1965

The Nature of the Suspension Effect, With Special Reference to Clay Suspensions

Gary E. Spalding

Recommended Citation

Spalding, Gary E., "The Nature of the Suspension Effect, With Special Reference to Clay Suspensions" (1965). *Electronic Theses and Dissertations*. 3079.
https://openprairie.sdstate.edu/etd/3079

THE NATURE OF THE SUSPENSION EFFECT, WITH SPECIAL REFERENCE TO CLAY SUSPENSIONS

BY

GARY E. SPALDING

A thesis submitted
in partial fulfillment of the requirements for the
degree Doctor of Philosophy, Major in
Agronomy, South Dakota
State University

1965

THE NATURE OF THE SUSPENSION EFFECT, WITH SPECIAL REFERENCE TO CLAY SUSPENSIONS

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Doctor of Philosophy, and is acceptable as meeting the thesis requirements for this degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Adviser Date

Head, Agronomy Department Date

Acknowledgements

The author wishes to express his gratitude to Professor L. O. Fine for his guidance throughout the course of the investigation. Appreciation is also expressed to Dr. Dwight Hovland and others of the Agronomy staff for helpful comments and criticisms.

Appreciation is expressed to the author's family for patience and sacrifice without which the investigation would not have been possible.

The aid of the United States Congress, through the National Defense Education Act of 1958, is gratefully acknowledged.

GES

THE NATURE OF THE SUSPENSION EFFECT, WITH SPECIAL REFERENCE TO CLAY SUSPENSION

Abstract

GARY E. SPALDING

Under the supervision of Professor L. O. Fine

The suspension effect has been explained on the basis of the Donnan potential and on the basis of a liquid junction potential. The purpose of the present study was to devise experimental means of distinguishing between these theories.

A theoretical equation was derived which related the e.m.f. measured between Donnan phases to transference numbers of ions in the bridges used to make contact with each phase. The equation predicted that a plot of e.m.f. vs. the difference in transference numbers would yield a straight line having a given slope. It was shown that the equation must be experimentally confirmable if the Donnan-potential theory is correct.

Cell e.m.f. values were measured for five K-bentonite + KCl Donnan systems, using bridges of differing composition in order to obtain several values for the difference in transference numbers of bridge ions. The experimental curves were not linear and their slopes were 250 to 290% greater than theoretical slopes. It was concluded that the suspension effect is not interpretable in terms of the Donnan potential and must be regarded as an error. The suspension effect is probably caused by non-ideal behavior of ionic mobilities giving rise to a liquid junction potential at the salt-bridge-suspension interface.

Table of Contents

Introduction

The recent development of practical cation-sensitive glass electrodes prompted the writer to investigate the feasibility of their application to the monitoring of nutrient-cation activities in natural soils. It soon became evident that the nature of the suspension effect must be more clearly understood if such application were to yield meaningful results.

The suspension effect may be defined as the pH (or pK, pNa, pCa, etc.) of solution in equilibrium with a suspension (e.g. of soil) minus the pH of the suspension, both pH values being measured potentiometrically. Two theories have been advanced to explain the cause of the suspension effect:

(1) The observed pH difference is real. The suspension effect is equivalent to the Donnan potential existing between a suspension and its equilibrium solution.

(2) The observed pH difference is largely an illusion. The suspension effect is an error caused by a liquid junction potential at the boundary between the saturated KCl salt bridge (of the reference electrode) and the suspension.

If theory (1) is correct, then potentiometric measurements on soil systems can be interpreted in terms of ionic activities. If theory (2) is correct, however, such interpretation is subject to error.

The purpose of the present study was to devise experimental means of distinguishing between theories (1) and (2) or assessing the importance of each.

Literature Review

Chemical Equilibria and Ionic Activities in Colloidal Systems

In contrast to solutions of simple electrolytes, some colloidal suspensions (e.g. those of soil and clay) display marked microheterogeneity. Homogeneity of ionic concentrations is disturbed by the presence of force fields originating in or at the surface of colloidal particles. Cationic concentrations decrease and anionic concentrations increase with distance from a negatively charged particle. The thermodynamic treatment of such systems must employ more general concepts than those commonly applied to electrolyte solutions. Davis (7), Low (9), and Babcock (2) have thoroughly discussed the electrochemical equilibria of these systems. The following discussion is patterned after that of Low.

Consider a suspension of charged colloidal particles (hereafter called "particles"). The particles represent seats of external force fields (originating externally with respect to the solution). In order for the system to be in equilibrium with respect to an ionic species, i, the partial molar free energy of i, $\overline{F}_i$, must be constant throughout the system. If a volume element in the diffuse part of the double layer of a particle is represented by double prime and one outside the practical limits of the double layer by prime, then at equilibrium

$$\overline{F}''_i = \overline{F}'_i \qquad (1)$$

The "total activity" of i, $\bar{a}_i$, is defined by

$$\bar{F}_i - \bar{F}_i^{\circ} = RT \ln \bar{a}_i \qquad (2)$$

where $\bar{F}_i^{\circ}$ is the partial molar free energy of i when i is in a specified standard state, R the molar gas constant, and T the absolute temperature.

From equations (1) and (2) it follows that, at equilibrium

$$\bar{a}_i'' = \bar{a}_i' \qquad (3)$$

That is, at equilibrium the total activity of i is constant throughout the system.

In the absence of external force fields other than pressure (as, for example, in electrolyte solutions), $\bar{F}_i$ is identical to the chemical potential, u_i. In the case of colloidal suspensions, however, external force fields cause variation in ionic concentrations, hence u_i varies. Low partitions $\bar{F}_i$ into u_i and positional potential, Θ_i. If the only force field present is an electrostatic field, then $\Theta_i = z_i F \psi$ and

$$\bar{F}_i = u_i + \Theta_i = u_i + z_i F \psi \qquad (4)$$

where z_i is the valence of i (with sign included), F the Faraday, and ψ the electrostatic potential of the volume element in which i resides.

The "activity," a_i, is defined by

$$u_i - u_i^\circ = RT \ln a_i \tag{5}$$

where u_i° is the chemical potential when i is in its specified standard state. a_i is the activity commonly referred to when considering electrolyte solutions. It is also frequently applied to colloidal systems, but in this application a_i varies with position in the system, as will now be seen.

The standard state for i may be conveniently chosen outside the influence of external force fields and at unit activity, that is, where $\Theta_i = 0$ and $a_i = \bar{a}_i = 1$. Then

$$\bar{F}_i^\circ = u_i^\circ \tag{6}$$

The relationship between activity of i in a volume element of the double layer, a_i'', and that in one outside the double layer, a_i', is found by combining equations (1), (4), (5), and (6). The result is

$$\psi' - \psi'' = \frac{RT}{z_i F} \ln \frac{a_i''}{a_i'} \tag{7}$$

Davis (7) showed that the two activity concepts are identical when applied to whole electrolytes, e.g. $\bar{a}_{NaCl} = a_{NaCl}$.

Low (9) pointed out that the total activity is a measure of the "escaping tendency" or change-toward-equilibrium while the activity may be thought of as an "effective concentration." The total activity is independent of the nature of Θ; even if Θ were different from $zF\psi$, equation (3) would hold. Equation (7), of course, depends on the nature of Θ. It must be noted that equations (3) and (7) apply only to equilibrium systems.

Equation (7) is frequently applied to equilibrium Donnan systems (1,2,7,10,18,25). A Donnan system is one in which a constraint is applied to the movement of some, but not all, of its constituents. The constraint may be gravity, as in the case of a soil suspension which segregates into a sediment phase and a supernatant phase. Or the constraint may be a membrane permeable to all constituents of a system except colloidal particles. In the application of equation (7) to Donnan systems, ψ'' is the potential of the suspension phase and ψ' is the potential of the solution phase. The quantity ($\psi' - \psi''$) is variously called the Donnan membrane potential, Donnan potential, membrane potential, or potential difference between phases; it is designated by E_m.

$$E_m = \psi_{soln} - \psi_{susp} = \frac{RT}{z_iF} \ln \frac{a_i(susp)}{a_i(soln)} \qquad (8)$$

ψ_{soln} may be assigned a value of zero; ψ_{susp} is then negative and E_m positive for negatively charged particles.

Babcock (2) has emphasized that E_m is the potential difference between phases and has the same value for all ion-species. From equation (8) it is seen that the following relationships must exist between ion-species 1, 2, 3, ..., n.

$$\left[\frac{a_i(\mathrm{susp})}{a_i(\mathrm{soln})}\right]^{1/z_1} = \left[\frac{a_2(\mathrm{susp})}{a_2(\mathrm{soln})}\right]^{1/z_2} = \cdots\cdots = \left[\frac{a_n(\mathrm{susp})}{a_n(\mathrm{soln})}\right]^{1/z_n} \tag{9}$$

E_m is commonly measured (1,7,10,25) by inserting a calomel electrode having a saturated KCl salt bridge into each phase of the Donnan system and measuring the potential difference between them. The potential difference between calomel electrodes is assumed to be the potential difference between phases, E_m. This assumption is the basis for the Donnan-potential explanation of the suspension effect, as will now be seen.

Overbeek* (21) has defined "Donnan-e.m.f.," E_D, as the e.m.f. of Cell A.

$$\mathrm{Hg;\ Hg_2Cl_2,\ sat\ KCl}\ \underset{E_x}{\overset{X}{\Big|}}\ \underset{\mathrm{I}}{\mathrm{susp}}\ \underset{E_m}{\overset{M}{\Big|}}\ \underset{\mathrm{II}}{\mathrm{soln}}\ \underset{E_y}{\overset{Y}{\Big|}}\ \mathrm{sat\ KCl,\ Hg_2Cl_2;\ Hg} \qquad \underline{\text{Cell A}}$$

If liquid junction potentials at X and Y are negligible or cancel, then $E_D = E_m$.

Applying equation (8) to the distribution of H^+ between phases we obtain

$$E_m = \frac{RT}{F} \ln \frac{a_H(\mathrm{susp})}{a_H(\mathrm{soln})} \tag{10}$$

---

*The author has transformed the polarity of Overbeek's cells to conform to that used by other authors. The effect is to reverse the sign of e.m.f.'s.

which can be written

$$\frac{E_m F}{2.303RT} = \log a_H(\text{susp}) - \log a_H(\text{soln}) \tag{11}$$

Since

$$- \log a_H = \text{pH} \tag{12}$$

equation (11) can be written

$$\Delta\text{pH} = \text{pH}_{\text{soln}} - \text{pH}_{\text{susp}} = \frac{E_m F}{2.303RT} \tag{13}$$

where ΔpH is the "suspension effect."

Overbeek (21) has shown that ΔpH calculated from Cell A is exactly equivalent to ΔpH calculated from pH measurements taken separately on each phase.

Equation (13) is the basis for the explanation of the suspension effect in terms of the Donnan potential E_m. This explanation assumes that $E_m = E_D$. Implicit in this assumption is the assumption that E_x and E_y (Cell A) are negligible or cancel.

The Liquid-junction-potential Theory of the Donnan-e.m.f.

Overbeek (21) clearly distinguished the Donnan-e.m.f., E_D, from the Donnan potential, E_m. E_D is the e.m.f. of Cell A--a measurable quantity. E_m is a conceptual quantity which cannot be measured with complete assurance because of the presence of liquid junctions at X and Y in Cell A. Many investigators (1,10,13,17,18,25) have regarded E_D as a good measure of E_m.

