

### 775. *Electrophoresis of Gold and Silver Particles.*

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The electrophoretic behaviour of particles of gold and silver in suspension in aqueous electrolytic solutions has been studied. Although the particles are conducting, the electrokinetic potentials calculated from the electrophoretic velocities, with the assumption that they are non-conducting, give results in reasonable agreement with those obtained from measurements of streaming currents. An explanation for this observation is suggested. The data are used to calculate electrokinetic charge densities for the various systems studied, and the adsorption of various ions by gold and silver is discussed.

THE electrokinetic potential ( $\zeta$ ) at the metal-solution interface is important in connection with adsorption and corrosion processes. In the past its determination has proved difficult because of the conducting nature of the metal which has rendered the usual techniques for measuring  $\zeta$  inapplicable. For example, Kruyt and Oosterman<sup>1</sup> and Zackryawski<sup>2</sup> have pointed out the difficulties encountered in attempting to measure  $\zeta$ -potentials with metallic capillaries by use of the streaming potential technique.

Eversole and Boardman<sup>3</sup> measured the streaming current through a platinum capillary by using an external measuring circuit with a resistance much lower than that of the capillary wall itself. Recently Hurd and Hackerman<sup>4</sup> have improved this technique, and used it to determine the  $\zeta$ -potentials of gold, platinum, and silver in distilled water, and in dilute solutions of potassium chloride and potassium hydroxide.

The more conventional method of measuring  $\zeta$ -potentials, namely, that of electrophoresis, has been somewhat neglected in this particular field, because it has been considered that the theory and assumptions involving the boundary conditions embodied in the classical theories of electrophoresis<sup>5,6</sup> would be no longer valid for conducting particles, where some kind of charge transfer involving discharge of ions takes place at the solid-liquid interface.

However, it appears that metals often behave effectively as non-conductors in electrophoresis, since the mobilities of colloidal metal particles are usually of the same order of magnitude as those of non-conducting particles. If Henry's theory<sup>6</sup> applied strictly, the mobilities would be extremely small, as the conductivity of the metal would be large compared with that of the electrolyte. The absence of conduction may be due either to

<sup>1</sup> Kruyt and Oosterman, *Kolloid-Beih.*, 1938, **48**, 377.

<sup>2</sup> Zackryawski, *Phys. Z.*, 1900, **2**, 146.

<sup>3</sup> Eversole and Boardman, *J. Phys. Chem.*, 1942, **46**, 914.

<sup>4</sup> Hurd and Hackerman, *J. Electrochem. Soc.*, (a) 1955, **102**, 571; (b) 1956, **103**, 316.

<sup>5</sup> Smoluchowski, *Bull. Acad. Sci. Cracovie*, 1903, 182; Huckel, *Phys. Z.*, 1924, **25**, 205.

<sup>6</sup> Henry, *Proc. Roy. Soc.*, 1931, *A*, **133**, 106.

the presence of a thin layer of non-conducting material (*e.g.*, oxide or hydroxide) between the metal and the electrolyte, or to polarisation at the metal-solution interface.<sup>7,8</sup>

The present paper, part of a study of adsorptive properties of noble-metal powders, deals with the application of the electrophoretic technique to suspensions of metal particles in aqueous media.

#### EXPERIMENTAL

*Materials.*—Silver and gold were chosen in order to avoid corrosion difficulties.

Silver powder was prepared by electrochemical precipitation from silver nitrate solution by fine copper powder previously cleaned in warm 5% oxalic acid solution. The precipitated silver was washed in alcohol, and a sample of silver powder, particle size  $\sim 6 \mu$ , was separated by fractional sedimentation. This sample was thoroughly washed in conductivity water before being treated with dilute ammonia solution to remove silver oxide. It was finally washed six times with conductivity water by successive centrifugation and resuspension.

Gold powder, particle size  $\sim 2 \mu$ , was separated from a spectrographically pure sample supplied by Johnson, Matthey and Co. The sample was washed in dilute ammonia solution, degreased in acetone and ether, and finally washed for several days in successive changes of conductivity water.

"Stock" solutions, containing approximately 1% of the metal powder, were made up in conductivity water, and aged for two days before being diluted 100-fold for use. Although none of the dilute suspensions showed any ageing effects, one hour was allowed to elapse before electrophoretic examination.

Electrolytes used in the examination were potassium chloride, barium chloride, lanthanum chloride, hydrochloric acid, and sodium hydroxide. Wherever possible, these were prepared from "AnalaR" materials by further recrystallisation. The last three substances were standardised by conventional techniques. Solutions were prepared from conductivity water, obtained by passing good-quality distilled water through a mixed-bed ion-exchange column. The specific conductivity of the water was in the neighbourhood of  $1 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ .

*Apparatus.*—Electrophoretic velocities were determined by a micro-electrophoretic technique, using an apparatus similar to that described by Alexander and Sagers.<sup>9</sup> The optical system was arranged to allow horizontal viewing of the particles, in order that the suspension might be in focus for as long as possible.

A Mattson<sup>10</sup> type electrophoresis cell (with grey platinum electrodes), immersed in a water bath at room temperature, was used. The "zero level" was located by application of Henry's optical formula.<sup>11</sup> The mobility of approximately 40 particles was recorded in both directions for each suspension. Although the scatter was sometimes quite large ( $\pm 10\%$ ), the average value was reproducible within 5%. When the mobility was rather small ( $< 10^{-4} \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$ ), a velocity-depth graph was constructed, and the velocity at the zero level determined by interpolation.

Measurements of electrophoretic velocities in the various electrolyte solutions were made over the range of concentration  $10^{-5} \text{N}$ — $10^{-2} \text{N}$ .

All experiments were carried out at room temperature ( $20^\circ \pm 5^\circ$ ), and the appropriate values of physical constants, such as viscosity and dielectric constant, were used in each case. No significant trend in  $\zeta$ -potential with temperature was observed.

#### RESULTS

$\zeta$ -Potentials were calculated from the well-known electrophoresis equation:

$$\zeta = \frac{f\pi\eta V_e}{DE} \dots \dots \dots (1)$$

where  $V_e$  is the electrophoretic velocity in cm./sec. under an applied field strength  $E$  (e.s.u./cm.) and  $D$  and  $\eta$  are the dielectric constant and viscosity of the dispersion medium respectively;  $f$  is a numerical factor whose value depends upon the size and shape of the dispersed particles and the thickness of the ionic double layer surrounding them ( $1/\kappa$ ).

<sup>7</sup> Frumkin, *J. Colloid Sci.*, 1946, **11**, 277.

<sup>8</sup> Kruyt, "Colloid Science," Elsevier, London, 1952, Vol. I, pp. 209, 236.

<sup>9</sup> Alexander and Sagers, *J. Sci. Instr.*, 1948, **25**, 374.

<sup>10</sup> Mattson, *J. Phys. Chem.*, 1933, **37**, 223.

<sup>11</sup> Henry, *J.*, 1938, 997.

The value of  $f$  can be computed from Henry's equation<sup>12</sup> and when  $\kappa a > 100$  (where  $a$  is the radius of the particle),  $f \rightarrow 4$ , and is independent of the particle shape.

In the present work, this condition was only satisfied in the more concentrated solutions, *viz.*,  $>ca. 5 \times 10^{-4}N$  for gold suspensions and  $>ca. 10^{-4}N$  for silver suspensions. However, the correction to be applied was rather small, *e.g.*, in  $5 \times 10^{-5}N$  solutions the correction was 11% for gold suspensions and 4% for silver suspensions.

The variation of  $\zeta$ -potential (calculated in this way) with concentration is illustrated in Figs. 1 and 2.

An attempt was also made to compute the effect of the "time of relaxation" and surface conductance upon the  $\zeta$ -potential. The effect of the former will be small in uni-univalent electrolytes,<sup>8</sup> and can be neglected. The results of the analysis using Overbeek's equation<sup>12</sup> for barium chloride and lanthanum chloride suspensions are recorded in Table 1 where  $\zeta'$  and  $f'$  refer to the corrected values of the electrokinetic potential and the "Henry factor" respectively.

TABLE 1. Corrections for relaxation effect in  $BaCl_2$  and  $LaCl_3$  suspensions.

System	Normality	$\zeta$ (mv)	$1/f$	$\zeta'$ (mv)	$1/f'$
Au- $BaCl_2$ .....	$10^{-5}$	41.1	4.57	46.3	4.95
" .....	$5 \times 10^{-5}$	33.1	4.23	34.2	4.37
" .....	$10^{-4}$	29.8	4.17	30.2	4.23
Ag- $BaCl_2$ .....	$10^{-5}$	28.9	4.21	29.7	4.32
" .....	$5 \times 10^{-5}$	24.0	4.10	24.0	4.10
Au- $LaCl_3$ .....	$10^{-5}$	22.5	4.35	23.7	4.58
" .....	$5 \times 10^{-5}$	13.7	4.16	13.8	4.17
" .....	$10^{-4}$	9.7	4.13	9.7	4.13
Ag- $LaCl_3$ .....	$10^{-5}$	11.4	4.21	11.4	4.21

The corrections to be applied are negligible at all concentrations for silver suspensions; for gold, the corrections are negligible when the ionic concentration is greater than  $5 \times 10^{-5}N$ .

