



A study of the suspension effect observed in a Dowex-50 - water system
by John Edward Robbins

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree
of Master of Science in Chemistry
Montana State University
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Abstract:

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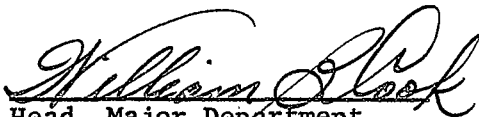
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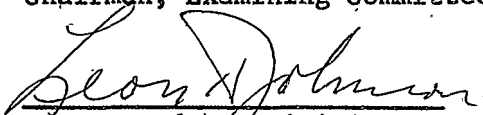
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Montana State College

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Head, Major Department


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Bozeman, Montana
August, 1961

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ABSTRACT

In this investigation, the distribution of ions in a Dowex-50-Water System, was considered. Within the limits of experimental error, the data support the "bound-water theory" as it relates to ion distribution.

The actual distribution of Cl as determined with Cl³⁶ was compared with the apparent distribution as determined potentiometrically with a Ag,AgCl--reference electrode pair. The discrepancy (corresponding to as much as 93 millivolts) was attributed to a liquid junction potential at the resin-salt bridge interface. The data are shown to provide qualitative, and to some extent quantitative, support to a theory proposed by Overbeek.

Any potentiometric measurement made in an exchanger-water system and employing reference electrode with salt bridge is considered to be subject to error from this source.

INTRODUCTION

The convenience and accuracy of the electrometric method has led to its widespread use for determination of pH of aqueous solutions. For this purpose, the glass electrode is commonly used with a reference calomel electrode. The potential difference between this electrode pair is related to the pH by the expression $E_{gl} - E_{ref} = 0.0591 \text{ pH}$. Electrical contact between the calomel electrode and solution is commonly made by means of a KCl salt bridge. Inasmuch as the equivalent conductance of K^+ and Cl^- are nearly the same (76 vs 79 mho), the liquid junction potential (E_j) at the calomel-solution interface is considered to be negligibly small (<2mv.). The observed potential difference is therefore considered to be a reliable quantitative measure of the pH of the solution.

The question of applicability of the electrometric method to exchanger-water systems has received attention in recent years. A difference of opinion still persists--some contending that E_j in these systems is negligibly small as it is in true solutions--others contending that the E_j may be so large as to completely invalidate the determination. The issue may be briefly outlined as follows: If the pH of an aliquot of the equilibrium aqueous phase of an exchanger is determined electrometrically, it is commonly found to differ from the pH of the slurry. The phenomenon has been termed the "suspension effect". In magnitude, it may range from zero to as high as 4 pH units, depending upon the type of exchanger, electrolyte content and other chemical properties of the system. With respect to the aqueous phase, the pH of the resin may be lower (positive suspension effect) or may be higher (negative suspension effect).

The original, and still popular, explanation for the positive suspension effect attributes the lower pH of the resin to the existence of H^+ ion "swarms" at the surface of the particles. Being constrained from free diffusion throughout the entire system by the oppositely charged exchange sites, they are nevertheless considered to be effective in increasing the activity of the H^+ ion near the particle surface. A glass electrode placed near the surface of the particle accordingly is exposed to solution of lower pH.

Recently, evidence has been published which is interpreted to mean that the suspension effect may be due to an error inherent in the electrometric method. According to this viewpoint, an appreciable E_j arises at the calomel-suspension interface upon bringing the calomel in close proximity to the charged particles. E_{ref} accordingly cannot be considered a constant and $E_{gl} - E_{ref}$ is accordingly not a reliable measure of the pH in exchanger-water systems.

As is readily apparent, the matter of determining the order of magnitude of E_j is a crucial problem. If it accounts for all of the suspension effect, it may be large enough in some systems to completely invalidate any electrometric measurements requiring the use of a salt bridge. If E_j is low (of the order of magnitude of several millivolts or less) it will not be objectionable in most electrometric determinations. The primary objectives of the present investigation were to (a) quantitatively determine E_j in a particular system and (b) to study the effect of several chemical properties of the system upon its magnitude.

LITERATURE REVIEW

The suspension effect was first reported independently by Bradfield (9) and Wiegner (28) in 1931. Bradfield observed that the potentiometrically measured pH of a H^+ -clay suspension was as much as 3 pH units lower than the pH of the equilibrium supernatant solution. The suspension effect was observed regardless of whether a glass, a hydrogen or a quinhydrone electrode was used.

Bradfield suggested that the chemical properties of the H^+ -clay were similar to those of a weak acid. Inasmuch as the negatively charged clay particles settled out, the associated H^+ ions also settled out in order to maintain electrical neutrality throughout the system. The clays, being weak acids, allowed some dissociation of H^+ ions and effectively lowered the pH of the suspension.

The explanation by Bradfield was widely accepted with little modification until about 1950. During this time interval, E_j was considered to be negligibly small, as it reportedly is, in true solutions (19). In 1950, Jenny et al. (20) published evidence which was interpreted to mean that the suspension effect is solely due to E_j . They interpreted their results to mean that the mobilities of K^+ and Cl^- are changed (increased and decreased respectively) by the presence of the negatively charged exchanger particles. As a result, an appreciable diffusion potential arose at the suspension-salt bridge interface.

Davis (32) and Du Reitz (33) have shown that the observed pH of comparable suspensions does not depend upon the position of the glass electrode but rather upon the position of the calomel electrode. Their observations

are depicted in Figure 1. Confirmatory observations were made in the present investigation. Following the publications of Davis (32) and DuReitz (33), however, a controversy arose regarding the interpretation of these observations. The interpretation of Jenny et al. appears to be as follows:

(1) If a glass-calomel electrode pair is immersed in the supernatant liquid as in (a), the E_j at the calomel-solution interface is negligibly small (< 2 millivolt) and the observed pH is a valid indication of the a_{H^+} in the medium.