In 1950, Jenny, Nielsen, Coleman and Williams (8) developed a theory attributing E_D primarily to a large liquid junction potential E_x, at X in Cells A and B. They studied

$$\mathrm{Hg;\ Hg_2Cl_2,\ sat.\ KCl} \;\Big|\; \underset{\mathrm{I.}}{\mathrm{KCl,\ a = a_2,\ c_2}} \;\underset{E_x}{\overset{X}{\Big|}}\; \underset{\mathrm{II.}}{\text{cation exchanger + KCl, } c_1}$$

$$\underset{E_m}{\overset{M}{\Big|}}\; \underset{\mathrm{III.}}{\mathrm{KCl,\ a = a_1,\ c_1}} \;\underset{E_y}{\overset{Y}{\Big|}}\; \mathrm{sat.\ KCl,\ Hg_2\,Cl_2;\ Hg} \qquad \underline{\text{Cell B}}$$

systems comprised of KCl solution and K-saturated cation exchangers (resins, clays and soils). Finding Hittorf transference numbers of Cl^-, t_{Cl}, to increase with increasing electrolyte concentration of the exchanger phase (compartment II) and decreasing charge density of the exchanger, the authors concluded that the relative movements of K^+ and Cl^- were seriously affected by the resin or colloid particles. Hence, a diffusion potential was to be expected at X (8).

Cell B was sectioned into three compartments by membranes at X and M. The exchanger in II was initially equilibrated against dilute KCl solutions in I and III. When the Cl^- concentration was determined on a filtrate obtained by rapid filtration from II, it was found to be the same as that in I and III. It was also found that H-resin added to one side of a two-compartment cell previously containing identical

HCl solutions in each compartment caused no redistribution of HCl to take place. Since no Donnan distribution (see equation 8) of Cl^- was observed across M, no membrane potential E_m was expected to exist (8).

Using experimentally determined relationships between t_{Cl} and a_{KCl}, the authors integrated the general equation for a liquid junction potential (applied to boundary X),

$$E_x = \frac{RT}{F} \int_{I}^{II} \sum \frac{t_i}{z_i} \, d \ln a_i \qquad (14)$$

obtaining, for a system in which K-saturated Ion-X resin was the exchanger,

$$E_x = \frac{RT}{F} \left(\ln \frac{a_2}{a_1} - 0.85 \ln \frac{1 + 6.36a_2}{1 + 6.36a_1} \right) \qquad (15)$$

The summation in equation (14) is over all diffusible species in the system, in this case K^+ and Cl^-. The symbols a_1 and a_2 refer to activities of KCl.

A series of measurements were made on Cell B, by replacing the equilibrium solution in I with KCl solutions of various concentration. This had the effect of varying the concentration of the bridge solution on the left of Cell A. Satisfactory agreement was obtained between calculated E_x values and measured e.m.f.'s of Cell B, E_B. A comparison of these values for the system K-Ion-X + KCl is presented in Table 1.

Results of other workers are also reported in Table 1 and will be discussed later.

Table 1. Observed E_B values and calculated E_x and $(E_m - E_x)$ values reported by Jenny (8) and Peech (23), for the system K-Ion-X + KCl, in millivolts.

a_{KCl} (eq/l)		E_B	E_x - calc.		$(E_m - E_x)$ - calc.,
a_1	a_2	observed (Jenny)	Jenny	Peech	Peech
.00463	.00902	18.0	17.7	98	18
.00463	.0441	53.7	53.7	58	58
.00463	.296	91.7	85.2	22	94
.00463	.432	96.5	89.3	15	101
.00463	2.32	113.0	102.0	4	112

Jenny et al. state that e.m.f. measurements can not distinguish between their theory and the Donnan theory because E_x and E_m are both of the same sign and are both included in E_D and E_B. Adhering to the membrane theory, however, requires one to conclude that E_m is a function of KCl concentration in the salt bridge used to measure it (c_2 in Cell B) (8).

The authors observed that when the calomel electrodes (including salt bridges) of Cell A were replaced by glass electrodes, the cell e.m.f. was zero. Since the membrane potential was believed to be negligible in the systems studied, two explanations were offered for the zero e.m.f. : (1) H^+ activity is constant throughout the system, or (2) the ions of the diffuse double layer do not influence the glass electrode. Explanation (1), of course, is equivalent to the concept of total activity. Also, if E_m is zero, then by equation (8) $a_1' = a_1''$ and there ceases to be a distinction between activity and total activity.

In a later paper (5), Coleman, Williams, Nielsen and Jenny employed a slightly different form of equation (15) for E_x.

$$E_x = \frac{RT}{F} \left(\ln \frac{a_2}{a_1} - \ln \frac{1 + ka_2}{1 + ka_1} \right) \qquad (16)$$

The selectivity constant, k, is defined as the ratio of solution conductance to surface conductance in the system studied. These quantities are determined by plotting the specific conductance of the system (the exchanger phase) against a_{KCl} in the system. Thus, the determination of Hittorf transference numbers was avoided.

Besides studying twelve K-saturated soils and reiterating their previous conclusions (8), the authors (5) determined pH's of soil sediments, stirred soil suspensions, and supernatant liquids, using Beckman glass and calomel electrodes. Natural soils were equilibrated with water in a 1:2 ratio. Supernatant liquids gave the highest pH's, followed in order by stirred suspensions and sediments. Removal of soluble salts from these soils generally resulted in a higher pH of the supernatant liquid and a larger suspension effect. In natural soils the pH difference between supernatant and sediment ranged from 0.2 to 1.5; the range for salt-free soils was 0.5 to 1.7.

The papers of Jenny et al. (8) and Coleman et al. (5) evoked a great deal of discussion concerning the seat and significance of the Donnan-e.m.f.

Marshall (13,14) criticized the work of Jenny et al. (8) and Coleman et al. (5). He argued that, as long as the concentration of KCl in the bridge is high compared to the concentration of electrolyte in the test system, E_x must be small. Mysels (19) wrote that while Marshall's argument applies to electrolyte solutions, it is not necessarily applicable to colloidal systems. The significance of E_x will depend on the kind of contact made between the bridge and the test system. If contact is made only in intermicellar solution E_x will be negligible. If, however, the dilute portion of the bridge enters the double layer, then micro Donnan-distributions will occur, the transference numbers of K^+ and Cl^- are altered, and E_x need not be negligible. The presence of a significant E_x is thus a consequence of Donnan equilibria (19). Marshall replied (15) that, for potentiometric results to be valid, the bridge solution must contact a representative cross section of the test system.

Marshall (13) was also critical of the manner in which Jenny et al. (8) determined the Cl^- concentration in compartment II of Cell B. He explained that, in filtering from II, a constraint (the filter) was applied to the movement of colloidal particles which was no different, in principle, from the constraint (membrane) at M.

Donnan theory predicts that the filtrate so obtained will, in the early stages of filtration, be identical to the solution in compartment III. Thus, there was no evidence to support the rejection of Donnan distributions in their systems (13). Marshall's analysis is supported by Mysels (19).

Marshall (13,14) recognized no fundamental difference in the boundaries X and M in Cell B; whatever takes place at X should take place at M. Williams (26) replied that M is an equilibrium boundary while X is not. This distinction was also emphasized by Overbeek (21,22). (Overbeek's analysis of Cell A will be reviewed later.)

Peech and McDevit (23) asserted that it was not possible for the potentials at X and M to have the same sign, as stated by Jenny et al. (8). They wrote that compartment II (Cell B) will be negatively charged with respect to solutions in I and III because of the presence of non-diffusible exchanger particles. Thus E_x is negative and E_m is positive. The e.m.f. of Cell B is then $(E_m - E_x)$ (23). In equating E_B to $(E_m - E_x)$, these authors apparently meant for absolute values of E_m and E_x to be used in the quantity $(E_m - E_x)$. Peech and McDevit applied the Planck equation to boundaries X and M, calculating E_x and E_m individually. Their values for the K-Ion-X + KCl system used by Jenny et al. (8) are presented in Table 1. These calculations show that E_x decreases with increasing a_2 (Cell B) and that $(E_m - E_x)$-calculated corresponds very closely to E_B (23).

Peech, Olsen and Bolt (24), while measuring Donnan-e.m.f.'s of clay suspensions, encountered instances in which measurements could not be explained by Donnan-potential theory. The sign of E_D was found to be positive for many H-, Na-, and K-saturated clays. When these clays were saturated with Ca^{+2}, however, the sign of E_B was negative despite the observation that Ca-clay particles were negatively charged; for these systems, it was concluded that a significant liquid junction potential was seated at X with sign opposite to that of E_m.

Cl^- was added to a Na-clay (as NaCl) and two Ca-clays (as $CaCl_2$) and the recovery of Cl^- was measured potentiometrically with Ag-AgCl and saturated calomel half-cells. If no liquid junction potential existed at the salt bridge-suspension contact, it would have been necessary to conclude from recovery data that Cl^- was positively adsorbed by Na-clays; the authors (24) rejected this possibility and concluded that a positive E_x was present. The effect of negative E_x on measurements of Ca-clay systems was to exaggerate the negative adsorption of Cl^- (24).

The authors state that the sign of E_x is indeterminate. Positive values were attributed to KCl bridge solution short-circuiting the potential drop across the double layer, while negative values were caused by the formation of $CaCl_2$ ahead of the KCl diffusion front (24).

Peech et al. (24) observed, as had Jenny et al. (8), that the Donnan-e.m.f. was dependent on the concentration of KCl in the bridge. At bridge concentrations greater than the concentration of the equilibrium solution, E_D was positive; at bridge concentrations less than equilibrium solution concentration, it was negative (24). Bower (4) also observed that the suspension effect varies with bridge concentration.

Marshall (16) believed that the reversal of the sign of E_D observed by Peech et al. (24) was caused by hydroxyl ions being strongly adsorbed by Ca-clay. This gave rise to a reversal of Donnan effects.

Low (10) used the Debye-Hueckel theory to derive an equation for the membrane potential. The result was

$$E_m = -\frac{Bn\zeta}{\sqrt{I}} \tag{17}$$

where n is the number of colloidal particles per cm^3, I the ionic strength, ζ is the zeta potential and

$$B = \frac{A}{F}\sqrt{\frac{125DRT}{\pi}} \tag{18}$$

where A is the surface area of a particle, D the dielectric constant, F the Faraday, and T the absolute temperature.

In an attempt to settle the question of whether or not E_D is a measure of E_m, Low measured Donnan-e.m.f.'s for 1% electrodialyzed-bentonite suspensions equilibrated against NaCl and KCl solutions. He stated that if results agreed with equation (17), then E_m exists and can be measured with enough accuracy to give semiquantitative information on ionic activities.

E_D was found to vary with clay concentration (n) as predicted by equation (17) except that the plot of E_D vs. clay concentration extrapolated to -3 mv at n = 0. It was suggested that the -3 mv value represents the difference in diffusion potentials at X and Y in Cell A.

E_D varied with I as predicted by equation (17). E_D varied with ζ as predicted except that the curve extrapolated to -13.3 mv at $\zeta = 0$. The -13.3 mv value was attributed to a difference in diffusion potentials at X and Y or to an assymetry potential across the membrane (10).

Low concluded that, since E_D varied as predicted by equation (17), E_x is not large enough to nullify the membrane potential measurement. It was emphasized that E_x does exist and that its magnitude should increase with the magnitude of the membrane potential.

Babcock and Overstreet (3) examined the question of whether or not Cell A could measure an equilibrium membrane-potential under the assumption that t_{Cl} and t_K are equal. They considered a system in which the suspension phase was K-colloid + KCl and the dialyzate phase was KCl solution. Upon adding all of the cell reactions and transference processes occurring when current is passed, they found the net cell reaction to be a transfer of KCl between bridge solutions. Since no free energy change occurs upon transfer of small amounts of KCl between identical solutions, E_D must be zero. When t_K and t_{Cl} are not equal across the membrane the net cell reaction involves transfer of KCl between suspension and dialyzate phases as well as between salt bridges. But since a_{KCl} must be the same in both phases, no E_D should be observed. The authors conclude that the only possible seats of e.m.f. are at the liquid junctions, X and Y. Babcock and Overstreet emphasized that their conclusion does not deny the possibility that E_m exists; they only concluded that it can not be measured with Cell A.

Mysels (20) criticized the analysis of Babcock and Overstreet (3). The assumption that $t_K = t_{Cl}$ is not realistic. Also, the authors (3) implicitly assumed the transference numbers were both equal 0.5, implying that the colloid has zero mobility; this is not realistic in a typical Donnan system (20). The mechanism by which Cell A could measure E_m and the limitations of its use is qualitatively explained by Mysels in the following quote.

