⁶. The performance of the 'surface conductivity correction' method as an approximate method of relaxation correction^{7,8} which gives comparable results has also been considered. Since the rigorous calculation of relaxation correction is extremely complicated, and despite its importance for all electrokinetic processes in general has been fully tackled (numerical computation) only in the case of one of the simplest systems (non-conducting solid spherical particle), over a limited range of values of the pertinent parameters (ζ , κa , and the ion-conductance values λ_{\pm})[†], therefore, it is of interest to consider how far the simple, though admittedly approximate, method of surface conductivity correction can be used as an alternative. It is the purpose of the present paper to consider this point a little more fully, in relation to the electrophoresis of non-conducting solid spherical particles.

The magnitude of the relaxation correction depends critically on the magnitude of the ζ potential⁵; it increases sharply, for example, and becomes significant at lower κa values, with increase in the value of ζ . With this dependence on the particular ζ value chosen, the results further show that for systems of constant ζ potential, which only are of immediate interest to us, the relaxation correction is (i) insignificant for both very small and very large values of κa , so that the electrophoretic mobility tends to be given in the first case by the Hückel equation

$$E' (= 6\pi\eta_1 eU/E\epsilon_1 kT) \rightarrow y_0 (= e\zeta/kT)$$

and in the second by the Smoluchowski equation ($E' \rightarrow 1.5y_0$); and (ii) significant over the intermediate

range of values of κa ($\sim 0.5-50$), leading eventually to a minimum in the E' versus κa curve, at a κa value ($\sim 1-10$) determined precisely by the particular ζ value chosen. Incidentally, over this range again the results of the analytical approximations of Overbeek and Booth fall rather conspicuously short of the correct (W-L-O) relaxation calculation results, for $\zeta > 75$ mV.

It is of interest to see how far the results of calculations by the surface conductivity correction method are in agreement with this, in the first instance.

Results and Discussion

In Fig. 1 the mobility functions E' calculated by the different relaxation correction treatments are compared with those calculated using the surface conductivity correction method. For two different values of ζ , the values of E' calculated by the computational method (W-L-O) as also the analytical approximation methods of Overbeek and Booth are shown as function of κa [all curves except I, $\zeta = 75$ mV, are taken from ref. 5, and refer to a uni-univalent electrolyte solution of equi-mobile ions with ion conductance equal to 70 ohms⁻¹ cm², at 25°C]. The mobility curves using the surface conductivity correction method, calculated in each case for some different typical values of the pertinent parameter σ_s/σ_1 , are also shown, and refer (because here κ must also be defined in addition to κa),

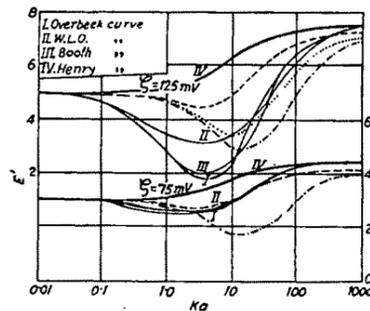


Fig. 1 — Comparison between the relation corrected (—), and surface conductivity corrected [$\sigma_s/\sigma_1 = 10^{-4}$ (---), 10^{-3} (— · — ·), and 5×10^{-4} (····)] mobility function versus κa curves

*Presented at the Convention of Chemists, Kharagpur, Dec. 1969.

†The different symbols used and the various theoretical equations, etc. referred to in this paper, have all been defined earlier¹.

for example, to a typical distilled water medium (sp. cond. = 1×10^{-6} ohm $^{-1}$ cm $^{-1}$) containing only H $^{+}$ and HCO $_3^{-}$ ions ($\lambda_{H^{+}} = 349.8$, $\lambda_{HCO_3^{-}} = 44.5$ ohm $^{-1}$ cm 2) at 25°C ($\kappa = 5.22 \times 10^4$ cm $^{-1}$). It may be noted that a change in the medium (i.e. κ) would merely alter, for any one of the surface conductivity corrected curves (i.e. $\sigma_s/\sigma_1 =$ a particular constant) the particular range of κa values over which it holds; alternatively, a different surface conductivity corrected curve ($\sigma_s/\sigma_1 =$ a different constant) would hold over the same range of κa values.