Booth<sup>13</sup> and Henry<sup>14</sup> have shown theoretically that the effect of surface conductance would be to lower the mobility of a particle by a factor  $1 + (\lambda_s/\lambda a)$  where  $\lambda_s$  is the surface conductance and  $\lambda$  is the bulk conductance.

The theoretical surface conductance can be calculated from Urban, White, and Strassner's equation, derived<sup>15</sup> on the basis of a simple double-layer theory. This was done for the metal-KCl and metal-HCl interfaces, and the results are recorded in Table 2, together with the

TABLE 2. Electrokinetic potentials corrected for surface conductance.

System	Normality	$\zeta$ (mv)	$10^{10}\lambda_s$ (ohm <sup>-1</sup> )	$\lambda$ (ohm <sup>-1</sup> cm. <sup>-1</sup> )	$\frac{\lambda_s}{\lambda a}$	$\zeta'$ (mv)
Au-HCl .....	$1 \times 10^{-5}$	25.6	0.41	$4.259 \times 10^{-6}$	0.096	28.1
" .....	$5 \times 10^{-5}$	18.0	0.57	$2.125 \times 10^{-5}$	0.026	18.5
" .....	$1 \times 10^{-4}$	14.9	0.63	$4.243 \times 10^{-5}$	0.015	15.1
Ag-HCl .....	$1 \times 10^{-5}$	37.5	0.67	$4.259 \times 10^{-6}$	0.052	39.5
" .....	$5 \times 10^{-5}$	26.7	0.97	$2.125 \times 10^{-5}$	0.015	27.1
" .....	$1 \times 10^{-4}$	18.6	0.85	$4.243 \times 10^{-5}$	0.007	18.8
Au-KCl .....	$1 \times 10^{-5}$	45.0	0.17	$1.490 \times 10^{-6}$	0.113	50.1
" .....	$5 \times 10^{-5}$	41.0	0.30	$7.420 \times 10^{-6}$	0.040	42.7
" .....	$1 \times 10^{-4}$	37.7	0.36	$1.480 \times 10^{-5}$	0.024	38.6
Ag-KCl .....	$1 \times 10^{-5}$	44.0	0.17	$1.490 \times 10^{-6}$	0.036	45.6
" .....	$5 \times 10^{-5}$	40.5	0.30	$7.420 \times 10^{-6}$	0.013	41.0
" .....	$1 \times 10^{-4}$	38.9	0.40	$1.480 \times 10^{-5}$	0.009	39.3

corrected  $\zeta'$  values. However, the experimental data tabulated in the literature<sup>8</sup> suggest that theoretical values for surface conductivity are somewhat lower than experimental values. For this reason, the corrected  $\zeta$ -potential in Table 2 may be somewhat lower than the "true" value.

As it is, the application of the correction leads to a 10% increase in the value of  $\zeta$  calculated for suspensions of gold in  $10^{-5}N$  solutions, and about 2% in  $10^{-4}N$  solutions; with silver the corresponding corrections are about 4%, and less than 1%, respectively.

<sup>12</sup> Overbeek, "Advances in Colloid Science," Interscience, New York, 1950, Vol. III, p. 113.

<sup>13</sup> Booth, *Trans. Faraday Soc.*, 1948, **44**, 955.

<sup>14</sup> Henry, *ibid.*, p. 1021.

<sup>15</sup> Urban, White, and Strassner, *J. Phys. Chem.*, 1935, **39**, 311.

In calculating the charge per unit area of surface ( $\sigma_2$ ) from the  $\zeta$ -potential, the expression given by Verwey and Overbeek<sup>16</sup> for an infinitely large plane interface, was used:

$$\sigma_2 = \left( \frac{NDkTC}{2\pi} \right)^{\frac{1}{2}} \left\{ \frac{1}{z_-} \left[ \exp(z_- e\zeta/kT) - 1 \right] + \frac{1}{z_+} \left[ \exp(-z_+ e\zeta/kT) - 1 \right] \right\}^{\frac{1}{2}}$$

where  $T$  is the absolute temperature,  $C$  the ionic concentration, and  $z_+$  and  $z_-$  are the valencies of the cation and anion respectively.

