[Contribution from the Avery Laboratory of Chemistry of the University of Nebraska]

A Study in Electrokinetics

By J. D. Quist* and E. Roger Washburn

In 1878 Dorn[1] discovered that when a powdered solid settled through a tube full of liquid a sedimentation potential, E, was produced between the upper and lower ends of the tube. Since that time no worker,[2,3,4,5] using water and water solutions, has obtained quantitative results for that experimental manifestation of electrokinetics. Only J. Stock,[6] using organic liquids, was able to harmonize his results with the familiar electrokinetic equation,[7] in which ζ is the poten-

$$E = \zeta DPR/4\pi\eta$$

tial existing across the boundary between the movable and immovable layers of liquid at the solid–liquid interface; D is the dielectric constant of the liquid; P is the hydrostatic pressure difference; R is the specific resistance of the liquid; and η is the coefficient of viscosity.

All the factors in the equation are measurable experimentally except ζ, which can be calculated when the other factors are known. For a given combination of powdered solid and liquid all the factors are constant except E and P. P equals the apparent weight of the material suspended in or settling through the liquid in the tube, between the electrodes.

The factor P can be further resolved into experimentally measurable quantities, as follows:

$$P = W(d - d_0)/Ad$$

in which W is the actual weight of material between the electrodes; d is the density of the powdered solid; d_0 is the density of the liquid, and A is the cross-sectional area of the tube. d, d_0 and A are constants for a given combination of powdered solid and liquid, studied by use of a given piece of apparatus. The factor W is variable, and changes in the value of W should cause corresponding changes in the value of the sedimentation potential, E.

It was the purpose of this research to show that the Dorn effect will also yield data, for water and water solutions, which agree with the above equation. That purpose will have been accomplished when it is shown that E is directly proportional to W whenever a given solid powder is allowed to settle freely and uniformly from the upper to the lower end of a tube full of water or a water solution.

Apparatus.—Since the potentials measured in this study originated in circuits of high resistance, it was necessary to use an instrument capable of detecting very small currents. The Leeds and Northrup no. 7673 thermionic amplifier was used in conjunction with a L. and N. student potentiometer, a no. 2500-b, type R galvanometer and a no. 2100 lamp and scale reading device. With this assembly of apparatus potentials could be measured with a precision of ±0.1 millivolt. The sensitivity was approximately 0.1 millivolt per millimeter of the scale.

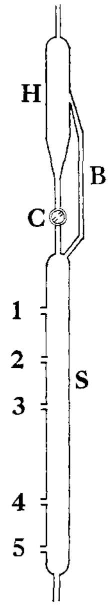

Fig. 1.

The apparatus which will be called the fall tube, Fig. 1, used in the experimental work, was constructed to meet the requirements for: (1) adequate control of the quantity of powder suspended in or settling through the liquid in the tube, between the electrodes; (2) protection against contamination; (3) repetition of measurements; (4) elimination of turbulence; (5) convenient removal and/or replacement of electrodes.

The fall tube was all glass and consisted of two parts: an upper compartment or "holder," H, and a lower compartment or "settling tube," S. These two compartments were connected by a 4 mm. stopcock, C, and a side-arm or bypass, B. The lower compartment was 64 cm. long and 38 mm. in diameter. To the lower end was sealed a 10 cm. length of 6 mm. tubing; to the upper end was sealed the stopcock; 1 cm. from the lower end was sealed a no. 5 ground joint (outside part); at distances of 10, 30, 40 and 50 cm. above the lower ground joint were sealed four other no. 5 ground joints, numbered (1), (2), (3), (4), (5), Fig. 1. The ground joints served to permit insertion of the electrodes which were fixed into the inside parts of the ground joints, so that they did not come in contact with the falling powder.

The "holder" was 38 mm. in diameter and 26 cm. long and was tapered at the lower end. The tapered end was sealed to the 4 mm. stopcock, while a 5 cm. length of 8 mm. tube was sealed to the upper end.

The bypass of 8 mm. tube, which was sealed into the upper end of the lower compartment and into the wall of the "holder" about 10 cm. from its upper end, served to permit the displacement of liquid when the powder flowed from

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[1] E. Dorn, *Wied. Ann.*, **10**, 46 (1880).

[2] J. Billitzer, *Ann. phys.*, [4] **11**, 937 (1903).

[3] H. Freundlich and E. Makelt, *Z. Elektrochem.*, **15**, 161 (1909).

[4] E. F. Burton and J. E. Currie, *Phil. Mag.*, [6] **49**, 194 (1925).