(2) As shown in (c), the a_{H^+} in both phases is equal, assuming that $E_m = 0$. (E_m , the membrane potential, represents the potential difference across the interface between slurry and supernatant solution. (See Appendix page 49.)

(3) If $E_m = 0$ then, as shown in (d), an E_j of 240 millivolts arises at the calomel-suspension interface upon immersing the calomel into the suspension.

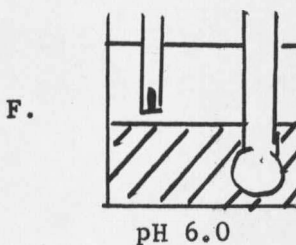
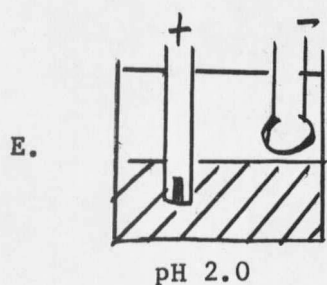
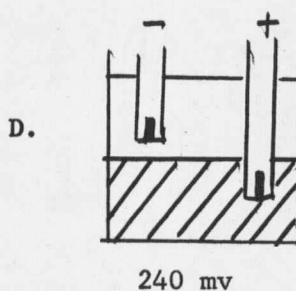
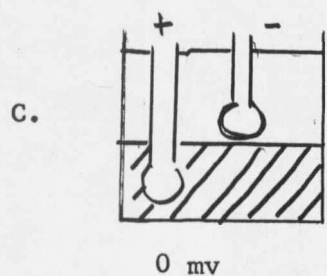
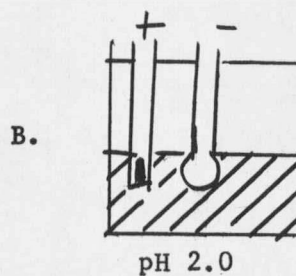
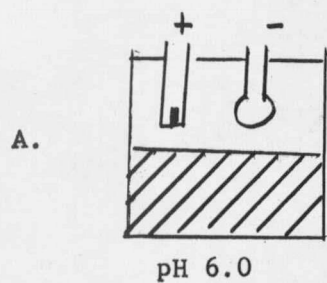
(4) The observed pH should therefore depend only upon the position of the calomel electrode and is unaffected by the position of the glass electrode. This is shown to be true by observations (a), (b), (e) and (f). According to this viewpoint, the observed EMF. for each cell would be given by the following:

$$E(a) = E_{gl}^o - E_{cal}^o + 0.0591 \log a_{H^+}'''$$

$$E(b) = E_{gl}^o - E_{cal}^o + 0.0591 \log a_{H^+}'' + E_j$$

$$E(c) = E_{gl}^o - 0.0591 \log a_{H^+}''' - E_{gl}^o + 0.0591 \log a_{H^+}'' = 0$$

$$E(d) = E_{cal}^o - E_{cal}^o + E_j = E_j$$



pH = 4.0 240 mv.

Key;  equilibrium solution  glass electrode
 suspension (colloidal particles)  calomel electrode

Figure 1. Electrometric observations made by Davis.

$$E(e) = E_{gl}^o - E_{cal}^o + 0.0591 \log a_{H^+}''' + E_j$$

$$E(f) = E_{gl}^o - E_{cal}^o + 0.0591 \log a_{H^+}''$$

and $a_{H^+}''' = a_{H^+}''$.

Eriksson (17) and others have suggested an alternative explanation of the observations depicted previously. From the Donnan (15) theory, (see Appendix, page 49), one can obtain the relationship:

$$E_m = 0.0591 \log a_{H^+}'' / a_{H^+}'''$$

Including this term in the expressions for the cell potentials where necessary, we obtain for cells a, b, c, d, e, and f the following:

$$E(a) = E_{gl}^o - E_{cal}^o + 0.0591 \log a_{H^+}'''$$

$$E(b) = E_{gl}^o - E_{cal}^o + 0.0591 \log a_{H^+}'' + E_j$$

$$E(c) = E_{gl}^o - E_{gl}^o + 0.0591 \log a_{H^+}'' / a_{H^+}''' - E_m$$

$$E(d) = E_{cal}^o - E_{cal}^o + E_j + E_m$$

$$E(e) = E_{gl}^o - E_{cal}^o + 0.0591 \log a_{H^+}''' + E_j + E_m$$

$$E(f) = E_{gl}^o - E_{cal}^o + 0.0591 \log a_{H^+}'' - E_m$$

Now if we substitute into the above expressions the value of E_m , and making the assumption the $E_j = 0$ we have:

$$E(a) = E_{gl}^o - E_{cal}^o + 0.0591 \log a_{H^+}'''$$

$$E(b) = E_{gl}^o - E_{cal}^o + 0.0591 \log a_{H^+}''$$

$$E(c) = 0$$

$$E(d) = E_m$$

$$E(e) = E_{gl}^o - E_{cal}^o + 0.0591 \log a_{H^+}''$$

$$E(f) = E_{gl}^o - E_{cal}^o + 0.0591 \log a_{H^+}'''$$

This treatment provides an alternative explanation for the observations made by Jenny et al., Davis (32) and Du Reitz (33). They point out that the observations can be explained satisfactorily by assuming that E_j is negligibly small and E_m correspondingly large. The observations may be explained equally well by the existence of an E_m or alternatively by the existence of an E_j .