> The colloidal ion in a typical Donnan system can escape through the salt bridge but not through the membrane. It is this tendency to escape and reach uniform concentration that could be measured by the potential of the cell (equal to the restraining Donnan membrane potential) if all other junction potentials were nullified. Salt bridges are an imperfect tool for such nullification and it is because of this imperfection that the potential depends on salt concentration.

It does not appear that Mysels was in fundamental disagreement with Babcock and Overstreet. They (3) concluded that <u>the membrane was not a seat of e.m.f.</u> and that the only possible seats were at X and Y. Mysels does not deny this. He does, however, attach a significance to the e.m.f. at X. The analysis of Babcock and Overstreet stopped short of considering the possibility that E_x may be of significance.

Overbeek (21,22) considered E_D to be the sum of junction potentials at X, M and Y (Cell A). The equation for E_D was, then

$$- E_D F = \int_{\text{left}}^{\text{right}} \sum \frac{t_i}{z_i} du_i \qquad (19)$$

In order to refer ionic chemical potentials to chemical potentials of neutral substances, the equation

$$0 = - \int_{\text{left}}^{\text{right}} \sum t_i du_K \qquad (20)^*$$

was added to equation (19) to give

$$- E_D F = \int_{\text{left}}^{\text{right}} \sum t_i \left(\frac{du_i}{z_i} - du_K\right) \qquad (21)$$

Overbeek showed that the expression in parentheses refers to a neutral substance. If i represents an anion, then

$$\frac{du_i}{z_i} - du_K = \frac{1}{z_i} (du_i - z_i du_K) = \frac{1}{z_i} du_{K_{z_i} i} \qquad (22)$$

---

*This is true because u_K is identical at each integration limit.

where $K_{z_i}i$ is the salt consisting of one i-ion and z_i K-ions. If i is a cation, then $[(du_i/z_i) - du_K]$ is the free energy change occurring when one K^+ is replaced by $1/z_i$ i-ion.

The integral of equation (21) can be split into integrals over each of the three boundaries occurring in Cell A.

$$- E_D F = \int_{\text{sat KCl}}^{\text{susp}} \sum t_i\left(\frac{du_i}{z_i} - du_K\right) + \int_{\text{susp}}^{\text{soln}} \sum t_i\left(\frac{du_i}{z_i} - du_K\right) + \int_{\text{soln}}^{\text{sat KCl}} \sum t_i\left(\frac{du_i}{z_i} - du_K\right) \qquad (23)$$

Since the transference number of non-diffusible ions is zero across the membrane and chemical potentials of diffusible salts do not change across the membrane, the second integral of equation (23) vanishes. Then,

$$- E_D F = \int_{\text{sat KCl}}^{\text{susp}} \sum t_i\left(\frac{du_i}{z_i} - du_K\right) + \int_{\text{soln}}^{\text{sat KCl}} \sum t_i\left(\frac{du_i}{z_i} - du_K\right) \qquad (24)$$

Thus, the situation at the membrane does not enter into the expression for the Donnan-e.m.f., E_D. Overbeek emphasized that this does not mean that E_m does not exist, it only means that E_m does not directly contribute to E_D.

Overbeek (22) applied equation (24) to a Cell A where K-colloid + KCl was the suspension phase and KCl solution the dialyzate phase. It was assumed that in the significant part of the liquid junction the colloidal particles are present at constant concentration. Ideal behavior of activities and mobilities of all constituents of the system was also assumed. Under these assumptions, the following relations hold (22).

$$t_i \ (i \neq K, Cl) = 1 - t_K - t_{Cl}$$

$$du_i = RT \ln \frac{dc_i}{c_i} \quad ; \quad du_K = RT \ln \frac{dc_K}{c_K} \tag{25}$$

$$dc_K = dc_{Cl}$$

Combining equation (24) and equation (25) yields

$$- E_D F = RT \int_{\text{sat KCl}}^{\text{susp}} \left[\left(\frac{t_K}{c_K} - \frac{t_{Cl}}{c_{Cl}} \right) dc_K - d \ln c_K \right]$$

$$+ \ RT \int_{\text{soln}}^{\text{sat KCl}} \left[\left(\frac{t_K}{c_K} - \frac{t_{Cl}}{c_{Cl}} \right) dc_K - d \ln c_K \right] \tag{26}$$

Since K^+ and Cl^- mobilities are nearly equal, the transference numbers of each are in about the same ratio as their concentrations and

$$\frac{t_K}{c_K} - \frac{t_{Cl}}{c_{Cl}} \doteq 0 \tag{27}$$

Equation (26) then reduces to

$$E_D = \frac{RT}{F} \ln \frac{c_K(\text{susp})}{c_K(\text{soln})} \tag{28}$$

which is equation (8) applied to K^+ under the assumption that $a_K = c_K$. Hence, for the system considered by Overbeek, E_D will be a good measure of E_m if activities and mobilities behave ideally.

Overbeek (22) does not believe the assumption of ideal behavior of ionic mobilities is an adequate approximation for Donnan systems unless E_m is small. The mobilities of counterions may be far below their mobilities in free solution while co-ion mobilities will be largely unchanged because they are expelled from regions of high charge density (22).

Overbeek cited work of others in which observed E_D's, when interpreted with equation (8), led to the conclusion that the degree of dissociation of colloidal particles increased with increasing salt concentration of the equilibrium dialyzate. This conclusion was rejected as unreasonable (22); however, "the interpretation with equation (24) . . . would mean that in the lower electrolyte concentration the mobility of the counterions is considerably decreased and this is wholly in line with the fact that at low ionic strengths the electrical potential around the particles is high" (22).

Although the explanation for the Donnan-e.m.f. (or suspension effect) in terms of liquid junction potentials was proposed by Jenny et al. fourteen years ago, there does not yet exist general agreement on whether or not this explanation is correct. Jenny et al. (8) remarked that measurements on cells of type A or B could not distinguish clearly between these theories. Much of their evidence was based on rejecting the importance of Donnan equilibria in their systems because of finding identical Cl^- concentrations in suspension and dialyzate phases. But the comments of Marshall (13), supported by Mysels (19), seem to properly discredit this observation. The reversal of the sign of E_D observed by Peech et al. (24) was interpreted by them in terms of liquid junction potentials, and by Marshall (16), in terms of Donnan equilibria. While strong theoretical arguments were brought forth in support of the liquid junction theory, it would seem that no experiment was performed which was capable of clearly distinguishing between these theories or of assessing their relative importance.

Theory

The following discussion is the basis for experiments which were performed in an attempt to distinguish between the liquid-junction-potential and Donnan-potential theories of the suspension effect or Donnan-e.m.f.

Let us consider a dialysis cell in which clay suspension has come to equilibrium with a dilute solution of strong electrolytes across a membrane permeable to all ionic constituents except clay particles. Identical bridges of a 1:1 strong electrolyte, AB, are then connected to each compartment of the dialysis cell and identical electrodes, reversible to A^+ or B^-, are inserted in the bulk of the bridge solution. The result is Cell C.

$$\text{revers. electr., AB}\ \overset{X}{\underset{E_x}{\Big|}}\ \begin{array}{c}\text{clay + dissociated cations}\\ \text{+ strong electrolytes}\\ \text{I}\end{array}\ \overset{M}{\underset{E_m}{\Big|}}\ \begin{array}{c}\text{strong}\\ \text{electrolytes}\\ \text{II}\end{array}\ \overset{Y}{\underset{E_y}{\Big|}}\ \text{AB, revers. electr.}\qquad \underline{\text{Cell C}}$$

Since the reversible electrodes are immersed in identical solutions, they will not contribute to the cell e.m.f., E_C. E_C is the algebraic sum of e.m.f.'s at X, M, and Y.

$$E_C = E_x + E_m + E_y \qquad (29)$$

Cell C differs from Cell A in that the bridges in Cell A are specified as saturated KCl while the composition of bridges in Cell C is unspecified. We now examine how E_C varies with bridge composition.

We shall assume that all constituents of the test system (compartments I and II) and bridges behave ideally with respect to activities and mobilities. It is further assumed that boundaries X and Y consist of a continuous series of mixtures of bridge solution and test-system solution or suspension. The potentials at X and Y may then be expressed by Henderson's integrated form of the equation for a liquid junction potential, equation (30). (An account of Henderson's integration is given by McInnes (11)).

$$E_{l.j.} = \frac{RT}{F} \frac{\sum (U_i/z_i)(c_i - \bar{c}_i)}{\sum U_i(c_i - \bar{c}_i)} \ln \frac{\sum \bar{c}_i U_i}{\sum c_i U_i} \qquad (30)$$

The symbol, c_i, is the concentration in equivalents per liter, U_i the mobility, and z_i the valence (with sign included) of ion-species i. Barred quantities (i.e. $\bar{c}_i$) refer to bulk solution to the left of the boundary and unbarred quantities refer to bulk solution to the right of the boundary. The summations are over all ions, including clay anions, present.

Let us specify that the electrolyte concentration of the test system is so small compared to the concentration of AB in the bridge, c_{AB}, that the $U_i c_i / z_i$ and $U_i c_i$ terms which apply to the test system become negligible in the logarithm coefficient. Equation (30) then reduces to

$$E_{l.j.} = \frac{RT}{F} \frac{U_A - U_B}{U_A + U_B} \ln \frac{\sum \bar{c}_i U_i}{\sum c_i U_i} \qquad (31)$$

At X, the bridge is on the left and we have

$$E_x = \frac{RT}{F} \frac{U_A - U_B}{U_A + U_B} \ln \frac{c_{AB}(U_A + U_B)}{\sum c_i'' U_i} \qquad (32)$$

where c_i'' is the concentration of i in the suspension. At Y, the bridge is on the right, therefore

$$E_y = \frac{RT}{F} \frac{U_A - U_B}{U_A + U_B} \ln \frac{\sum c_i' U_i}{c_{AB}(U_A + U_B)} \qquad (33)$$

Where c_i' is the concentration of i in the dialyzate.

Adding equations (32) and (33) yields

$$E_x + E_y = \frac{RT}{F} \frac{U_A - U_B}{U_A + U_B} \ln \frac{\sum c_i' U_i}{\sum c_i'' U_i} \qquad (34)$$

In the bulk solution of the bridges the transference numbers may be defined by

$$t_A = \frac{U_A}{U_A + U_B} \text{ and } t_B = \frac{U_B}{U_A + U_B} \tag{35}$$

thus,

$$\frac{U_A - U_B}{U_A + U_B} = t_A - t_B \tag{36}$$

Equation (34) may then be expressed more simply as

$$E_x + E_y = (t_A - t_B)\,\frac{RT}{F}\,\ln \frac{\Sigma c_i' U_i}{\Sigma c_i'' U_i} \tag{37}$$

We now seek to eliminate all c_i'' 's in equation (37). We assume that the distribution of diffusible ions between phases is given by equation (8).

$$E_m = \frac{RT}{z_i F}\,\ln \frac{a_i''}{a_i'} \tag{8}$$

Assuming ideal behavior of activities, we have

$$E_m = \frac{RT}{z_i F}\,\ln \frac{c_i''}{c_i'} \tag{38}$$

which can be transformed into the exponential form

$$c_i'' = c_i' \exp\left[\frac{z_i F E_m}{RT}\right] = c_i' \exp(z_i E_m k) \tag{39}$$

where

$$k = \frac{F}{RT} \tag{40}$$

In order for electroneutrality to be satisfied, the concentration of clay, c_p, (in equivalents per liter) must be

$$c_p = \Sigma c_{+i}'' - \Sigma c_{-i}'' \tag{41}$$

where $\Sigma c_{+i}''$ is the summation of the concentrations of all cations in the suspension and $\Sigma c_{-i}''$ is the summation of the concentrations of all anions, except clay, in the suspension. Combining equations (39) and (41) we obtain

$$c_p = \Sigma c_{+i}' \exp(z_i E_m k) - \Sigma c_{-i}' \exp(z_i E_m k) \tag{42}$$

Separating the $c_p U_p$ term from the summation in equation (37) and specifying that the summations now apply only to small ions, we obtain

$$E_x + E_y = (t_A - t_B)\,\frac{RT}{F}\ln\frac{\Sigma c_i'U_i}{c_pU_p + \Sigma c_i''U_i} \tag{43}$$

Equations (39) and (42) are now used to eliminate c_p and all c_i'' from equation (43). Also, $\frac{1}{k}$ is substituted for RT/F.

$$E_x + E_y = (t_A - t_B)\,S \tag{44}$$

Where

$$S = \frac{1}{k}\ln\frac{\Sigma c_i'U_i}{[\Sigma c_{+i}'\exp(z_iE_mk) - \Sigma c_{-i}'\exp(z_iE_mk)]U_p + \Sigma c_i'U_i\exp(z_iE_mk)} \tag{45}$$

If E_m does not directly contribute to E_C (i.e. if M is not a seat of e.m.f.), then $E_C = E_x + E_y$, hence

$$E_C = (t_A - t_B)\,S \tag{46}$$

If E_m contributes to E_C, then $E_C = E_m + E_x + E_y$ and

$$E_C = E_m + (t_A - t_B)\,S \tag{47}$$

Consider, now, an experiment in which E_C is measured on a given test system using bridges of differing composition in order to obtain different values of $(t_A - t_B)$. Equation (46) then predicts that a plot of E_C vs. $(t_A - t_B)$ will yield a straight line passing through the origin and having slope S. Equation (47) predicts that plotting E_C vs. $(t_A - t_B)$ will yield a straight line of E_C-intercept E_m and slope S.