[5] H. B. Bull, *J. Phys. Chem.*, **33**, 656 (1929).

[6] J. Stock, *Anz. Akad. Wiss. Krakau*, (A) 131 (1913); (A) 95 (1914).

[7] M. v. Smoluchowski, "Graetz Handbuch der Elektrizität und des Magnetismus," Verlag Johann Barth, Leipzig, 1914, Vol. 2, p. 366.

the "holder," through the stopcock, into the "settling tube."

To the stopcock was attached a graduated scale which made it possible to reproduce settings of the stopcock. The 4-mm. hole bored through the stopcock plug was enlarged to a diameter of 6.4 mm. about half its length.

The fall tube was shielded against electrostatic effects by means of a wire screen grounded to a water pipe.

Procedure.—The apparatus was filled by drawing the liquid to be studied up into the tube with suction. When the level of liquid was above the point where the side arm was sealed into the "holder," the powder was run into the top end of the "holder" through a funnel. The whole tube was then filled with liquid and closed at both ends. Two of the electrodes were then connected to the amplifier and allowed to come to equilibrium, after which the stopcock was opened and the sedimentation potentials set up by the falling powder were measured. After the powder had flowed from the "holder," it was returned by inverting the tube.

Preliminary work with water and acid solutions as liquids and sand as powdered solid, showed that electrodes of platinum, nickel, nichrome and carbon were not suitable for this work because they would not come to a constant equilibrium potential, were too easily polarized, and subject to oxygen electrode effects. Silver chloride electrodes[8] of sufficient surface area to prevent polarization were therefore used to obtain data with 40–50 mesh Pyrex glass powder. The powder was first soaked in *aqua regia*, then washed with distilled water and dried in a flask which was evacuated while being heated over a hot plate. The glass was kept in the evacuated flask until used. The water used was redistilled from alkaline permanganate, using a block tin condenser. Solutions were mixed in the fall tube by adding to the distilled water in the tube a quantity of solution which, when diluted to the volume of the tube (720 ml.), would give the desired concentration. The sedimentation potentials were measured after the powder had been flowing a minute or two to assure a steady rate of flow of powder. The apparatus was cleaned with "cleaning solution," then rinsed with boiling water, and steamed out before any measurements were made.

Results and Discussion

The Effect of Variations in W upon the Magnitude of E.—The magnitude of the sedimentation potential, E, should be directly proportional to the weight, W, of material suspended or falling between the electrodes. The factor, W, is equal to the product of the quantity of powder, q, flowing per minute through the stopcock times the time, t (minutes), required for the powder to fall from the upper to the lower electrode; or, $W = qt$. The time, t, was directly proportional to the distance between the electrodes, hence E should be directly proportional to the distance between the electrodes. This was found to be true, within experimental error. The potential gradient was uniform throughout the length of the tube.

A study also was made of the variation of E with rate of flow of powder. The data are summarized in Table I. Values of W were calculated from the equation $W = qt$. The time, t, required for the powder to fall from the upper to the lower electrode was found by taking the average of about 90 measurements. Values of q were obtained by measuring with a stopwatch the periods of time required for weighed quantities of powder to pass through the stopcock.

The sedimentation potentials were found to be almost directly proportional to the rate of flow, q, and the weight, W, of material between the electrodes at any time. There was a slight tendency for the potentials to fall off at larger values of W or q. The most probable cause of the deviation was the change in the conductivity because of surface conductivity. As is evident from the electrokinetic equation, E is directly proportional to R. The specific conductivity is the sum of the specific conductivity of the liquid and the surface conductivity of the particles suspended in the liquid. The surface conductivity increases as W increases, or R varies inversely with W, but the proportionality is not direct.

TABLE I[a]

DEPENDENCE OF THE POTENTIAL, E, UPON RATE OF FLOW

Rate of flow, q	Values of E				Powder between electrodes, W
	Water	Concn. of NaCl, mols/l. 5×10^{-7}	1×10^{-5}	1×10^{-4}	
1.5	1.5	1.2	0.5		0.39
2.1	2.0	1.6	.7	0.2	.54
2.6	2.6	2.0	.9		.67
3.1	3.1	2.3	1.1	.3	.80
4.1	3.9	3.0	1.5		1.06
5.0	4.8	3.8	1.8	.4	1.30
6.0	5.6	4.3	2.0		1.55
7.2	6.7	5.0	2.5	.6	1.86

[a] E in millivolts ± 0.1 mv.; q in grams per minute; W in g.; t in seconds $= 15.5 \pm 0.5$; electrode distance $= 40$ cm.; data for 40–50 mesh glass powder. E was called positive when the upper electrode became positive relative to the lower electrode.