In 1952, M. Peech, G. H. Bolt and R. A. Olsen (27) reported some anomalies that they attributed to a liquid junction potential between the saturated KCl and clay suspension interface. They measured the membrane potential of several clay suspensions by use of two saturated calomel electrodes using the Donnan (14) equilibrium method for measuring ion activities in suspensions. ΔE_{cal} was given a positive sign when the electrode in the dialyzate was positive with respect to the electrode in suspension. This is in accordance for a membrane potential of a negatively charged colloid.

$$\Delta E_{cal} = E_m + E_j.$$

The sign of ΔE_{cal} was found to be positive for suspensions of many different clays saturated with H^+ , Na^+ and K^+ . However, when certain clays were saturated with Ca^{++} , the ΔE_{cal} was negative. One possible explanation for this observation would be the reversal of sign on the colloid particle. This possibility was checked independently by zeta potential measurements. It was found that the sign of the charge on the particles had not been reversed. The reversal of sign was therefore attributed to a negative E_j .

In conjunction with the above work, the osmotic pressure of the clay

suspension was determined by experimental measurements and also by calculation. The activities determined the Donnan method were used in calculating osmotic pressure, Π , by the equation:

$$\Pi = RT (Z + 2Y - 2X)$$

$Z = \text{Na}^+$ concentration (dissociated from clay)

$Y = \text{NaA}$ salt concentration in the suspension

$X = \text{NaA}$ concentration in the dialyzate.

These values were calculated from the following relation to ΔE_{cal} .

$$\Delta E_{\text{cal}} = \frac{RT}{F} \ln \frac{X}{Y} = \frac{RT}{F} \ln \frac{Z + Y}{X}$$

The osmotic pressure that was calculated showed serious deviation from the osmotic pressure that was measured. The discrepancy was attributed to the error introduced in the experimental evaluation of E_m , and the resultant error in calculation of osmotic pressure.

In 1953, Overbeek (26) published a theoretical treatment of the suspension effect. He considered the suspension effect and the Donnan potential to be identical and made up of the sum of E_j and E_m . Attempts at separately evaluating E_j and E_m were considered to be unsatisfactory because of the necessity of arbitrary assumptions. He showed that the suspension effect (referred to as E_D) can be calculated approximately from the composition of the system by the relationship:

$$E_D = \frac{RT}{F} \ln \frac{\text{conductance of exchanger}}{\text{conductance of equilibrium liquid}}$$

Overbeek's treatment was tested experimentally by Bloksma (2), using mobilities of the adsorbed ions. He concluded that the agreement was sufficiently good to be confirmative.

Recently, Bower (5)(6) studied the suspension effect with a glass electrode which is selective for Na^+ . Bower found good support for Overbeek's theory. He also checked the effect of the concentration of the salt bridge on the magnitude of the suspension effect. It was found that the suspension effect became negligible when the concentrations of salt in the salt bridge and equilibrium liquid are the same.

At the present time, there seems to be, judging from the published information, two schools of thought regarding E_j in colloidal systems. One school (24) is apparently of the opinion the E_j is negligible. The other (20), is apparently of the opinion the E_j is of sufficient magnitude to entirely account for the suspension effect. In this investigation, an attempt has been made to obtain a more reliable estimate of E_j than is currently available and thereby contribute to our understanding of the suspension effect.

EXPERIMENTAL

Characteristic Suspension Effects of Selected Ion Exchange Resins

The initial objective was to select an exchanger which exhibited a large suspension effect. It was reasoned that if the exchanger exhibited only a small suspension effect, the accuracy with which E_j could be measured would be correspondingly low. So far as is known, the largest suspension effect reported in the literature is the value of 4 pH units reported by Jenny (20) for a Dow product called Ion-X. Accordingly, several synthetic cation and anion exchangers were selected for comparison.

All resins were treated in the following way:

- (1) A sample of approximately 20 g. was placed in a Buchner funnel under suction.
- (2) Cation exchangers were washed with 0.1 N HCl and the anion exchangers were washed with 0.1 N NaOH.
- (3) The resins were transferred to 500 ml. Erlenmeyer flasks and were equilibrated with excess acid or base for one half hour on a wrist action shaker.
- (4) The samples were then washed in the Buchner funnel without suction until indicator paper indicated that the effluent had become approximately neutral. Prior to the determination of the suspension effect, ten milliliters of water were added to approximately two grams of resin. The flask was shaken periodically for three hours and then allowed to stand over night. The suspension effect was measured with a glass electrode and a saturated calomel electrode. Values, obtained for the suspension effect

for the various resins, are shown in Table I (page 19). Other characteristics are also listed in the table. These will be discussed later. As a result of the findings here, Dowex-50 was selected as the resin to be used in the investigation. This particular resin is characterized by the following; 8% cross-linkage; particle size 100-200 mesh. In the H^+ form, it was found to exhibit a suspension effect of approximately 3 pH units; which was believed satisfactory for the purposes of this investigation. A comparison of the suspension effect for a weak acid and a strong acid and of a weak base and strong base is depicted in figure 2.