It is of interest to examine the predictions of equations (46) and (47) when the bridge is composed of KCl. In this case, Cell A and Cell C are identical and $E_C = E_D$. Since K^+ and Cl^- are nearly equitransferent, $(t_A - t_B) \doteq 0$. Equation (46) then predicts that $E_D \doteq 0$. But it is well known that E_D is, in general, not equal to 0. Since $(t_A - t_B)$ is not exactly equal to 0, *some* deviation from 0 is expected for E_D, however, not nearly as much as is commonly found. Hence, we must conclude that equation (46) is not valid. Equation (47) predicts that $E_D \doteq E_m$; thus, it is in agreement with the explanation of E_D in terms of the Donnan potential.

If equation (47) is experimentally confirmable, this would provide very strong evidence for the Donnan-potential theory of the suspension effect. If E_D is a liquid junction potential caused by non-ideal behavior of ionic mobilities it would seem very unlikely that equation (47) could be obeyed; recall that equation (47) is based on the assumption of ideal behavior of mobilities. Thus, plots of E_C vs. $(t_A - t_B)$ should provide a basis for differentiating between the theory of the Donnan potential and the theory of the liquid junction potential.

Experimental Methods and Procedures

In order to test equation (47), simple examples of systems represented in Cell C were studied. These examples are represented more specifically in Cell C'.

$$\mathrm{Ag;\ AgCl,\ 1\underline{N}\ ACl}\ \overset{X}{\underset{E_x}{\Bigg|}}\ \begin{matrix}\text{1\% K-bentonite}\\ \text{+ KCl}\\ \text{I}\end{matrix}\ \overset{M}{\underset{E_m}{\Bigg|}}\ \begin{matrix}\text{KCl}\\ c_K = c_{Cl} = c_{KCl}\\ \text{II}\end{matrix}\ \overset{Y}{\underset{E_y}{\Bigg|}}\ \mathrm{1\underline{N}\ ACl,\ AgCl;\ Ag}$$

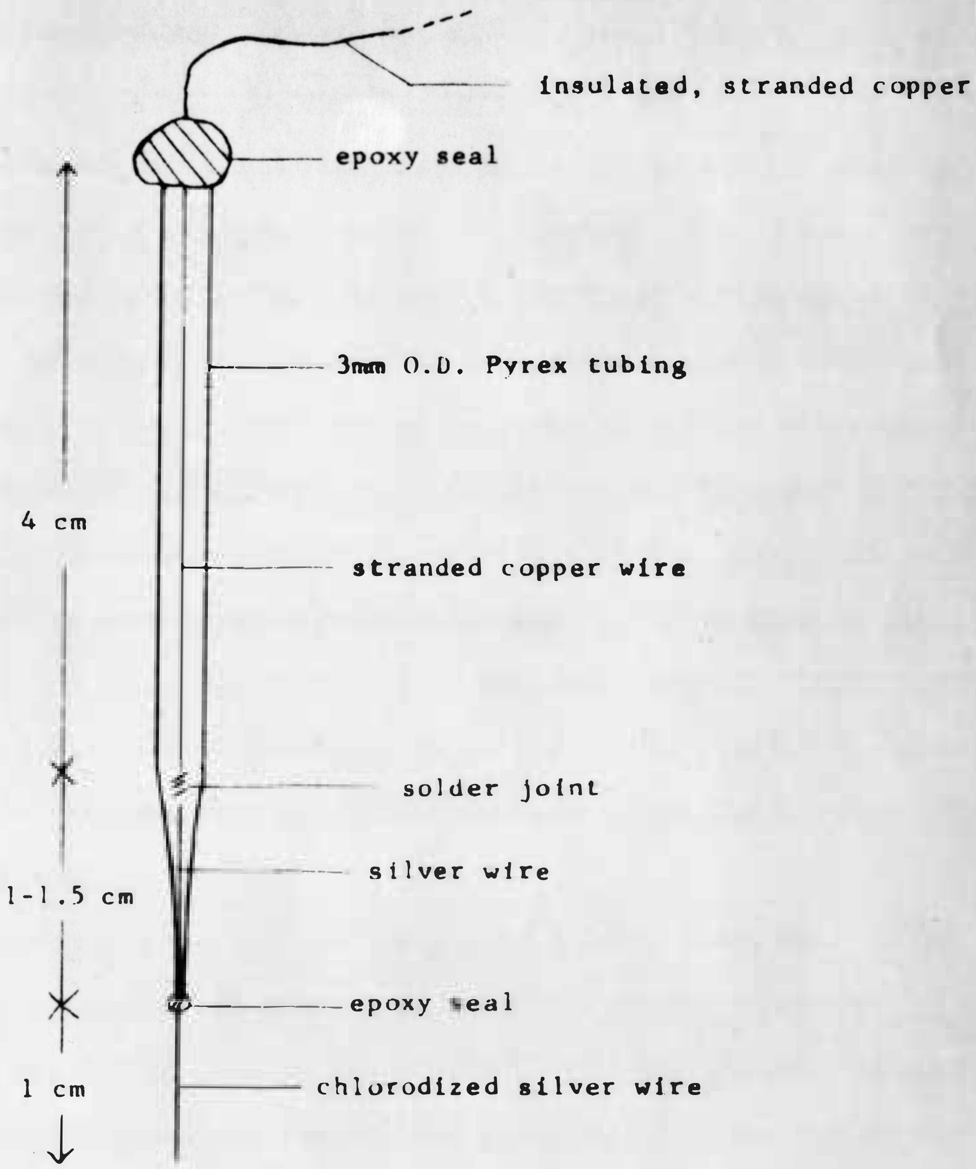
Cell C'

Bridges of 1.00 N LiCl, NaCl, KCl and HCl were used to measure e.m.f.'s of Cell C', i.e. bridges in which $A^+ = Li^+$, Na^+, K^+, or H^+. Five dialysis cells were prepared. All contained 1% K-bentonite in compartment I. Each of the five cells contained a different concentration of KCl electrolyte than the other four; KCl concentration of cells was varied from 1×10^{-4} N to 9×10^{-4} N.

Electrode Construction

Ag-AgCl electrodes were constructed as shown in Figure 1. After sealing the silver wire in the glass, it was cleaned by soaking a few seconds in warm (ca. 50°C) 8 N HNO_3, wiping with absorbent paper, soaking about 1 minute in concentrated NH_4OH, wiping with absorbent paper, and rinsing thoroughly with water. The silver wire

Figure 1. Construction of Ag-AgCl electrode.



was chlorodized in 0.1 N HCl against a platinum wire (sealed in glass) cathode. A current density of 15 ma/cm^2 was passed for 5 minutes.

Bridge tubes were prepared by drawing a 0.5 to 1 mm diameter straight capillary from 4 mm I.D. Pyrex tubing. Tubes accepted for use had evenly cut openings and tapered gently for about 1 cm from the capillary tip upwards. Overall lengths of bridge tubes were about 7.5 cm, the 4 mm tubing accounting for about 6 cm.

Alkali-chloride agar was prepared by dissolving 1.5 g of agar in 50 ml of 1.00 N LiCl, NaCl or KCl at 97-99°C. Bridge tubes were filled with hot solution to a height of about 1.5 - 2 cm above the capillary opening; they were held in a vertical position until the agar gelled. HCl-agar could not be prepared in this manner because agar was decomposed and would not gel. To prepare HCl-agar, 1.5 g of agar was dissolved in 25 ml of water at 97-99°C. The solution was allowed to cool, with constant stirring, to 65°C; then 25 ml of 2.00 N HCl was added and stirred in. The ends of bridge tubes were immediately filled with HCl-agar and held vertically until the agar gelled. No decomposition of gelled HCl-agar was visible, even after several weeks.

After preparing agar bridges, 1.00 N LiCl, NaCl, KCl, or HCl was added to a height of about 2 cm above the agar. A Ag-AgCl electrode was dipped into bridge solution and held securely in place by cementing (DeKhotinsky cement) its glass shank to the top of the bridge tube. The top of the bridge tube was not sealed from the atmosphere. Electrodes + bridges (hereafter called electrodes) were fitted in No. 0 rubber stoppers and stored in 125 ml Erlenmeyer flasks containing the appropriate 1.00 N chloride solution; lead wires extended out of the flask and the flask was stoppered as tightly as possible in order to prevent evaporation.

Testing the Henderson-boundary Approximation

To determine how well the Henderson equation expresses the junction potentials between agar bridges and dilute KCl solutions, measurements were taken on Cell E.

$$\begin{array}{ccccc} & O & \text{standard KCl} & P & \\ \text{Ag; AgCl, 1 }\underline{\text{N}}\text{ ACl} & | & \text{solution} & | & \text{1 }\underline{\text{N}}\text{ KCl, AgCl; Ag} \\ E_1 & E_2 & & E_3 & E_4 \end{array}$$

Cell E

Junctions at O and P were made by means of agar bridges. The concentration of standard KCl was varied from 10^{-4} to 10^{-3} N. The cell e.m.f., E_E, is the algebraic sum of E_1, E_2, E_3, and E_4.

$$E_E = E_1 + E_2 + E_3 + E_4 \tag{48}$$

E_1 and E_4 were calculated as follows.

$$E_1 = -E^\circ + \frac{RT}{F} \ln a_{Cl} \qquad (49)$$

$$E_4 = E^\circ - \frac{RT}{F} \ln a_{Cl} \qquad (50)$$

E° is the standard reduction potential of the Ag-AgCl electrode; $E^\circ = 0.2224$ at 25°C. The value of a_{Cl} was calculated from the mean ionic activity coefficient of ACl ($A^+ = Li^+$, Na^+, or H^+) or KCl.

E_2 and E_3 were calculated from the Henderson equation, equation (31). Mobility values (infinite dilution) were taken from a table presented by Daniels and Alberty (6).

Cell e.m.f.'s were measured with a Keithly Model 600A electrometer. Cells in which the HCl-agar electrode formed the left half-cell required 3-5 minutes for the e.m.f. to become steady; the final e.m.f. was usually 2 mv different from the initial. The e.m.f. of other cells was steady almost immediately. Measurements were taken with two (designated a and b) of each kind of ACl-agar electrode. ACl-agar electrodes were allowed to stand in 1.00 <u>N</u> ACl solution for several minutes between readings. Measurements were taken at 25° ± 1°C.