The assumptions implicit in the use of this equation are (a) that it can be used for double layers of finite size,<sup>17</sup> and (b) that the boundary between the Stern and Gouy layers coincides with the electrokinetic slipping plane, hence  $\psi_a$  the boundary potential, can be equated to  $\zeta$ .

#### DISCUSSION

(a) *Comparison of the Results with Those obtained from Streaming Currents.*—The only reliable electrokinetic data available for the gold- and silver-solution interfaces are those of Hurd and Hackerman,<sup>4b</sup> which are given in Table 3 for comparison.

TABLE 3. Graphical electrokinetic potential data of Hurd and Hackerman by the streaming current technique.

Normality	$\zeta$ -Potential (mv)			Normality	$\zeta$ -Potential (mv)		
	Au-KCl	Au-KOH	Ag-KCl		Au-KCl	Au-KOH	Ag-KCl
$1 \times 10^{-5}$	54	65	55	$5 \times 10^{-4}$	32	78	23
$5 \times 10^{-5}$	48	73	43	$1 \times 10^{-3}$	24	67	18
$1 \times 10^{-4}$	44	80	36				

For the gold-potassium chloride system, the micro-electrophoretic technique gives results which are *ca.* 5 mv more positive than those of Hurd and Hackerman. However, this difference decreases with increasing electrolyte concentration, and at  $10^{-3}N$  identical  $\zeta$ -potentials (24 mv) are obtained. For the silver-potassium chloride interface there is good agreement over the middle portion of the concentration range studied, but in dilute solution ( $10^{-5}N$ ) and in concentrated solution ( $10^{-3}N$ ) the  $\zeta$  values differ by *ca.* 10 mv. (Hurd and Hackerman reported variations of  $\pm 4$  mv in the results obtained with different silver capillaries in distilled water, although they did not record the degree of variation in potassium chloride.)

It was also possible to compare our results for the gold-sodium hydroxide interface with those of Hurd and Hackerman for the gold-potassium hydroxide interface, since the two cations, sodium and potassium, have similar adsorption properties. Although the variation of  $\zeta$  with concentration is similar in the two cases, the values differ by *ca.* 20 mv.

It is realised that this type of comparison is restricted, even when the adsorbents are identical, because ultimately their surface properties depend upon their pretreatment. Any difference in the character of the surfaces studied would probably be more apparent in alkaline solutions than in neutral salt solutions, owing to specific adsorption of the hydroxide ion.

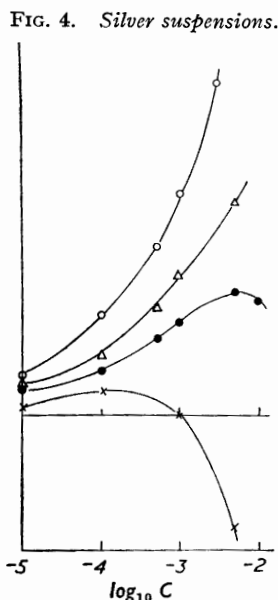
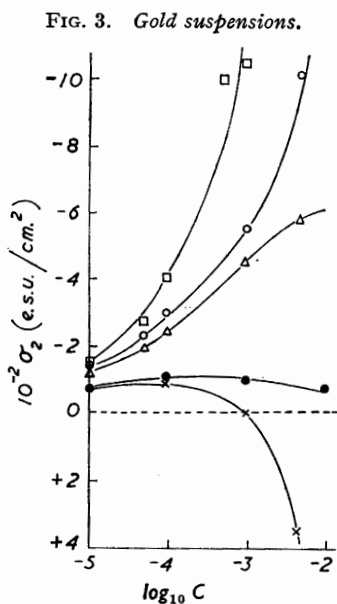
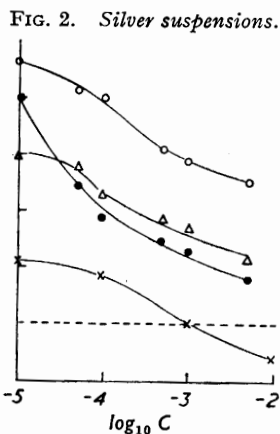
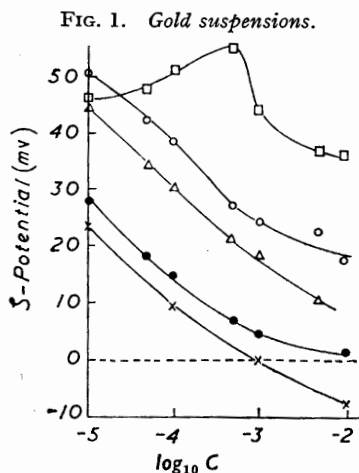
In fact, Hurd and Hackerman etched their metal capillaries with dilute acid and followed this with copious washing, a treatment which would tend to activate the surface and probably result in greater adsorption of hydroxide ion.