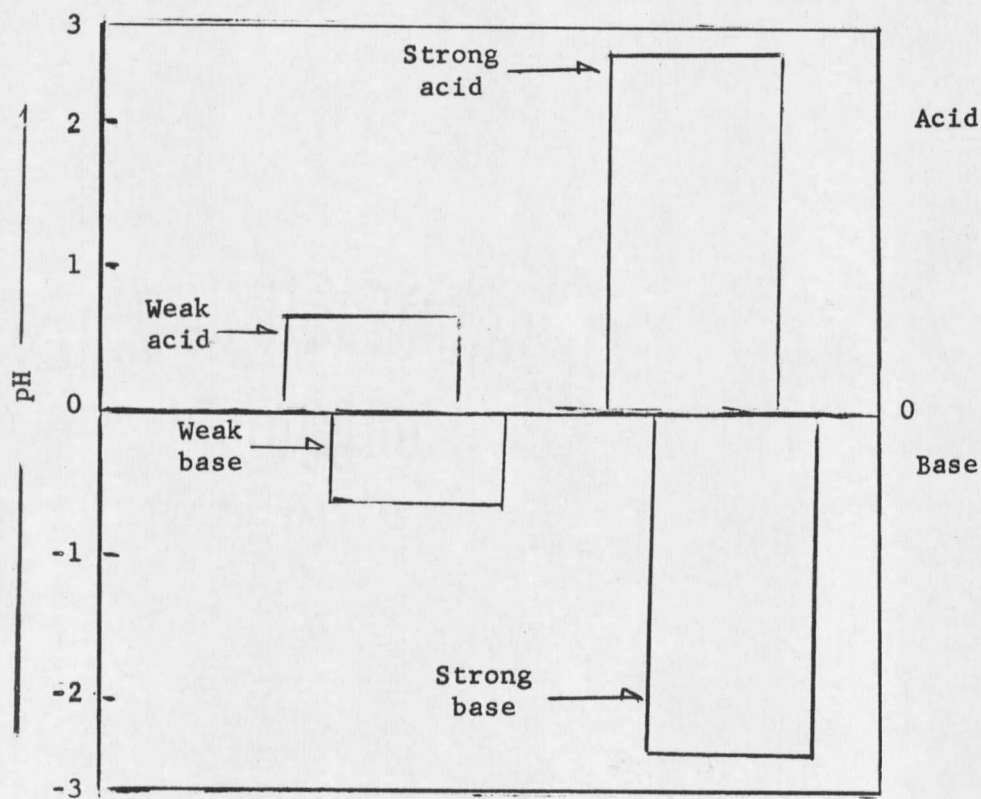


Figure 2: Comparison of the Suspension Effect between Strong Acid and Base Resins and Weak Acid and Base Resins

TABLE I

Characteristics of Ion Exchange Resins

<u>Exchangers</u>	<u>Wet Resin Capacity*</u>	<u>Suspension Effect Aqueous-Resin</u>	<u>Acid or Base Strength</u>
<u>Cation</u>			
Dowex-50	1.7 meq/ml	3.26 pH units	strong
Dowex-50W	1.7 meq/ml	2.64 pH units	strong
Amberlite IR-120	1.9 meq/ml	3.05 pH units	strong
Amberlite IRC-50	3.5 meq/ml	0.81 pH units	weak
<u>Mixed bed</u>			
IR MB-3	0.55 meq/ml	2.88 pH units	
<u>Anion</u>			
Dowex-1	1.33 meq/ml	-2.79 pH units	strong
Dowex-2	1.33 meq/ml	-2.05 pH units	strong
IR-45	2.00 meq/ml	-0.70 pH units	weak
IR-400	1.00 meq/ml	-3.07 pH units	strong
IR-410	1.20 meq/ml	-2.46 pH units	strong
Duolite A-40	1.40 meq/ml	-3.30 pH units	strong
Duolite 42	1.30 meq/ml	-2.53 pH units	strong

*All exchange capacities are reported as milliequivalents per milliliter of wet resin, with the cation exchanger in the H^+ form; the anion exchangers in the Cl^- form. For the suspension effect, the H^+ and OH^- forms were used.

Ion Distribution in a Dowex-50 - Water System

A. Donnan Theory versus "Bound Water" Theory

In a recently published thesis, Moreno (34) has considered the relative merits of the Donnan theory and of the "bound water" theory (15) for describing ion distribution in an exchanger-water system. The following is based upon his treatment of the two theories. In the "bound water" theory, it is postulated that a certain volume of water, V_b , is tightly adsorbed at the surface of an exchanger so that it does not function as a solvent for an electrolyte. By making this assumption, one can formulate the following:

Let X = amount of Cl^- *

$[Cl^-]$ = concentration of Cl^-

V_b, V_r, V_t = volume of bound water, volume of remainder of water, and the total volume of water respectively.

$$\text{Then } \frac{X_r}{V_r} = \frac{X_t}{V_t - V_b}$$

and multiplying by V_t we obtain,

$$\frac{X_t V_t}{V_t(V_t - V_b)} = \frac{X_r}{V_r}, \text{ this may also be written as } [Cl^-]_t = \frac{(V_t - V_b)}{V_t} [Cl^-]_r$$

Thus, by keeping V_t, V_r, V_b constant and varying X_t , we should get a plot of X_t/V_t versus X_r/V_r as a straight line which passes through the origin and has a slope of $(V_t - V_b)/V_t$. Since V_t is known, V_b can be determined from the slope. (See figure 3, page 26).

* Cl^- was chosen because it can be analyzed for by potentiometric, radiometric, and volumetric methods.

If the Donnan theory provides the most satisfactory treatment of chloride distribution in an exchanger-water system, then there is not a definite region in which Cl^- is excluded, but rather an exponential relationship between the electrical potential and Cl^- . (See Appendix C, page 49). The nearer one approaches the resin surface, the lower the $[\text{Cl}^-]$ becomes. The one theory requires a diffuse double layer - the other a distinct double layer.

According to the Donnan treatment for uni-univalent electrolyte

$$a'_{\text{M}^+} \times a'_{\text{Cl}^-} = a''_{\text{M}^+} \times a''_{\text{Cl}^-}, \quad (1)$$

$$\text{and also } (a'_x + a'_{\text{Cl}^-}) (a'_{\text{Cl}^-}) = (a''_{\text{Cl}^-})^2. \quad (2)$$

Where a'' is the activity of an ion in the supernatant and a' refers to the slurry and where a_x is the activity of the adsorbed cation. That the total chloride in the system equals the sum of the chloride in the parts requires that,

$$X_t = [\text{Cl}^-]' V' + [\text{Cl}^-]'' V'' \quad (3)$$

$$[\text{Cl}^-]_t = X_t/V_t = \frac{[\text{Cl}^-]' V'}{V_t} + \frac{[\text{Cl}^-]'' V''}{V_t} \quad (4)$$