Calculated and observed values of E_E are presented in Table 2. In every case, observed values were lower (more negative) than those calculated with the Henderson equation. The difference between calculated and observed values does not seem to depend on the concentration of KCl standard solution; in 4 out of 6 cases, this difference agreed within 1 mv for the most concentrated and most dilute KCl

Table 2. Comparison of calculated and observed values of E_E at 25°C, in millivolts.

	$A^+ = Li^+$					$A^+ = Na^+$					$A^+ = H^+$				
c_{KCl}		obs.		calc.-obs.			obs.		calc.-obs.			obs.		calc.-obs.	
eq/l X 10^4	calc.	a	b	a	b	calc.	a	b	a	b	calc.	a	b	a	b
1	-65	-72	-74	7	9	-42	-46	-47	4	5	181	170	173	11	8
2	-59	-68	-69	9	10	-38	-42	-44	4	6	169	159	162	10	7
3	-56	-65	-65	9	10	-36	-40	-42	4	6	162	153	155	9	7
4	-54	-64	-64	10	10	-35	-39	-40	4	5	157	143	150	9	7
5	-52	-62	-62	10	10	-34	-38	-39	4	5	153	144	146	9	7
6	-50	-60	-60	10	10	-33	-37	-37	4	4	150	141	143	9	7
7	-49	-58	-59	9	10	-32	-36	-36	4	4	148	138	140	10	8
8	-48	-57	-57	9	9	-32	-35	-36	3	4	146	136	138	10	8
9	-47	-55	-56	8	9	-31	-34	-35	3	4	144	133	135	11	9
10	-46	-56	-56	10	10	-31	-34	-34	3	3	142	130	133	12	9
column average:				9	10				4	5				10	8
column range:				7-10	9-10				3-4	3-6				9-12	7-9

standards. Thus, even though the Henderson equation does not describe the observations exactly, it is only necessary to add a constant to it in order to obtain an equation which does. In measurements of E_C it is not necessary to consider such a "correction constant" because it cancels out. In other words, the Henderson equation correctly predicts differences in liquid junction potentials. Hence, it may be applied to the quantity $(E_x - E_y)$ if activities and mobilities are as ideal in the suspension phase as in the dialyzate phase.

Preparation of K-bentonite

Seventy-five grams of Upton Wyoming bentonite (A.P.I. No. 25) were dispersed in approximately 3 liters of water using a Hamilton Beach mixer. Coarse particles were removed by centrifuging for 10 minutes at 1000 rpm in an International No. 2 centrifuge equipped with 250 ml tubes. One liter of 0.4 N KCl was then stirred into the 3 liters of suspension. The suspension was stirred occasionally over a period of 3 days and was then passed through a Sharples supercentrifuge operating at 50,000 rpm. The clear effluent solution was discarded and the clay sediment redispersed in 3 liters of water using the Hamilton Beach mixer. The clay was KCl-washed two more times; centrifugation was begun about 10 minutes after stirring the KCl solution into the suspension. After the final KCl-wash, the clay was repeatedly washed with water until the supercentrifuge effluent contained no Cl^- as indicated by the $AgNO_3$ test. The clay remaining after the final washing was dispersed in 1 liter of water. The clay concentration was determined by drying a known weight of the suspension at 90°C until free water was expelled and then drying to constant weight at 130°C. The clay concentration was found to be 1.60% by weight.

Dialysis Cells

Five dialysis cells were constructed from 1/4" Plexiglas sheet and 2" O.D.-, 1 1/2" I.D.-Plexiglas cylinder. One of these is illustrated in Figure 2. Ethylene chloride was used to cement pieces together. Internal dimensions of each compartment are 3 X 3 inches. The two compartments are connected by cylinders cemented into one side of each compartment and protruding 1/2 inch from the side; rubber "O" rings are mounted on the protruding ends of cylinders. A 10-millimicron Millipore filter is mounted between "O" rings and compartments are fastened together with 1/8-inch machine bolts. After filling a compartment, its lid is fastened on with four 1/8-inch machine bolts and sealed by brushing a melted mixture of paraffin and petrolatum (approximately 1:1 by volume) over edges where the lid contacts the rest of the compartment. The lid has two 1/2-inch diameter holes which accommodate electrodes set in No. 0 rubber stoppers. Holes were plugged with solid rubber stoppers when measurements were not being taken.

The initial compositions of dialysis cells were made up as shown in Table 3.

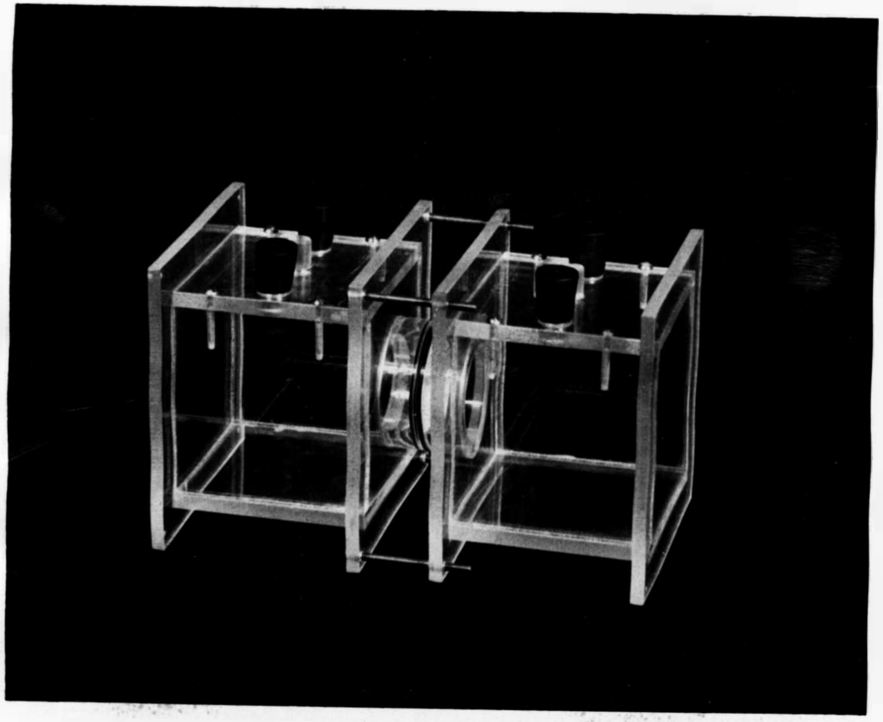


Figure 2. Dialysis cell.

Table 3. Initial compositions of dialysis cells.

Cell No. and compartment	ml 1.60 % K-bentonite	ml 0.100 N KCl	ml H_2O	% clay	c_{KCl} eq/l X 10^4
1 - dial	-	0.4	400	-	1.0
- susp	250	0.4	150	1.0	1.0
3 - dial	-	1.2	400	-	3.0
- susp	250	1.2	150	1.0	3.0
5 - dial	-	2.0	400	-	5.0
- susp	250	2.0	150	1.0	5.0
7 - dial	-	2.8	400	-	7.0
- susp	250	2.8	150	1.0	7.0
9 - dial	-	3.6	400	-	9.0
- susp	250	3.6	150	1.0	9.0

Volumes of 1.60% clay and of water were measured with a 500 ml graduated cylinder; volumes of 0.100 N KCl were measured with a 5 ml graduated pipette.

After filling dialysis cells, they were placed on a mechanical shaker and shaken for 5 days in a direction parallel to the membrane. After this period the phases were at equilibrium as evidenced by an e.m.f. of less than 0.2 mv between Ag-AgCl electrodes, one immersed in each phase.

Prior to each measurement of $E_{C'}$, the e.m.f. between a and b ACl electrodes was measured. This e.m.f. was subtracted from $E_{C'}$ in order to correct for small differences in the characteristics of electrodes a and b. When measuring E_C, it usually required about 25-40 minutes for cell e.m.f.'s to become steady. The e.m.f. was recorded when it became sufficiently steady that no change was observed during a period of at least five minutes. The Keithley Model 600A electrometer was used to measure cell e.m.f.'s.

Results and Discussion

The results of $E_{c'}$ determinations on five K-bentonite + KCl systems are presented in Table 4.

Table 4. Observed $E_{c'}$ values for five K-bentonite + KCl systems, in millivolts. At 25°C.

Cell No.	$A^+ = Li^+$	$A^+ = Na^+$	$A^+ = K^+$	$A^+ = H^+$
1	68	57	35	-10
3	59	50	30	-7
5	52	45	25	-8
7	46	38	24	-7
9	44	39	22	-7
$(t_A - t_{Cl})$:	-0.327	-0.206	-0.018	+0.643

The $(t_A - t_{Cl})$ values were calculated from mobilities at infinite dilution and 25°C; mobility values were taken from a table presented by Daniels and Alberty (6). In Table 4, the (dialysis) cell number is equal to the KCl concentration in the system (suspension + dialyzate), in units of 10^{-4} equivalents per liter. Values reported are averages of two measured values. In no case did individual measurements differ by more than 2 mv from the average, i.e. duplicate determinations always agreed within 4 mv; they usually agreed within 2 mv.

In Figure 3, $E_{C'}$-observed is plotted against $(t_A - t_{Cl})$ for dialysis cells 1, 3, 5, 7 and 9. It appears that these plots do not yield the straight line predicted by equation (47). It would not seem reasonable to draw a best-fitting straight line for each curve because the curves are similar for the 5 systems studied. Upon connecting points by line segments it is seen that inflections occur at $(t_A - t_{Cl}) = -0.018$ and $(t_A - t_{Cl}) = -0.206$ for each of the five curves. Such similarity would not be expected if points deviated from a straight line because of random experimental error. Thus, the deviation from linearity is believed to be real.

For the K-bentonite systems studied, the theoretical expression for $E_{C'}$, equation (47), becomes

$$E_{C'} = E_m + (t_A - t_{Cl}) \frac{1}{k} \ln \frac{U^*}{U_p \sinh(E_m k) + U^* \cosh(E_m k)} \qquad (51)$$

where

$$U^* = \frac{U_K + U_{Cl}}{2} \qquad (52)$$

In obtaining equation (51) from equation (47), the approximations $U_K = U^*$ and $U_{Cl} = U^*$ were used. Marshall (12) reported a value of 3.8×10^{-4} cm^2.volt^{-1}.sec^{-1} for U_p when p is K-bentonite. Substituting the values of U_K and U_{Cl} at infinite dilution (and 25°C) into equation (53), it is found that $U^* = 7.76 \times 10^{-4}$ cm^2.volt^{-1}.sec^{-1}.