It is seen that the general nature of the correct W-L-O relaxation corrected mobility curve can, within limits, be surprisingly well reproduced by the approximate method of surface conductivity correction. In the case of the curve for $\zeta = 75$ mV, for example, the difference between the two (for $\sigma_s/\sigma_1 = 10^{-4}$ cm) nowhere exceeds (except for κa very large, see below) that between the analytical approximation and the computer calculation solution of the relaxation treatment itself, which is known to be small for $\zeta \leq 75$ mV. The same is true also in the case of the curve for $\zeta = 125$ mV (for $\sigma_s/\sigma_1 = 5 \times 10^{-4}$ cm), at least over that range of moderately large κa values (~ 10 -200) which generally is of practical importance for ordinary colloidal suspensions, and where again the analytical expressions themselves are known (see Fig. 1) to be satisfactory approximations to the correct relaxation treatment.

The occurrence of the minimum in the theoretical E' versus κa curves, which has been considered⁹ to be a rather stringent test of the relaxation correction theories, is also seen to be reproduced by the surface conductivity correction treatment*. Its position shifts depending upon the value chosen for the parameter σ_s/σ_1 , and at higher ζ values is seen to differ somewhat from that predicted by the correct relaxation treatment. It may, however, be mentioned again that for most of the ordinary colloidal suspensions of common interest the κa values (generally > 20) are such that only the right ascending portion of the E' versus κa curves is of interest, the position of the minimum falling mostly well below the lowest κa values practically encountered.

For $\kappa a \rightarrow 0$, the surface conductivity corrected curves, like the relaxation corrected curves, can be shown to reduce to the Hückel curve, irrespective of the magnitude of the specific surface conductivity σ_s . On the other hand, even for such large values of κa where the relaxation corrected curves already practically reduce to the Smoluchowski curve, the surface conductivity corrected curves still fall below it by a factor $1/(1 + \sigma_s/\sigma_1 a)$, the merger occurring theoretically only in the region of infinite radius of curvature of the particle. From the mobility values for particles of varying sizes over this range of large κa values the parameters ζ and σ_s/σ_1 can be determined experimentally for constant ζ systems. The surface conductivity corrected curve then becomes fully determinate from experimental data over the entire range of κa values, just as

*That there should be such a minimum was already apparent from the occurrence of the maximum in the 'reciprocal mobility versus size at constant ζ ' curves; see ref. 2.

is the relaxation corrected curve, for which the corresponding constant value of ζ is obtained from the individual ζ values, by some sort of averaging, say.

We now cite some illustrations of the actual comparative application of the two methods discussed for the calculation of the theoretical mobility curves from experimental data. For this purpose we choose, from among the meagrely recorded data for systems where ζ may plausibly be assumed to remain constant†, some of Stackelberg *et al.*'s¹⁰ more recent and Mooney's¹¹ later set of data, because these are (a) fairly representative (showing everywhere the generally observed, and anticipated over this range of κa values, trend of increase of mobility with particle size), (b) complete (mobility variation over some fifty-fold increase of particle size being given; also the temperature is mentioned, that of 75°C being of special interest), and (c) reasonably precise. All details regarding the procedures followed in the case of the different theoretical treatments applied, the method of obtaining the data, and the minor assumptions made [$\sigma_2 = 0$, $\eta_2 = \infty$, KCl as the 'impurity' ($1 \times 10^{-5}N$) in Stackelberg's distilled water ($\kappa = 1 \times 10^5$)] having already been discussed earlier¹, only the final results are shown in Figs. 2-4. [The values of the constants used are^{6,12}: $\lambda_{K^{+}} = 66.56$ (20°), 73.52 (25°), 147.5 (75°); $\lambda_{Cl^{-}} = 69.15$ (20°), 76.34 (25°); $\lambda_{H^{+}} = 324.9$ (20°); $\lambda_{OH^{-}} = 182.5$ (20°), 367.0 (75°) ohm $^{-1}$ cm 2 ; also $\eta_1 = 10.05$ (20°), 8.95 (25°), 3.79 (75°) mpoise; $\epsilon_1 = 80.36$ (20°), 78.54 (25°), 62.62 (75°)]. Only the following need be mentioned regarding the intermediate steps in the relaxation calculations:

(i) Generally, all three methods³⁻⁵ were used for the ζ potential calculations except (a) in the $10^{-4}N$ and $10^{-3}N$ HCl (20°C) solutions, where (ζ being high, generally > 150 mV) only the Overbeek and Booth approximations were used; and (b) in Stackelberg systems¹³ where only one analytical approximation (Overbeek) was used besides the computational (W-L-O) method.