The effect of surface conduction on E should be smaller in solutions of electrolytes, the effect decreasing with increasing concentration. The data conform to this idea, the E-W curves for 10^{-5} and 10^{-4} M sodium chloride being more nearly straight lines.

Effect of Electrolytes upon the Magnitude of E.—Since glass is negatively charged in water,

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(8) A. S. Brown, THIS JOURNAL, **56**, 646 (1934).

the cations of an electrolyte would tend to decrease the charge, and hence decrease ζ. Some electrolytes tend first to increase ζ, then reduce ζ in higher concentrations. According to the Hardy–Schulze rule, the effectiveness of an ion in decreasing ζ depends upon the valence of the ion. Since E is directly proportional to R and ζ, therefore proportional to the product $R\zeta$, electrolytes will increase or decrease E depending upon variations in the product $R\zeta$. Additions of electrolytes to water will always decrease R, but may increase or decrease ζ.

In making a study of the effect of salts on the magnitude of the E, difficulty in reproducing "water values" was encountered. Figure 2 shows some values of E plotted against the logarithm of the molarity, starting with approximately the same "water values" for E. In general, it was found that when a sample of water gave low values of E, the effect of small additions of electrolyte was not appreciable or, in some cases, a slight tendency for E to increase was noted. Since the low "water values" were undoubtedly due to contamination of the water to start with, it was not surprising that small amounts of electrolytes (1×10^{-7} to 1×10^{-6} mole per liter) had the above-mentioned effects. It was found that regardless of the "water value" started with, the value of E was always the same by the time the concentration had reached 1×10^{-4} molar. At this concentration, therefore, the concentration of the electrolyte was too high for any contamination of the water to have an effect on the magnitude of E.

The curves, Fig. 2, show that, starting with comparatively pure water, the effect of electrolytes was to decrease E. The decrease in E was less with sodium chloride than with barium chloride, and less with barium chloride than with aluminum chloride. E became negative (upper electrode more negative) at a concentration approximately 5×10^{-6} mole of aluminum chloride per liter, showing that Al^{+++} reversed the sign of the charge on glass. The curves are in agreement with the Hardy–Schulze rule regarding the effectiveness of ions of increasing valence. The fact that the curves descend for even slight traces of electrolytes indicates that the percentage change in R was greater than the percentage change in ζ. That is, the product, $R\zeta$, decreased.

Calculation of ζ for the Glass–Water Interface.—A calculation of the ζ potential for the glass–water interface from the data in Table I requires the knowledge of the specific resistance of the liquid, R. This was estimated by placing in the tube a solution of 10^{-3} M sodium chloride and measuring the potential E_1 between the electrodes. The potential, E_1, was either the equilibrium potential between the electrodes or the e. m. f. of a battery connected in series with the tube. Across the electrodes was then placed a shunt resistance, R_2, approximately equal to the resistance of the tube, and the potential E_2 was measured with the shunt in the circuit. The resistance of the tube was then equal to

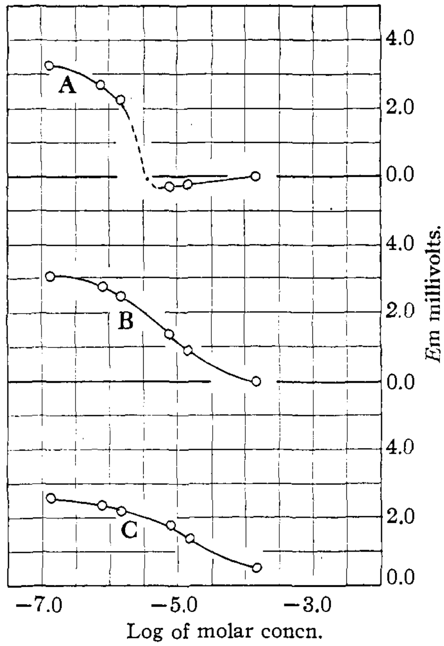

Fig. 2.—A, aluminum chloride; B, barium chloride; C, sodium chloride.