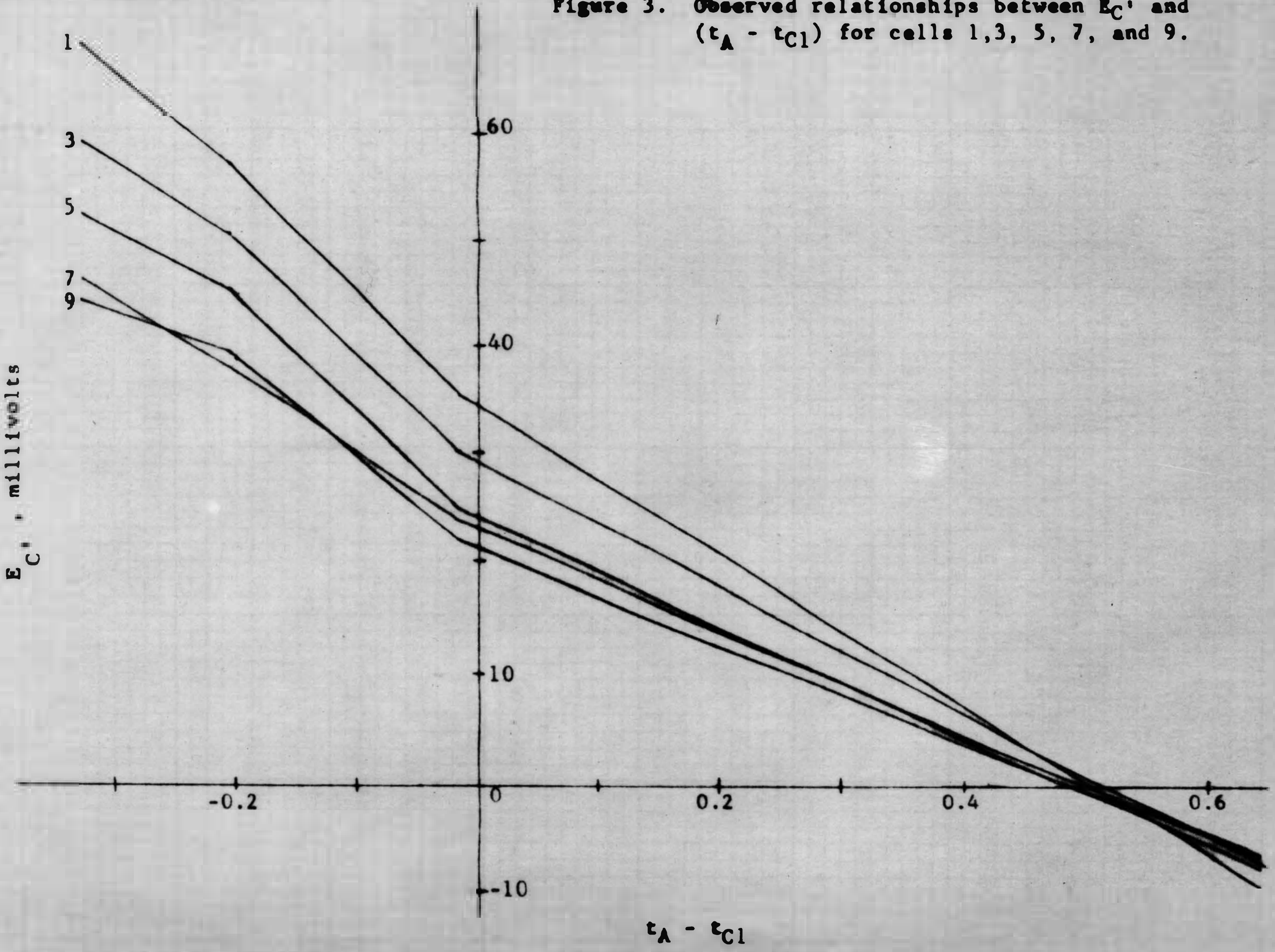


Figure 3. Observed relationships between E_C' and $(t_A - t_{Cl})$ for cells 1,3, 5, 7, and 9.

At 25°C, $k = (38.9/1000)\ \mathrm{mv}^{-1}$ and $1/k = 25.7$ mv. Substituting these values into equation (51) it is found that

$$E_{C'} = E_m + (t_A - t_{Cl})(25.7)\ \ln \frac{7.76}{3.8\sinh\left[\frac{38.9E_m}{1000}\right] + 7.76\cosh\left[\frac{38.9E_m}{1000}\right]} \qquad (53)$$

where $E_{C'}$ and E_m are expressed in millivolts. Equation (53) predicts a slope, S', of

$$S' = 25.7\ \ln \frac{7.76}{3.8\sinh\left[\frac{38.9E_m}{1000}\right] + 7.76\cosh\left[\frac{38.9E_m}{1000}\right]} \qquad (54)$$

for a line obtained by plotting $E_{C'}$ vs. $(t_A - t_{Cl})$.

Figures 4, 5, 6, 7 and 8 present observed and theoretical (equation 53) relationships between $E_{C'}$ and $(t_A - t_{Cl})$ for dialysis cells 1, 3, 5, 7 and 9 respectively. The value of E_m used in equation (53) was taken from the experimental-curve intercept on the $E_{C'}$-axis, hence the two curves must necessarily intersect at that point. It is evident that the magnitude of theoretical slopes is much smaller than that of observed slopes. A comparison of theoretical and minimum-observed slopes is presented in Table 5.

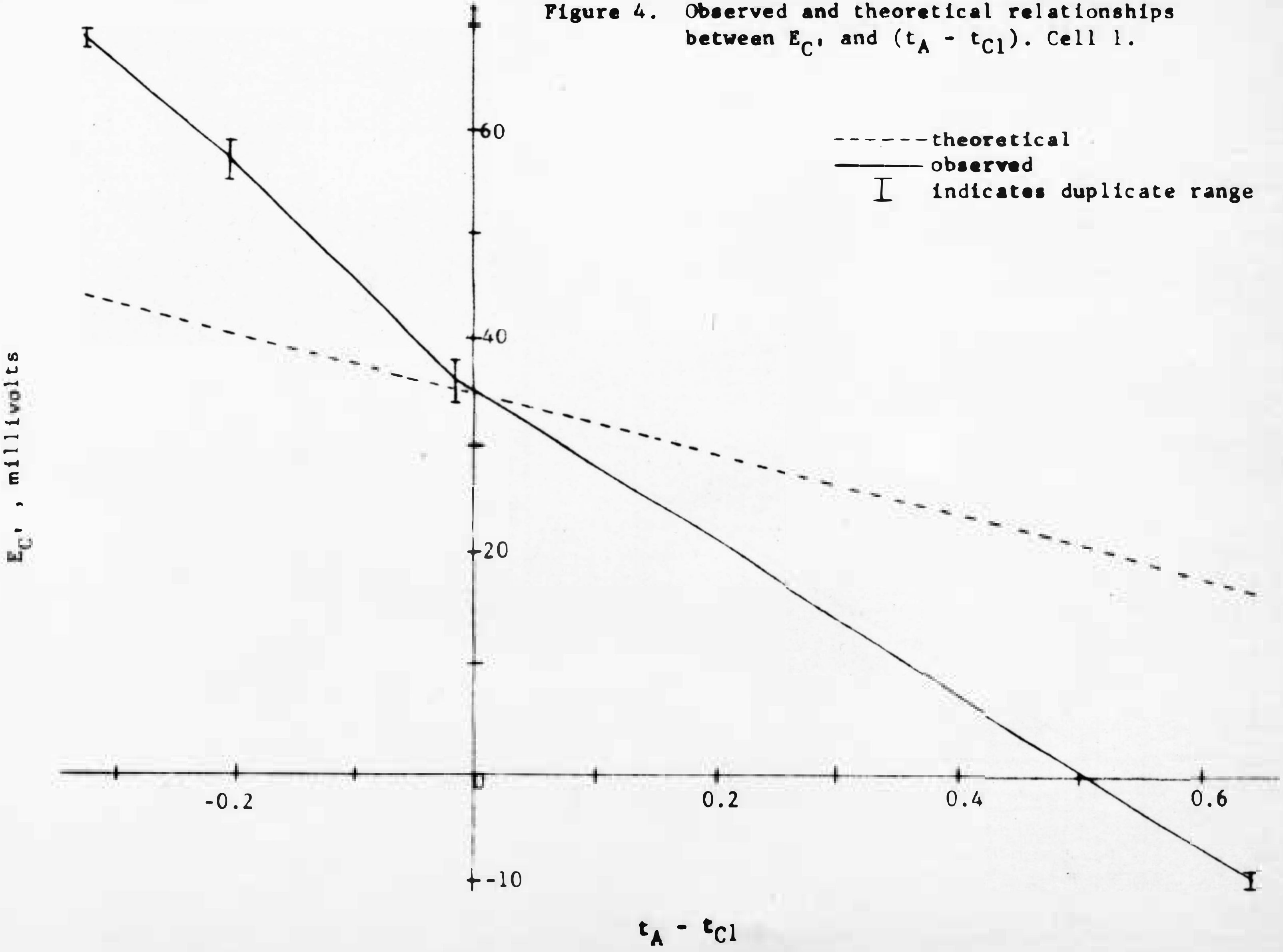


Figure 4. Observed and theoretical relationships between $E_C{}'$ and $(t_A - t_{Cl})$. Cell 1.

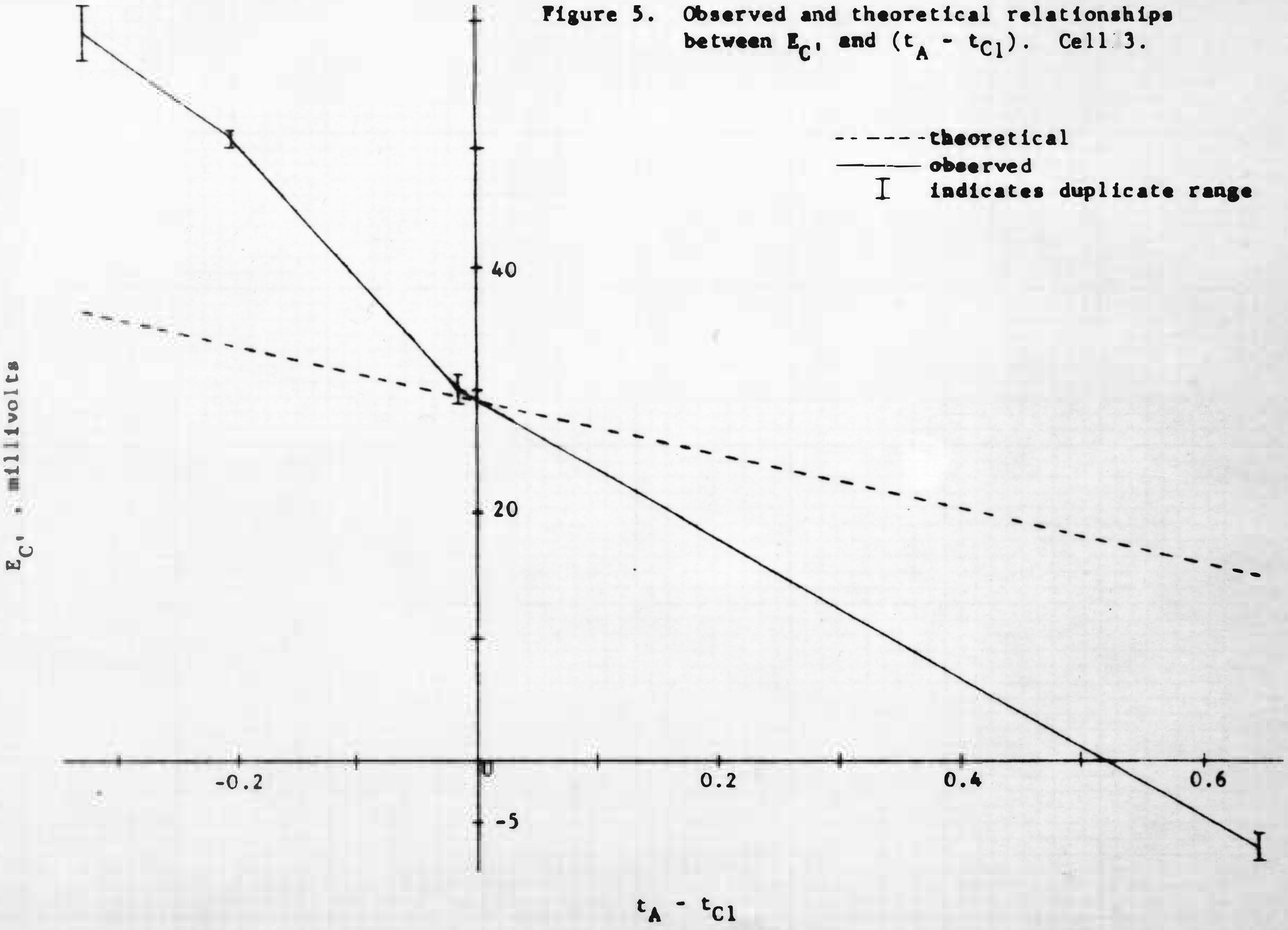


Figure 5. Observed and theoretical relationships between $E_{C'}$ and $(t_A - t_{Cl})$. Cell 3.