The great difficulty usually experienced in reproducing electrokinetic results of other workers, even using the same technique, being borne in mind, there is satisfactory agreement between our results (from electrophoretic data and the assumption that the particles are effectively non-conducting) and those of Hurd and Hackerman (from streaming current).

<sup>16</sup> Verwey and Overbeek, "Theory of the Stability of Lyophobic Colloids," Elsevier, London, 1948, p. 33.

<sup>17</sup> Müller, *Kolloid-Beih.*, 1928, **26**, 257.

Overbeek<sup>12</sup> states that complete electrical polarisation of small metallic particles can be produced by a polarisation tension of a few microvolts. In the present experiments, where particles with diameters of the order of  $10\ \mu$  were subject to an electrical field of strength about 10 volts/cm. the polarisation potential over the particle was of the order



For all diagrams:  $\circ$  KCl,  $\bullet$  HCl,  $\triangle$  BaCl<sub>2</sub>,  $\times$  LaCl<sub>3</sub>,  $\square$  NaOH.

of 10 mv, so that virtually complete polarisation would occur. In these circumstances, use of the electrophoretic method for metallic particles appears to be permissible.

(b) *Adsorption of Ions by Gold and Silver.*—The  $\zeta$ -potential at the metal-solution interface, for all the electrolytes studied here, was negative in dilute solutions, indicating a preponderance of anions in the fixed part of the electrical double layer. As the ionic content of the suspension was increased the  $\zeta$ -potential decreased, the rate of decrease depending upon the type of cation present (Figs. 1 and 2). The increasing negative charge

indicates that preferential adsorption of the anion is taking place, except in the case of lanthanum chloride suspensions at ionic concentrations greater than  $10^{-3}N$ , where  $\zeta$  (and hence  $\sigma_2$ ) becomes positive.

For both barium chloride and lanthanum chloride solutions, the charges and potentials are lower than for corresponding concentrations of potassium chloride, owing to the increased ease with which the bi-valent and ter-valent cations are taken into the fixed (Stern) part of the double layer. By comparing the values of  $\sigma_2$  for the highest electrolyte concentrations studied (Figs. 3 and 4), the following cation adsorption series can be derived:  $K^+ < Ba^{2+} < H^+ < La^{3+}$ . On general grounds, it is to be expected that in such a series of salts (with common anion), and in the absence of any specific effect, the valency of the cation would be of prime importance. The position of the  $H^+$  ion in the series appears to be somewhat anomalous, indicating the occurrence of specific adsorption.

Preferential adsorption of a multivalent ion into the Stern layer is shown to a considerable extent in suspensions containing lanthanum chloride, for which the isoelectric point is reached at concentrations approaching  $10^{-3}N$ , the surface thereafter becoming highly positively charged. Owing to the small value of the electrophoretic mobility for particles in suspensions of hydrochloric acid and lanthanum chloride at relatively high concentrations, the accuracy of the measurements is lower than in other cases. However, the  $\zeta$ -potential is so low at these concentrations that the uncertainty in mobility does not lead to an error in  $\zeta$  of more than about 1 mv.

In most cases, the charge density bears a linear relation to the cube root of the concentration and at zero concentration the surface charge is zero or very nearly so.

It is noteworthy that this type of relation has been observed before with silica and carborundum surfaces in solutions of acids and salts of various valency types.<sup>18</sup>

Values of  $A$  and  $B$  (the latter zero unless stated) in the equations  $\sigma_2 = 1000AC^{\frac{1}{3}} - B$  governing the adsorption, are:

Gold suspensions: NaOH,  $A$  12.0,  $B$  140; KCl,  $A$  5.4; BaCl<sub>2</sub>,  $A$  4.6

Silver suspensions: KCl,  $A$  6.85; BaCl<sub>2</sub>,  $A$  4.2; HCl,  $A$  2.4

Finally these results indicate the non-ionogenic nature of the gold and silver surfaces, since the charge density tends to zero as the bulk ionic concentration approaches infinite dilution.

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<sup>18</sup> Benton and Elton, "Proc. 2nd Int. Congr. Surface Activity," Vol. III, Butterworths, London, 1957, p. 28.