Some Anomalies Resolved in Colloid Mobility by Electrodeposition Analysis: Depletion *versus* Turbulence

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Since the logarithm of the sol electrodeposition current varies linearly with time (as required by theory) only if uniform composition is maintained by turbulence, a mechanism involving vortical motion is shown to set in after a period and to account for hitherto unremarked 2-fold factors between parameters of the theory, as well as other observations.

Colloid mobilities u are obtained *inter alia* from photon correlation spectroscopy (PCS), or from sol electrodeposition[1] between closely spaced cylindrical electrodes (gap $L \approx$ 5 mm usually). The current i decay is observed[2] to become logarithmic with time t, the slope yielding a transit time τ for traversal by a typical particle of the distance L, hence u may be calculated. The adduced[2] theory, however, rests on unfulfilled diffusion conditions, an initial non-linearity remains unaccounted for, and there is, we find, an unexplained factor of just 2 between the actual initial current i_0 and that logarith-

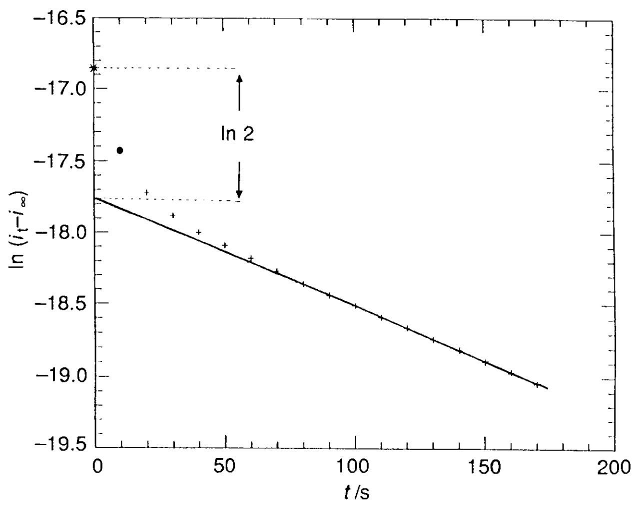

Fig. 1 Plot of ln (i_t − i_∞) against t (where i_∞ is small background current) showing 2-fold ratio between back-extrapolated and observed current values at t = 0, as also seen (without explanation) in seminal paper.[2] (Colloid was carbon black + surfactant $\mathrm{Zr^{IV}}$ mixed-octanoate + acrylic polymer Neocryl B-702 in mixed octane medium.)

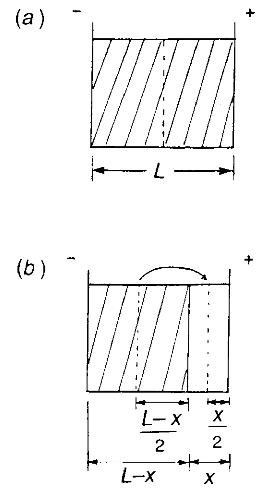

Fig. 2 The gap between the electrodes depicted as length L. (a) Under depletion conditions the average distance traversed[2] is $L/2$ (all sol material if concentrated in halfway plane, dotted, involves nil net vectorial motion; its transfer then to cathode involves pathlength $L/2$). (b) If depleted region on the right is to be restored to uniform distribution by back-transfer (curved arrow) from the populated region, left, then the extra backward distance is $L/2$. One half of the initial population needs to be thus back-transferred to maintain uniformity.

mically back-extrapolated to t = 0, i_0' (Fig. 1). (A related factor 2 also arises between u values calculated from i_0 and those from τ.) We propose a novel mechanism encompassing the observed phenomena which avoids these shortcomings and yields u values confirmed by PCS.

In summary recapitulation,[3] $-\mathrm{d}n/\mathrm{d}t \propto n\mathrm{v} = n/\tau$ (n = particle number density, assumed uniform, $\mathrm{v} = uE$ where E = field), hence $n = n_0 \exp(-t/\tau)$. Given $i = q\mathrm{v}nA$ (q = average particle charge, A = electrode area), $\ln(i/i_0) = -t/\tau$, as derived.[2] However, for compositional uniformity, the depletion arising from deposition needs to be replenished by diffusion,[2] but since the rate of diffusion, from a simple model, is $\ll$ rate of migration (by $\approx 10^3$ fold), this requirement is not met, and compositional uniformity is simply not maintained in the first instance. Instead, a sol-free depletion region grows, extending a distance x, Fig. 2, from the repelling electrode (anode in our