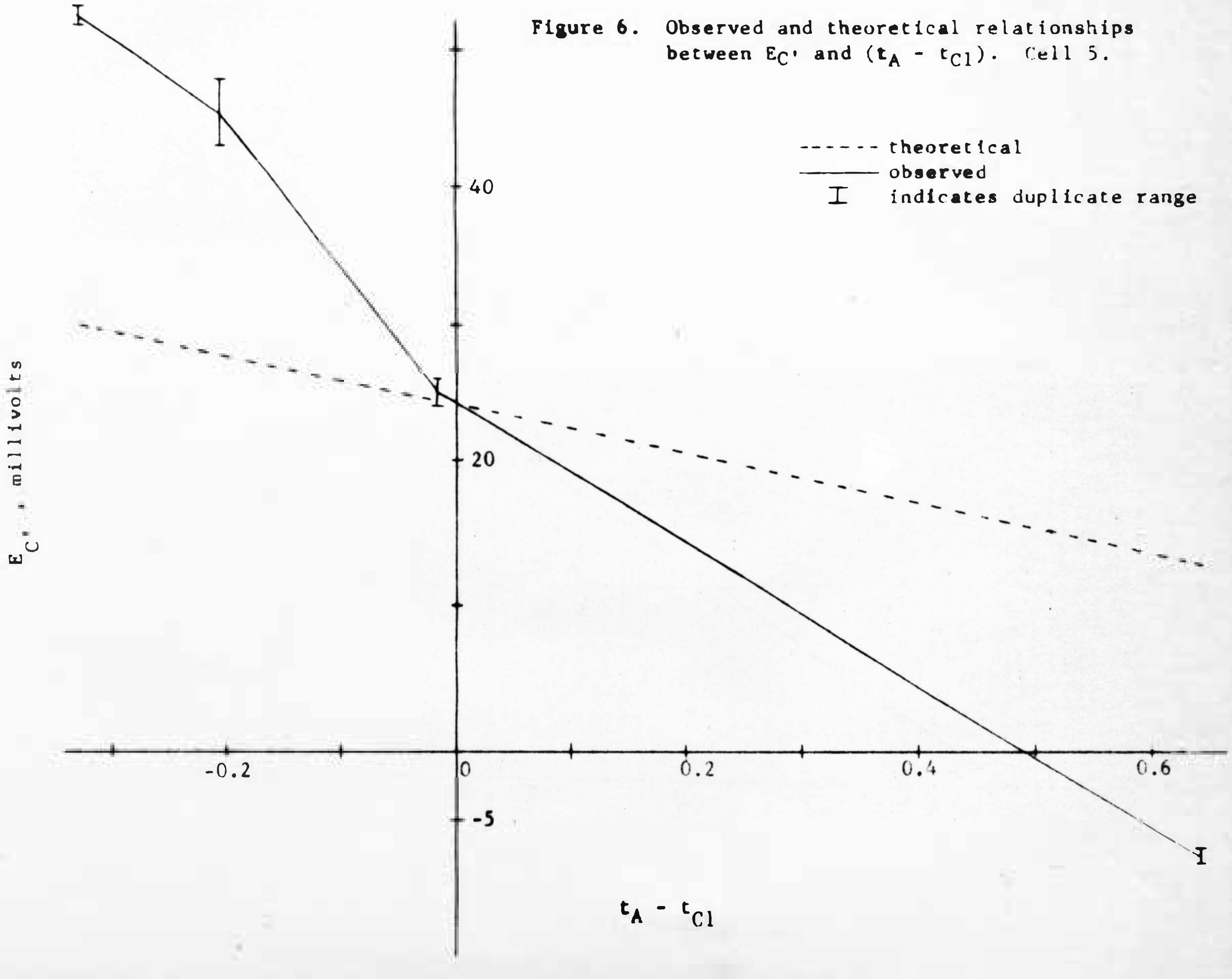


Figure 6. Observed and theoretical relationships between $E_{C'}$ and $(t_A - t_{Cl})$. Cell 5.

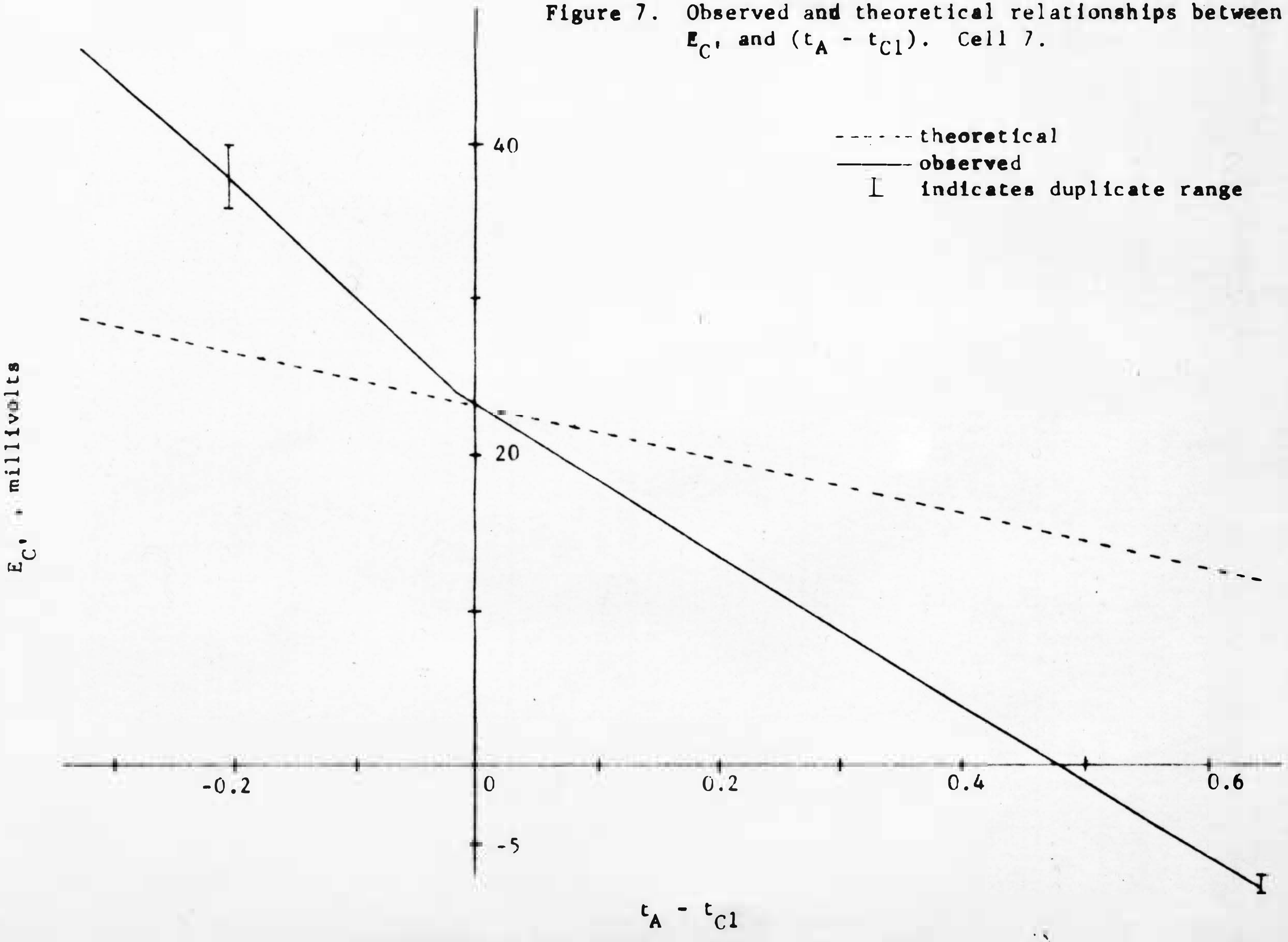


Figure 7. Observed and theoretical relationships between $E_{C'}$ and $(t_A - t_{Cl})$. Cell 7.

Figure 8. Observed and theoretical relationships between $E_{C'}$ and $(t_A - t_{Cl})$. Cell 9.

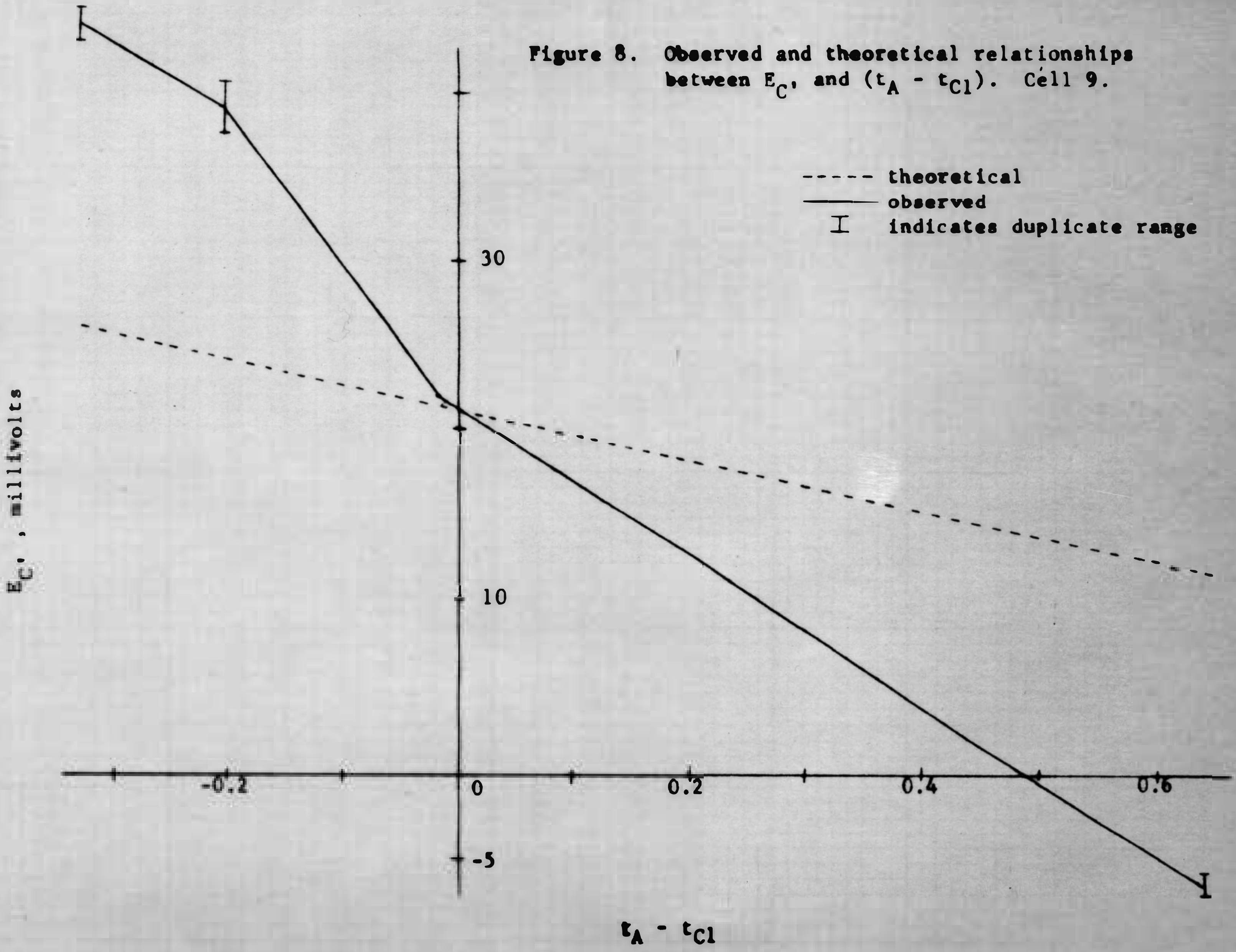


Table 5. Theoretical and minimum-observed slopes for $E_{C'}$ vs. $(t_A - t_{Cl})$, in millivolts.