$$R_1 = R_2 \frac{E_1 - E_2}{E_2}$$

Knowing the equivalent conductance of 10^{-3} M sodium chloride, the tube constant was calculated. The specific resistance of the sample of water, with which the data in Table I were obtained, was calculated to be about 7.0×10^5 ohms. Using the following data: $d = 2.23$ g./ml., $d_0 = 1.00$ g./ml., $A = 8.55$ sq. cm., $R = 7.0 \times 10^3$ ohms, $D = 80$, $\eta = 0.0089$ poise, $g = 980$ cm./sec.^{2}, in the equation

$$E = \frac{\zeta DRW(d - d_0)g}{4\pi\eta Ad9 \times 10^{11}}$$

for $E = 0.0015$ volt and $W = 0.39$ g., $\zeta = -0.110$ volt; for $E = 0.0067$ volt and $W = 1.86$ grams, $\zeta = -0.102$ volt.

In the above calculation, the resistances of the 10^{-3} *M* sodium chloride and the water for which the data were obtained were the resistances when no powder was flowing; no correction was made for surface conductivity. It is assumed that the concentration of the salt is high enough to allow the surface conductivity to be neglected.

A Brief Study of the Charge on Galena.—The potential produced when some 80–150-mesh galena was allowed to settle through water, was measured and was of such a sign as to show that the galena was negatively charged in contact with water.

Summary

An apparatus and method for obtaining quantitative results for the Dorn effect has been developed. The apparatus provides for adequate control of the flow of powder and also provides for protection against contamination. It allows for indefinite repetition of measurements with the same sample of liquid and powdered solid.

It has been found that silver chloride electrodes are ideally suited for use in the study of the Dorn effect, both because they are not easily polarized and are conveniently manipulated.

It has been shown that the data obtained for ground glass and water conform to the electrokinetic equation.

The effect of electrolytes on the sedimentation potentials was found to be in accord with the Hardy–Schulze rule.

A calculation of the ζ potential for the glass-water interface from the data obtained gave a value of the correct order of magnitude.

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Amperometric Titrations. V. The Titration of Cobalt with α-Nitroso-β-naphthol

BY I. M. KOLTHOFF AND A. LANGER[1]

It may be expected that many of the organic reagents which yield precipitates with metal ions will be very useful in the amperometric titration of the latter. In a previous paper[2] it was shown that nickel can be titrated accurately, even at high dilutions, with dimethylglyoxime as reagent, using the dropping mercury electrode as indicator electrode. In the present paper it is shown that with the same indicator electrode the amperometric titration of cobalt with α-nitroso-β-naphthol can be carried out with accuracy and precision. This organic reagent was one of the first which found application in qualitative and quantitative inorganic analysis.[3] Ilinski and von Knorre[4] found that upon addition of a solution of the potassium salt of α-nitroso-β-naphthol to an excess of a neutral cobalt solution a reddish-brown precipitate is formed of the composition $Co[C_{10}H_6O(NO)]_2$ or CoR_2.[5] Upon heating with dilute acids the precipitate was transformed into a purple compound of the composition CoR_3 in which the cobalt was assumed to be trivalent. This precipitate is also formed upon addition of a solution of the reagent in alcohol or acetic acid to a weakly acid cobalt solution. Since the composition of the compound was found to vary, the precipitate was not weighed as such but as cobalt oxide or sulfate or metallic cobalt after ignition and the proper treatment. Mayr and Feigl[6] claim that the cobalt in the precipitate is present partly in the divalent and partly in the trivalent form. In order to get all of the cobalt in the trivalent form they first precipitated the cobalt with alkali hydroxide and hydrogen peroxide as $Co(OH)_3$, dissolved the precipitate by heating with a large excess of concentrated acetic acid and, after dilution, precipitated the solution with an excess of α-nitroso-β-naphthol. After drying at 130° to constant weight the purple-red precipitate was weighed as $CoR_3 \cdot 2H_2O$. Our investigations make it doubtful that the above formula is correct.

In preliminary work it was found that α-nitroso-β-naphthol yields well-defined waves and diffusion currents at the dropping mercury electrode at relatively positive potentials. This is advantageous from the viewpoint of amperometric titrations. It may be mentioned that

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[2] I. M. Kolthoff and A. Langer, THIS JOURNAL, **62**, 211 (1940).

[3] M. Ilinski, *Ber.*, **17**, 2592 (1884).

[4] M. Ilinski and G. v. Knorre, *ibid.*, **18**, 699 (1885).

[5] For the sake of simplicity we will write in the following R instead of $[C_{10}H_6O(NO)]$.

[6] C. Mayr and F. Feigl, *Z. anal. Chem.*, **90**, 15 (1932).