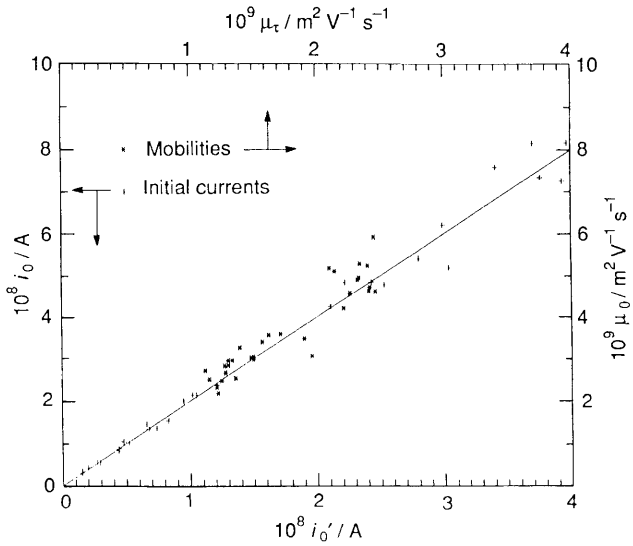

Fig. 3 Plot of observed i_0 value *versus* back-extrapolated i_0' value (both corrected for small background current) for sols as Fig. 1 but of various compositions and at a range of applied potentials. Also, plot of u_0 calculated from i_0 *versus* u_τ from τ. Line has a slope of exactly 2.

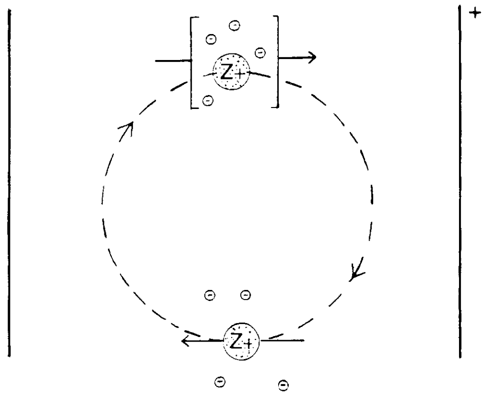

Fig. 4 Simplified diagram of mechanism of vortex-controlled motion. The vortex is maintained by the field-driven motion of the (nether) Z+ sol particle without surrounding anion migration, and in turn effects the counter-field motion of [(upper) Z+ sol particle plus counterbalancing anions] as [square-bracketed] neutral fluid. Both sol particles move with speed v towards electrodes. (In a real vortex, many sol particles will be involved, in pro- and anti-field motions in approximatlly equal number.)

experiments), such depletion being clearly visible in experiments in glass tubes with endface electrodes. In the depletion region, charge-uncompensated anions maintained by the field give rise to a growing counter-field which decelerates the sol particles, giving the sharp initial current fall; the net field at sol particles may decrease as $\approx 1/x$ or approximately as $1/t$, and the consequent linearity expected of i *versus* ln t is indeed found for the initially decremental excess current.

Growing instability from the free-charge accumulation then results in the convulsive onset of turbulence, which we suggest persists as vortices on the micro scale, a 'circular motion' indeed being observed[3] in sol electrodeposition. This restores uniformity of composition (Fig. 2) and, so, justifies the ln(i), t relationship, allowing calculation of u values which agree with PCS measurements.

The external current up to the onset of turbulence is capacitor-like, the sol deposited being charge-uncompensated (and, in post-deposition short-circuit experiments, slowly releasing *just* the charge so entrapped). With the turbulent convulsion, anions, electrochemically depleted at the anode by the initial current pulse at $t = 0$, are restored in concentration, and in our sols, reactions $RCO_2^- \rightarrow RCO_2^\cdot + e$, $RCO_2^\cdot \rightarrow R^\cdot + CO_2$ and $2R^\cdot \rightarrow R_2$ ensue.[4] The corresponding cathode electrochemistry involves the metal cation required[5] as a surfactant component attached to sol particles: here $Zr^{IV} + 2e \rightarrow Zr^{II}$ is involved,[6] and neutral solid, now *not* storing charge, is thus deposited.

In restoring uniformity, the turbulence causes the average particle to traverse an *extra* distance $L/2$ over and above the pathlength, also $L/2$, on average traversed under depletion conditions, Fig. 2. This confers the factor 2 on i_0/i_0', and on mobilities from i_0 and from τ. Both relations are plotted in Fig. 3. Vortical motion giving local turbulence would allow the extra distance to be traversed *via* a backward transport of sol + counter-anion, *i.e.* neutral fluid, on the far side (diametrically opposite, in the vortex, Fig. 4) of current-bearing charge motion by sol particle alone. The former also allows nil-current motion of anions to the anode, to maintain the electrochemistry occurring there.

This interpretation provides for the (late) establishment of uniform composition, the initial logarithmic non-linearity, the post-deposition charge release, the two 2-fold relationships, a vortical turbulence mechanism for both replenishment and the counter-ion motion required for the electrochemistry, and, additionally, for sol behaviour (the circular motion) in other circumstances. It also provides three virtually independent sources of $u : i_0$, i_0' and τ, concordance between which (as here) provides strong support for the proposed mechanism.

Received, 13th February 1991; Com. 1/00675D

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