Since $V' = V_t - V''$

$$\frac{V' [\text{Cl}^-]'}{V_t} = [\text{Cl}^-]_t - \frac{[\text{Cl}^-]'' V''}{V_t} \quad (5)$$

$$\text{and } [\text{Cl}^-]' = [\text{Cl}^-]_t - \frac{[\text{Cl}^-]'' V''}{V_t - V''}$$

$$= \frac{[\text{Cl}^-]_t V_t - [\text{Cl}^-]'' V''}{(V_t - V'')} \quad (6)$$

According to (2) $(a'_{Cl-})(a_x) + (a'_{Cl-})^2 = (a''_{Cl-})^2$ (7)

$$(a'_{Cl-})^2 + (a'_{Cl-})(a_x) + \frac{1}{4}a_x^2 = (a''_{Cl-})^2 + \frac{1}{4}(a_x)^2 \quad (8)$$

and $(\frac{1}{2}a_x + a'_{Cl-})^2 = (a''_{Cl-})^2 + \frac{1}{4}(a_x)^2$ (9)

thus $(\frac{1}{2}a_x + a'_{Cl-}) = (a''_{Cl-})^2 + \frac{1}{4}(a_x)^2$ (10)

and $(a'_{Cl-}) = (a''_{Cl-})^2 + \frac{1}{4}(a_x)^2 - \frac{1}{2}a_x$ (11)

If we assume that $a'_{Cl-} = Cl^-$ then we equate (11) and (6).

$$(a''_{Cl-})^2 + \frac{1}{4}(a_x)^2 - \frac{1}{2}a_x = \frac{[Cl^-]_t V_t - [Cl^-]'' V''}{(V_t - V'')} \quad (12)$$

$$(a''_{Cl-})^2 + \frac{1}{4}(a_x)^2 - \frac{1}{2}a_x + \frac{[Cl^-]'' V''}{(V_t - V'')} = \frac{[Cl^-]_t V_t}{(V_t - V'')} \quad (13)$$

$$((a''_{Cl-})^2 + \frac{1}{4}(a_x)^2 - \frac{1}{2}a_x)(V_t - V'') + [Cl^-]'' V'' = [Cl^-]_t V_t \quad (14)$$

$$[Cl^-]_t = ((a''_{Cl-})^2 + \frac{1}{4}(a_x)^2 - \frac{1}{2}a_x) \frac{(V_t - V'')}{V_t} + \frac{[Cl^-]'' V''}{V_t} \quad (15)$$

$$\frac{[Cl^-]_t}{[Cl^-]''} = \frac{((a''_{Cl-})^2 + \frac{1}{4}(a_x)^2 - \frac{1}{2}a_x)(V_t - V'')}{[Cl^-]'' V_t} + \frac{V''}{V_t} \quad (16)$$

As shown by equation (16) one would not expect a linear relationship between $[Cl^-]_t$ and $[Cl^-]''$ if the Donnan theory is applicable to the system.

To check the applicability of these two theories to chloride distribution in a Dowex resin-water system, a series of samples were equilibrated for twenty-four hours, with concentration of HCl^{36} being the independent variable. A one milliliter sample of the supernatant solution was pipetted out, neutralized with sodium hydroxide, evaporated to dryness and

counted with a Geiger-Mueller counter. Solutions of equal volumes of water and equal amounts of chloride but with no resin were prepared for each concentration and counted in the same manner. The former measurements were used as a measure of (X''/V'') and the latter as (X_t/V_t) . A plot of these two values was then made; (see figure 3, page 26). The linearity observed between (X''/V'') and (X_t/V_t) is considered to constitute evidence of the applicability of the "bound water" theory.

Another supporting piece of evidence for the "bound water" theory was published recently by Anderson and Low (1). Their studies deal with the density of water near the surface of clay particles. They found that within $10\text{\AA}$ of the surface of a clay particle that the density decreased continuously. The densities approached 0.97 g/cc. as a lower limit. This would suggest that the water molecules are taking on some type of ordered arrangement presumably similar to water of hydration. This volume of water would probably cease to function as a solvent. The present investigators feel that this is the same volume element that is occupied by the "bound water".

TABLE IIa
Bound Water Data

<u>Sample</u>	<u>Weight</u>	<u>Volume of HCl^{36}</u>	<u>Volume of H_2O</u>	<u>Total Volume</u>
1a	1.0000 g.	5 ml.	5 ml.	10 ml.
1b	0.9999 g.	5 ml.	5 ml.	10 ml.
blank		5 ml.	5 ml.	10 ml.
2a	0.9996 g.	4 ml.	6 ml.	10 ml.
2b	1.0003 g.	4 ml.	6 ml.	10 ml.
blank		4 ml.	6 ml.	10 ml.
3a	1.0001 g.	2 ml.	8 ml.	10 ml.
3b	0.9999 g.	2 ml.	8 ml.	10 ml.
blank		2 ml.	8 ml.	10 ml.
4a	0.9997 g.	1 ml.	9 ml.	10 ml.
4b	0.9997 g.	1 ml.	9 ml.	10 ml.
blank		1 ml.	9 ml.	10 ml.
5a*	1.0000 g.	5 ml.	5 ml.	10 ml.
5b	1.0000 g.	5 ml.	5 ml.	10 ml.
blank		5 ml.	5 ml.	10 ml.

*The HCl^{36} used in the first four samples was a 0.00769 N solution whereas the HCl^{36} used for the last sample was a tenfold dilution of this acid.