(ii) The particles being all negatively charged (U negative¹⁰, so also, therefore, is E') the ionic mobility correction to E' [applied for KOH (20°, 75°) solutions only] in the W-L-O method† was made in the appropriate manner¹, which signifies in brief, an interchange of the roles which the quantities $\partial E'/\partial m_{\pm}$ and $\partial E'/\partial m_{\pm}$ (taken with their appropriate signs, here positive) play in the ionic-mobility correction to E' expression for positive particles.

†The other possible assumption, that the surface charge density remains constant instead, would not alter the relaxation correction calculations. The surface charge densities calculated from the ζ potentials obtained by the computational equation⁸ show, however, the same lack of constancy as do the ζ potentials themselves, because, over the range of values of κa involved (> 20), the relation between the two is nearly linear.

‡The net corrections ($\Delta E'$, negative) are insignificantly small ($< 1\%$ of E'), because the counter-ion conductance factor ($m_{K^{+}}$) is not greatly different at any temperature from the reference value 0.184, in spite of $\lambda_{K^{+}}$ being substantially different from 70 ohm $^{-1}$ cm 2 at 75°. Here (KOH, 75°, 20°), $m_{\pm} < 0.184$; hence the corrections for the two ions have the same (negative) sign. (For NaOH, 25°C, ref. 1, $m_{\pm} > 0.184$ while $m_{\pm} < 0.184$ so the said corrections were opposite in sign, and $\Delta E'$ was always positive because the correction due to the slower counter-ion Na $^{-}$ was more significant).

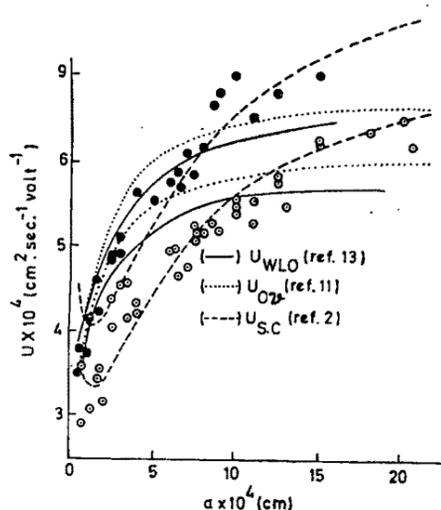


Fig. 2—Theoretically calculated electrophoretic mobilities compared with Stackelberg *et al.*'s data for paraffin oil (with 1% oleic acid) droplets of different sizes in distilled water (25°) [(●) oil weighted with C_2Cl_4 : $\zeta_{WLO(av)} = \zeta_{Ov(av)} = 90$ mV, $\zeta_{s.c.} = 120.4$ mV, $\sigma_s = 0.79 \times 10^{-9}$ ohm $^{-1}$; (○) oil weighted with $C_2H_2Cl_4$: $\zeta_{WLO(av)} = \zeta_{Ov(av)} = \zeta_{WLO} = 80$ mV, $\zeta_{s.c.} = 101.1$ mV, $\sigma_s = 0.83 \times 10^{-9}$ ohm $^{-1}$]

Also, only the following need be considered regarding the corresponding results:

(i) None of the calculated ζ values (not even ζ_{W-L-O}) remain constant over the range of κa values studied: (a) In intermediate ζ -systems [75-110 mV: $10^{-5}N$ (25°) KCl, and $10^{-3}N$ and $10^{-4}N$ KOH (20°)], $\zeta_{W-L-O} > \zeta_{Booth} > \zeta_{Overbeek}$ (the first difference, at $\kappa a \sim 15$, about 8% of ζ_{W-L-O} , and the second about 4% of ζ_{Booth}), but the differences decrease steadily with increasing κa to about 2% and 0% respectively at $\kappa a \sim 100$; (b) In high ζ -systems [~ 150 mV: HCl and $10^{-3}N$ KOH (75°)] the difference ($\zeta_{Booth} \sim \zeta_{Overbeek}$) is quite large ($\sim 12\%$ of either) at $\kappa a \sim 60$, and still remains significant ($\sim 6\%$) at $\kappa a \sim 100$. (c) In the very high ζ -system (> 200 mV: $10^{-4}N$ HCl), the calculated $\zeta_{Overbeek}$ values may thus be significantly different from the correct ζ -potentials involved, because of the anticipated still larger extent of uncertainty in the calculated ζ values.