Cell No.	theoretical	minimum observed	obs. - theor.	$\frac{\text{obs.}}{\text{theo.}}$
1	-28	-69	-41	2.5
3	-22	-57	-35	2.6
5	-18	-50	-32	2.8
7	-17	-47	-30	2.8
9	-15	-44	-29	2.9

The "minimum-observed" slope is the slope of the line segment to the right of the origin. Other line segments of experimental curves have larger slopes; thus, for these segments, the difference between observed and theoretical slopes is larger than shown in Table 5.

The failure of equation (53) to describe the experimental results is evident. It predicts a linear relationship between $E_{C'}$ and $(t_A - t_{Cl})$, whereas a non-linear relationship was observed. Also, minimum-observed slopes are 240 to 290% greater than theoretical slopes. In line with the discussion presented in the Theory section, it is concluded that the Donnan-e.m.f., E_D, is a very poor measure of the Donnan membrane potential, E_m.

Overbeek (21,22) considered the Donnan-e.m.f. to be a poor measure of E_m unless the charge density of colloidal particles is low; the condition that E_D be low is not sufficient. Table 5 shows that the arithmetic difference between observed and theoretical slopes is larger for systems having lower KCl concentrations; Table 4 and Figure 3 show these systems to have high values of $E_{C'}$. In other words, the agreement between theory and experiment is poorer for systems having larger $E_{C'}$ values. A comparison of observed slope/theoretical slope (Table 5), however, shows that the percentage difference between slopes is greater for systems of higher KCl concentrations and lower $E_{C'}$ values. This supports Overbeek's statement that the condition that E_D be low is not sufficient to imply that it will be a good measure of E_m.

Babcock and Overstreet (3) and Overbeek (21,22) showed that the membrane potential, E_m, does not contribute directly to the Donnan-e.m.f. or suspension effect; i.e. the membrane is not a seat of e.m.f. (see equation 24). The author can find no fault with their theoretical analyses in this regard. Accepting this viewpoint requires one to choose equation (46),

$$E_C = (t_A - t_B)\, S \tag{46}$$

as the correct expression for E_C, if assumptions upon which it is based are valid. But, as noted in the theoretical discussion, this requires that E_D ($E_C = E_D$ when AB is KCl) be approximately zero; this contradicts much experimental evidence, including that presented above.

This leads one to question the validity of assumptions on which equation (46) is based. It was previously shown (in Experimental Methods and Procedure section) that the Henderson-boundary assumption is valid for experiments reported here, if activities and mobilities are as ideal in the suspension phase as in the dialyzate phase. Activities are well known to behave almost ideally in dilute solutions. Since activities differ from concentrations only because of interaction between small ions, they must behave as ideally in suspension phases as in solution phases; recall that the chemical potential, in terms of which activities are defined (equation 5), does not include interaction between small ions and force fields of colloidal particles. The assumption that equation (8) expresses the distribution of ions between phases seems reasonable in view of the single assumption used in its derivation; i.e. the assumption that the only force field originating in colloidal particles and affecting ions is an electrostatic force field; in any case, this assumption is essential to the interpretation of the Donnan-e.m.f. in terms of the Donnan potential. The remaining assumption upon which equation (46) was based is that ionic mobilities behave ideally.

Jenny et al. (8), Coleman et al. (5) and Overbeek (21,22) attributed the Donnan-e.m.f. to non-ideal behavior of mobilities. Results of the present study support this view if it is granted that the correctness or reasonableness of other assumptions has been established.

Mysels (20) seems to have argued that, although the membrane is not a seat of e.m.f., the membrane potential, E_m, would be reflected in the liquid junction potential, E_x, if mobilities behaved ideally. Overbeek (22) showed analytically how such a reflection could take place, again, if mobilities are ideal (see equation 28). But it was his view that the assumption of ideal behavior of mobilities is not valid for systems containing particles of high charge density. Results of the present study show that the membrane potential is not accurately reflected in the liquid junction potential E_x.

Since the Donnan-e.m.f. or suspension effect is not interpretable in terms of the Donnan membrane potential (nor, as far as is known, in terms of any other quantity of direct significance) it must be regarded as an error. Also, since E_m is not measurable, the conceptual distinction between "activities" and "total activities" can not be given a physical distinction, in systems containing charged colloids. Although Low considered E_D to be an approximate measure of E_m (10), he seemed to prefer total-activity measurements to activity measurements because the former are of greater thermodynamic significance than the latter (9,10). The results of the present study support Low's preference.

As was pointed out by Babcock and Overstreet (3) and by Overbeek (22), the view that E_D is not a measure of E_m (supported by results reported here) does not deny the possibility that E_m exists; it only denies the usefulness of potentiometric methods used to measure E_m. It must be emphasized that the results of the present study in no way deny that Donnan distributions of ions exist in the systems studied or in analogous systems (e.g. in soils).

Since the Donnan-e.m.f. must be explained in terms of changed ion mobilities, it is of interest to examine a mechanism by which mobility changes could give rise to the observed e.m.f. Since it is impossible to observe the movements of ions on a molecular scale, the following discussion must, in part, fall into the realm of speculation.

Consider Cell A, in which KCl bridges are employed to measure E_D. Assuming that E_y is negligible and that M is not a source of e.m.f., then $E_D = E_x$. Since positive E_D's are observed, E_x must be positive; i.e. the boundary X is of polarity $- \mid +$. In order to obtain a positive E_x, it must be true that K^+ moves from the bridge into the suspension at a faster rate than Cl^-. To see why this should be so, consider the approach of the KCl diffusion front to a single negatively charged particle (e.g. a clay particle). As bridge-KCl begins to enter the double layer of the particle (i.e. the electrostatic force field), K^+ will be accelerated toward the particle and Cl^- will be repelled by the particle; there is also a tendency for K^+ and Cl^- to be held in the same location due to attraction between them. The result of these opposing forces is to cause a slight excess of positive charge to accumulate in the double layer with a corresponding deficiency of positive charge outside the double layer; this gives rise to a positive potential, E_x, the magnitude of which depends on the charge excess or deficiency, and on the separation of locations where positive charge is in excess and locations where it is deficient. When KCl solution is concentrated, the electrostatic field of the double layer should be very small; however, since bridge-KCl enters the system by diffusion, there will be locations (at the diffusion front) where bridge-KCl is dilute. At these locations, the particle's electrostatic field is large, giving rise to E_x.

As mentioned earlier, it usually required 25 to 40 minutes to obtain steady $E_{C'}$ measurements. During this time, $E_{C'}$ always <u>increased</u>. This can be explained by the mechanism proposed above: The observed e.m.f. increased with time because the KCl diffusion front became more dilute with time, hence the influence of the electrostatic field of particles became greater. When the diffusion front became as dilute as KCl in the system, the observed e.m.f. became steady.

It is of interest to mention how the conclusions of the present study affect the interpretations of results of potentiometric measurements on soils. Since the Donnan-e.m.f. or suspension effect must be regarded as an error, it should be avoided wherever possible. This can be done by making measurements (e.g. pH or pK measurements with glass electrodes and saturated calomel electrodes) on a solution which is at equilibrium with the soil under study. Each investigator must, of course, decide whether or not the suspension effect will contribute sufficient error to be of significance in his studies. The significance of the suspension-effect error will depend on the particular soil under study and on the purpose of the study.

Summary

There has been a great deal of discussion in the literature on how potentiometric measurements in colloidal systems should be interpreted. The suspension effect, which is generally observable when such measurements are made, is attributed, by some, to the Donnan potential and, by others, to a liquid junction potential. The purpose of the present study was to devise experimental means of distinguishing between these theories.

A theoretical equation was derived which related the e.m.f. measured between Donnan phases to transference numbers of ions in the bridges used to make contact with each phase. The equation predicted that a plot of e.m.f. vs. the difference in transference numbers would yield a straight line having a given slope. It was shown that the equation must be experimentally confirmable if the interpretation of the suspension effect in terms of the Donnan potential is valid.

Cell e.m.f. values were measured for five K-bentonite + KCl Donnan systems, using bridges of various compositions in order to obtain several values for the difference in transference numbers of bridge ions. The experimental data did not obey the theoretical equation; curves obtained by plotting experimental data were not linear and observed slopes were 250 to 290% greater than predicted slopes. It was concluded that the suspension effect is not interpretable in terms of the Donnan potential and that it must be

regarded as an error in measured e.m.f. values. The suspension effect is probably caused by non-ideal behavior of ionic mobilities giving rise to a liquid junction potential at the salt-bridge-suspension interface.

Literature Cited

1. Adair, G. S., and Adair, M. E. The determination of the electric charge of colloidal ions. Trans. Faraday Soc. 31:130-135. 1935.

2. Babcock, K. L. Some Characteristics of a model Donnan system. Soil Sci. 90:245-252. 1960.

3. __________, and Overstreet, R. On the use of calomel half-cells to measure Donnan potentials. Science 117:686-687. 1953.

4. Bower, C. A. Studies on the suspension effect with a sodium electrode. Soil Sci. Soc. Am. Proc. 25:18-21. 1961.

5. Coleman, N. T., Williams, D. E., Nielsen, T. R., and Jenny, H. On the validity of interpretations of potentiometrically measured soil pH. Soil Sci. Soc. Am. Proc. 15:106-110. 1951.

6. Daniels, F., and Alberty, R. A. Physical Chemistry. John Wiley and Sons, Inc., New York, p368. 1961.

7. Davis, L. E. Significance of the Donnan equilibria for soil colloidal systems. Soil Sci. 54:199-219. 1942.

8. Jenny, H., Nielsen, T. R., Coleman, N. T., and Williams, D. E. Measurements of pH, ion activities and membrane potentials in colloidal systems. Science 112:164-167. 1950.

9. Low, P. F. Force fields and chemical equilibria in heterogeneous systems with special reference to soils. Soil Sci. 71:409-418. 1951.

10. __________. Ionic activity measurements in heterogeneous systems. Soil Sci. 77:29-41. 1954.

11. MacInnes, D. A. The Principles of Electrochemistry. Dover Publications, Inc., New York, pp231-232. 1961.

12. Marshall, C. E. The Colloid Chemistry of the Silicate Minerals. Academic Press Inc., New York, p148. 1949.

13. __________. Measurements in colloidal systems. Science 113:43-44. 1951.

14. __________. Comments on references 5 and 8. Soil Sci. Soc. Am. Proc. 15:110-112. 1951.

15. __________. Potentiometric measurements in colloidal systems. Science 115:361-362. 1952.

16. __________. A critical review of the two preceding papers. Soil Sci. Soc. Am. Proc. 17:218-220. 1953.

17. __________, and Deshpande, K. B. The validity of electrometric methods as applied to clay-water systems. Trans. 7th International Congr. Soil Sci., Madison, Wis. II:337-341. 1960.

18. McLean, E. O., and Franklin, R. E. Cation activities in clay suspensions and equilibrium dialyzates. Soil Sci. 97:260-267. 1964.

19. Mysels, K. J. (Potentiometric) measurements in (some) colloidal systems. Science 114:424-425. 1951.

20. __________. On (the interpretation of) the use of calomel half-cells to measure Donnan potentials. Science 118:603-604. 1953.

21. Overbeek, J. Th. G. Donnan-e.m.f. and suspension effect. Jour. Coll. Sci. 8:593-605. 1953.

22. __________. The Donnan equilibria. Progr. Biophys. and Biophys. Chem. 6:58-84. 1956.

23. Peech, M., and McDevit, W. F. Comments on references 5 and 8. Soil Sci. Soc. Am. Proc. 15:112-114. 1951.

24. Peech, M., Olsen, R. A., and Bolt, G. H. The significance of potentiometric measurements involving liquid junction in clay and soil suspensions. Soil Sci. Soc. Am. Proc. 17:214-218. 1953.

25. __________, and Scott, A. D. Determination of ionic activities by means of the Donnan membrane equilibria. Soil Sci. Soc. Am. Proc. 15:115-119. 1951.

26. Williams, D. E. Reply to reference 14, Soil Sci. Soc. Am. Proc. 15:111. 1951.