TABLE IIb

"Bound Water" Data (counting data from Cl³⁶)

Sample	X_t/V_t counts/min.	X_t/V_t meq/ml. $\times 10^3$	X_r/V_r counts/min.	X_r/V_r meq/min $\times 10^3$
1a			13,677	4.10
1b			13,674	4.11
blank	12,795	3.84		
2a			10,848	3.35
2b			10,615	3.28
blank	9,967	3.08		
3a			5,865	1.78
3b			5,719	1.74
blank	5,084	1.54		
4a			2,719	0.83
4b			2,584	0.78
blank	2,529	0.77		
5a			1,452	0.44
5b			1,432	0.43
blank	1,345	0.40		

All counts are corrected for background.

Sample calculation: $X_t/V_t = 5 \times 0.00769/10 = 0.00384$ meq/ml

$X_r/V_r = 13,667 \frac{c}{min} \times 0.3001 \frac{meq \ min}{ml \ counts} \times 10^{-6} = 0.0041$ meq/ml.

Calculations for V_b from the slope in figure 3

$$\frac{3.8}{4.1} = 0.927 = \frac{V_t - V_b}{V_t} \text{ and } V_t = 10 \text{ ml.}$$

solving for V_b

$$V_b = 0.73 \text{ ml.}$$

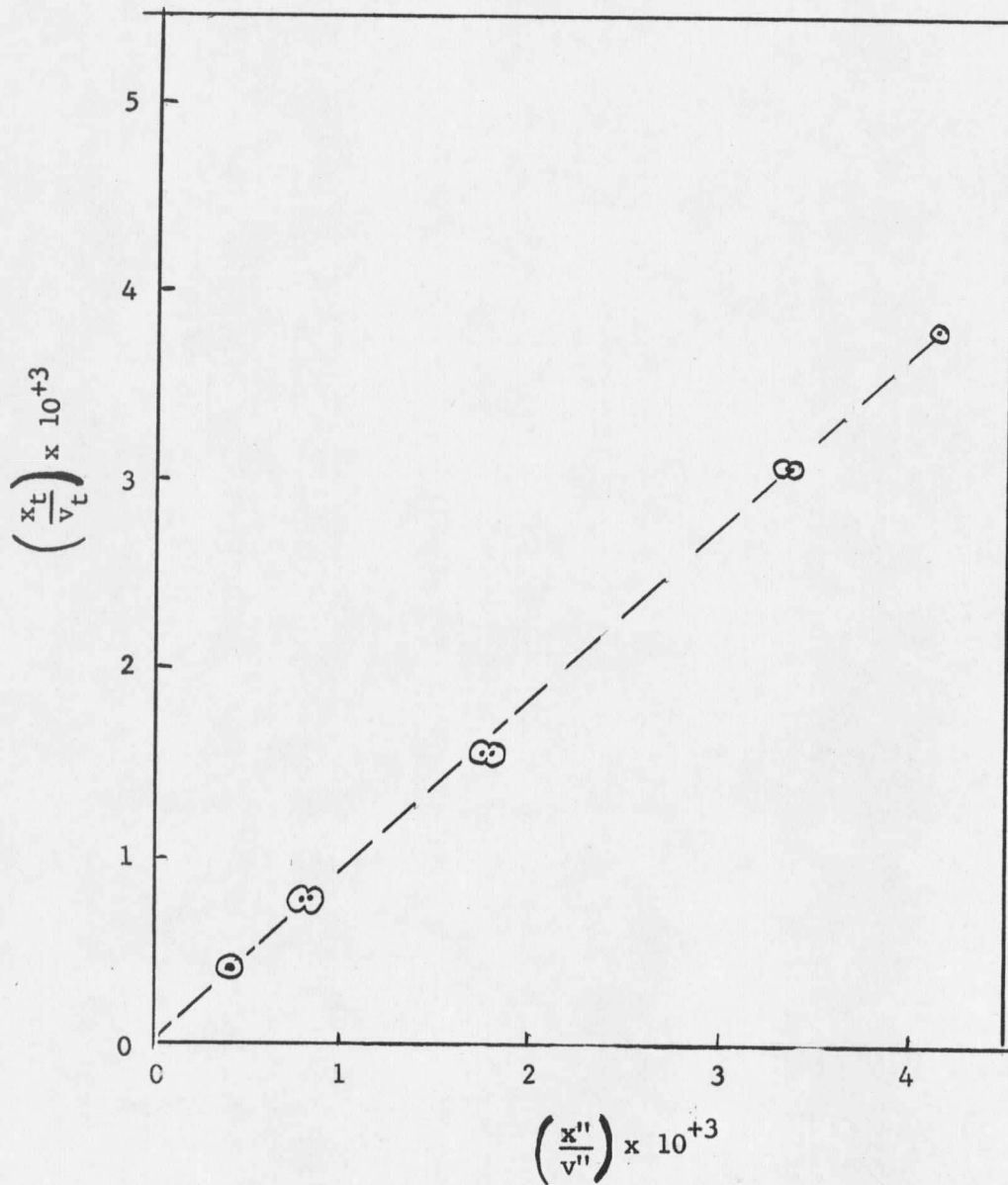


Figure 3: Bound Water Theory

Distribution of Cl^{36} in a Dowex-50 - Water System.

The objective of this section was to determine the actual distribution of Cl^- in the resin-water system. The values obtained are later compared with the apparent distribution of Cl^- as determined potentiometrically. Any discrepancy between the apparent and actual distribution will be attributed to an E_j at the calomel-resin interface.

The resin-water system is divided into three arbitrary divisions which will be referred to as phases. Phase''' refers to the equilibrium solution. Phase'' refers to the interstitial solution, i.e., the solution between the particles. Phase' refers to the solution in the interior of the resin particles.

H^+ resin samples were equilibrated with aliquots of dilute HCl tagged with Cl^{36} . After equilibrium was attained, the three phases were physically separated using the technique suggested by Grigor et al. (18) as stated in Appendix D, page 51. The concentration of Cl^- in the three phases was determined by means of standard counting techniques. Results obtained for a series of 1.000 gram samples are listed in Table III.