(ii) The counter-ion being slower than the co-ion, and the particles being negatively charged, $\zeta_{Booth} > \zeta_{Overbeek}$ (as in ref. 1) in the KOH solutions¹³; the counter-ion being faster than the co-ion, $\zeta_{Overbeek} > \zeta_{Booth}$ in the HCl solutions.

The above findings are in general agreement with those reported^{1,13,14} and also with the theoretical anticipations⁵.

The final mobility versus κa curves (Figs. 2-4) deserve fuller discussion. It is seen that

(i) The experimental points in the systems shown lie mostly on the right ascending portion of the E' versus κa curves, and the relaxation and the surface conductivity corrections give an almost equally good account of the results over this range of κa values (for ζ not very high). The same is also true in case of most other data analysed^{1,13}.

(ii) For a few smallest particles ($a \sim 10^{-4}$ cm) in almost electrolyte-free (distilled water, $\kappa \sim 10^5$) solutions, the calculated surface conductivity correct

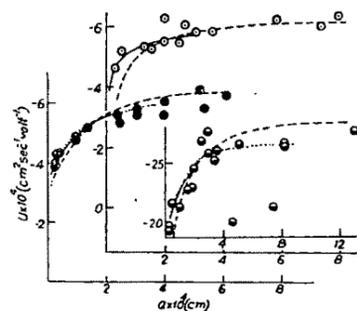


Fig. 3—Same as in Fig. 2 for Mooney's data for various organic oil droplets in aq. KOH solutions [(●) $10^{-4}N$, 20° ($\zeta_{WLO(av)} = \zeta_{Ov} = 87.14$ mV; $\zeta_{s.c.} = 95.5$ mV, $\sigma_s = 1.03 \times 10^{-9}$ ohm $^{-1}$); (○) $10^{-3}N$, 20°: $\zeta_{WLO(av)} = 81.6$ mV, $\zeta_{s.c.} = 90.1$ mV, $\sigma_s = 7.14 \times 10^{-9}$ ohm $^{-1}$]; (●) $10^{-3}N$, 75°: $\zeta_{WLO(av)} = 189.2$ mV, $\zeta_{Ov(av)} = 188.1$ mV; $\zeta_{s.c.} = 201.3$ mV, $\sigma_s = 1.89 \times 10^{-8}$ ohm $^{-1}$]

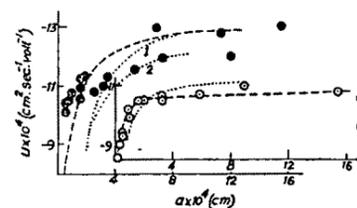


Fig. 4—Same as in Fig. 2 for aq. HCl solution (20°) [(●) $10^{-4}N$: $\zeta_{Ov} = 201$ mV (1), 187.2 mV (2), $\zeta_{s.c.} = 188.6$ mV, $\sigma_s = 1.52 \times 10^{-9}$ ohm $^{-1}$]; (○) $10^{-3}N$: $\zeta_{Ov(av)} = 162$ mV, $\zeta_{s.c.} = 152.1$ mV, $\sigma_s = 2.97 \times 10^{-9}$ ohm $^{-1}$]

mobility versus κa curves (Fig. 2) show the minimum mentioned at $\kappa a \sim 10-20$, while the relaxation corrected curves do not yet do so, and the experimental data are rather uncertain in this region to decide in favour of either, because of the experimental errors inherent in micro-electrophoretic measurements with such small particles. However, in better controlled experiments with synthetic latices, the position of the minimum has been established⁹ and reported to be in agreement with that predicted by the relaxation corrected curve corresponding to a suitable assumed value of ζ .