The mean value obtained for $[\text{Cl}^-]''' / [\text{Cl}^-]''$ was 1.32 and 1.34 for the 1.0000 gm. and 2.0000 gm. samples respectively. The corresponding values of $[\text{Cl}^-]''' / [\text{Cl}^-]'$ were 6.7 and 6.4.

An attempt was made to double check these values in the following way: using a lambda pipette and covering the tip with a tissue (swipe) which was impermeable to the resin particles, a sample of phase''' was withdrawn from three different samples. Phase''' was extracted with a

pipette. These were counted and the ratios compared. The mean value for $[Cl^-]''' / [Cl^-]''$ was 1.17, indicating a relatively small difference in chloride concentration between these two phases. Whether or not the lack of agreement (1.32 and 1.34 vs 1.17) is attributable to experimental error is not known.

According to the "bound water" theory, chloride is excluded from the "bound water" at the particle surface; the $[Cl^-]$ throughout the remainder of the system is constant. If we now think of this distribution applied to the system depicted in Appendix B, page 49, then it would seem as though $[Cl^-]''' = [Cl^-]'' = [Cl^-]'$ provided phase'' and phase' are corrected for the loss of solvent to "bound water". We have seen that $[Cl^-]''' = [Cl^-]''$ according to the radiometric data. Therefore one might expect the "bound water" to affect the amount of water available as solvent in phase' to the greatest extent. A correction can be made for the volume of water acting as a solvent for Cl^- in phase' if we assume all the "bound water" volume, V_b , to be contained in this phase. The actual $[Cl^-]'$ would be calculated by subtracting V_b , as determined from figure 3, page 26, from the total volume of phase'.

$$\text{Actual } [Cl^-]' = \frac{\text{apparent } [Cl^-]' \times \text{volume of phase'}}{\text{volume of phase}' - V_b}$$

Using the values from Table III the actual $[Cl^-]'$ was calculated for each sample. These values are listed in Table IV along with the concentrations for phase'''. Statistical treatment of the data indicates no significant difference at the 5% level between $[Cl^-]'''$ and $[Cl^-]'$ when corrected for "bound water". The results, therefore, provide

supporting evidence for the applicability of the bound water theory to the resin-water system under consideration.

Study of a_{H^+} By Ester Hydrolysis Rates

The rate of hydrolysis of an ester is reportedly a function of the a_{H^+} in the medium (22). Presumably the measured rate of hydrolysis of an ester could therefore be used to determine a_{H^+} . The purpose of the study reported here was to determine a_{H^+} in Dowex-50 resin in this way. The value obtained could then be compared with the apparent a_{H^+} as determined potentiometrically. Any discrepancy could be attributed to the E_j involved in the pH determination.

With this objective in mind, a series of hydrochloric acid solutions of varying pH were used to study the relation between pH and rate of hydrolysis. For a more detailed account of the experimental procedure see Appendix D, page 57. The results from this study are plotted in figure 4, page 30. Resin samples were equilibrated with enough water to make the volumes of the solutions comparable. Then the rate of hydrolysis for these samples was measured. The triangular point on the graph in figure 4 shows the results of these determinations. A second set of determinations was made using HCl solutions and Dowex-50 of comparable equivalents of H^+ per unit volume of solution. These determinations indicated that the H^+ resin was slightly more effective than HCl containing equal meq H^+ per unit volume in catalyzing the hydrolysis reaction. The results are listed in Table V, page 32. From these observations it seems as though the rate of hydrolysis is influenced by other factors, possibly the absorption of the ester by the resin. It was concluded that the rate of hydrolysis

could not be used as a reliable measure of a_{H^+} in the resin-water system. The results of McAuliffe and Coleman (22) also help substantiate this conclusion.