(iii) The ζ values obtained in the case of the relaxation and surface conductivity corrections generally agree* with one another within 10% in all the systems shown (see also refs. 1, 13). This may be considered encouraging in view of the fact that $\zeta_{W-L-O(av)}$ is generally obtained from the data for the smallest particles (κa small), whereas $\zeta_{s.c.}$ is obtained from those for the largest particles ($\kappa a > 100$ for $10^{-4}N$, and > 30 for $10^{-3}N$ solutions). Also, in spite of the scatter which the calculated ζ values show (due to experimental errors), it is still possible to discern, however, with increasing κa ,

*The linear extrapolations, made for deriving the $\zeta_{s.c.}$ and σ_s/σ_1 values reported, do not involve the least square method; also, the averaging represents more properly a suitable average choice over the calculated ζ_{WLO} or ζ_{Ov} values so as to ensure a good fit of the calculated mobility curves with experimental data.

In Stackelberg's distilled water (as also Mooney's $10^{-4}N$ KOH) systems the ζ values for U_{WLO} calculations were taken to be the same ($\zeta_{Overbeek}$) for which the $U_{Overbeek}$ curves were available¹¹, in order to be better able to compare the two mobility curves with the same value of ζ .

an increasing trend in ζ in most of the systems studied^{1,13}. [The sharp increase of ζ_{Overbeek} with decreasing κa in the HCl solutions is due to the inapplicability of the Overbeek approximation at the high ζ values involved (>150 mV); also the minimum at lower κa ($\sim 20-30$) in the alkali solutions only (cf. ref. 1) is too ill-defined to merit consideration]. This general increase in ζ (and the derived quantity 'surface charge density' σ) points most likely to the fact that the assumption that in systems of constant electrolyte concentration, ζ or σ_s , plausibly remain constant, is not fully justified.

(iv) The values of specific surface conductivity σ_s (see Figs. 2-4) calculated from σ_s/σ_1 for the different systems by making use of the specific conductivity (σ_1) values of the different media, show a tendency to increase with (a) increase of electrolyte concentration of the solutions at constant temperature, and (b) increase of temperature at constant concentration. Though the magnitudes of σ_s found generally agree with those obtained from the theoretical equations for surface conductance at a plane double layer¹⁵, it remains to be seen how far the said variations of σ_s do so. Also, it is interesting to note that the magnitudes ($\sim 10^{-4}$ cm) of the quantities σ_s/σ_1 for the surface conductivity corrected mobility curves shown to be in good agreement with the relaxation corrected curves in Fig. 1 are generally similar to those found in Fig. 2 for the surface conductivity corrected curves in distilled water systems; while the corresponding quantities found in $10^{-4}N$ and $10^{-3}N$ solutions (Figs. 3 and 4) are naturally smaller in order of magnitude.

Conclusion

As is well known¹⁶ the relaxation and the normal surface conductivity effects are fundamentally identical, being essentially the corrections to include the effect of polarization of the electrical double layer near the charged particle surface. The relaxation treatment is, however, more comprehensive and rigorous mathematically. The dependence of the mobility on the characteristics of the ions in solution, such as valency, mobility (counter-ion, co-ion effect), etc., can not yet be reproduced by the surface conductivity correction method, at least in the present stage of development of the latter. However, the complete treatment (computation) of the relaxation effect is as yet available only up to moderately large values of ζ (≤ 150 mV), while the analytical approximations thereto (which involve rather tedious calculations) are known to be incomplete above $\zeta \sim 100$ mV (see Fig. 1), and

distinctly inaccurate for still higher values of ζ (cf. the HCl systems, Fig. 4). The surface conductivity correction method, which is known to give equally correct results for low ζ , has thus a distinct advantage for application to high ζ systems also. Moreover, the precise contribution of the ionic diffusion terms in the equations describing the steady state condition in the atmosphere round the moving charged particle in the derivation of the relaxation corrected electrophoresis equation is yet to be assessed properly; the performance of the surface conductivity correction method which essentially ignores this effect only while considering the others involved, would show that the said contribution is not very significant and certainly not decisive. This being so, the question becomes pertinent whether in the numerous instances, where the polarization of the atmosphere⁶ effect would profitably be taken into account, it is worth while to go in for a rigorous treatment by way of relaxation correction, or else a tolerably approximate surface conductivity correction treatment could profitably be used instead¹⁷.

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