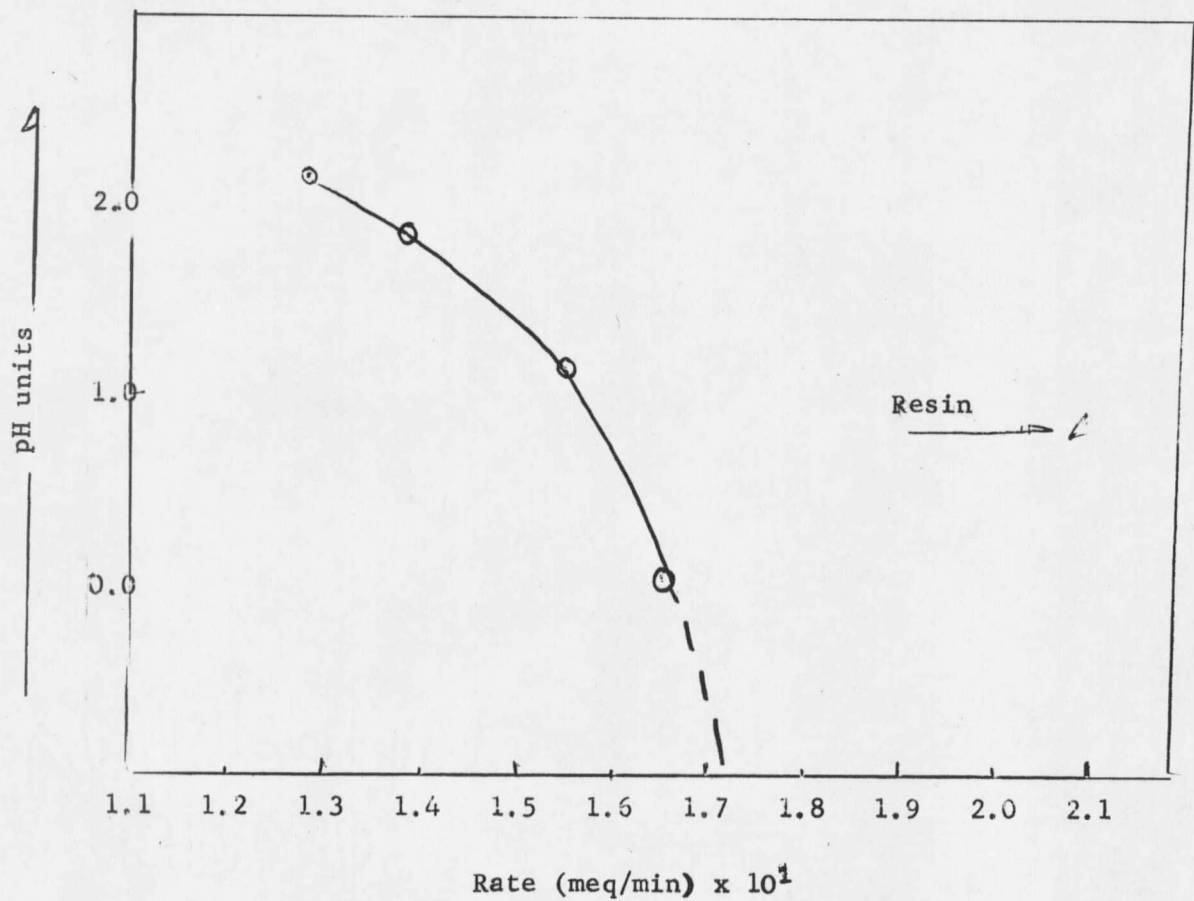


Figure 4: Hydrolysis of Methyl-acetate H^+ catalyzed

TABLE III
Distribution of Cl^{36}

Sample	Weight (grams)	Phase	c/min (Corr. for B.G.)	c/min/ml	Concentration meq/ml x 10 ⁴
1a	1.0002	"	1260	1260	7.84
		"	810	900	5.60
		"	132	152	0.95
2a	1.0006	"	1219	1219	7.58
		"	853	948	5.90
		"	180	206	1.28
3a	1.0000	"	1352	1352	8.43
		"	914	1013	6.30
		"	184	212	1.33
4a	1.0003	"	1269	1269	7.80
		"	857	956	5.87
		"	165	190	1.17
5a	1.0004	"	1305	1305	8.02
		"	851	946	5.83
		"	174	201	1.23
Blank				1123	6.99
1b	2.0011	"	1410	1410	8.34
		"	1846	1085	6.43
		"	367	211	1.26
2b	2.0006	"	1350	1350	8.00
		"	1808	1060	6.28
		"	391	225	1.33
3b	2.0001	"	1341	1341	7.92
		"	1679	978	5.78
		"	376	216	1.28
4b	2.0004	"	1401	1401	8.12
		"	1787	1021	5.90
		"	355	204	1.18
5b	2.0001	"	1392	1392	8.06
		"	1809	1063	6.17
		"	367	211	1.22
6b	2.0003	"	1419	1419	8.21
		"	1688	993	5.75
		"	400	230	1.33
Blank for samples 1-3				1188	6.99
Blank for samples 4-6				1207	6.99

TABLE IV

Concentration of Cl^- Corrected for "Bound Water"

Sample	$[\text{Cl}^-] \times 10^4$ in phase" as determined from Cl^{36} data	$[\text{Cl}^-] \times 10^4$ in phase' as calculated by correcting for "bound water"
1a	7.84 meq/ml	5.90 meq/ml
2a	7.58	7.95
3a	8.43	8.26
4a	7.80	7.30
5a	8.02	7.77
1b	8.34	7.84
2b	8.00	8.26
3b	7.92	7.97
4b	8.12	7.34
5b	8.06	7.59
6b	8.21	8.26
mean	7.90*	7.68*

*No significant difference at 5% level.

TABLE V

Comparative Rates of Ester Hydrolysis
of
Equivalent amounts of H^+ Per Unit Volume

<u>HCl</u>	<u>Dowex-50</u>
1.028×10^{-1} meq/min.	1.263×10^{-1} meq/min.
1.113×10^{-1} meq/min.	1.233×10^{-1} meq/min.

Potentiometric Determination in Exchanger-Water System

Some of the cells to be considered in this section are depicted below.

Cell #1. glass el. /HCl_(m)/KCl_(sat.)/Hg₂Cl₂, Hg

Cell #2. glass el. /HCl_(m) and resin//KCl(sat.)/ Hg₂Cl₂, Hg

Cell #3. Ag, AgCl/HCl_(m)//NH₄NO₃(10%)//KCl(sat.) AgCl(sat.)/ AgCl, Ag

Cell #4. Ag, AgCl/HCl_(m) and resin//NH₄NO₃(10%)//KCl(sat.) AgCl(sat.)//
AgCl, Ag

Cell #5. Hg, Hg₂Cl₂/KCl(sat.)//HCl_(m)/ HCl and resin// KCl(sat.)//
Hg₂Cl₂, Hg

See figure 1. D, page 12.

Cell #6. glass el./HCl(m)/ HCl(m), resin/glass el.

See figure 1. C, page 12. Where // indicates a liquid junction,
and / indicates a membrane or other mechanical means of separation. The
potentials of the cells, as depicted, will be referred to as E₁.

E₂, E₃ etc. These potentials may be expressed by the following:

$$E_1 = E_{g1}^0 - E_{cal} - E_j'''(KCl) - 0.0591 \log a_{H^+}'''$$

$$E_2 = E_{g1}^0 - E_{cal} - E_j''(KCl) - 0.0591 \log a_{H^+}''$$

$$E_3 = E_{Ag,AgCl}^0 - E_{ref} - E_j'''(NH_4NO_3) + 0.0591 \log a_{Cl^-}'''$$

$$E_4 = E_{Ag,AgCl}^0 - E_{ref} - E_j''(NH_4NO_3) + 0.0591 \log a_{Cl^-}''$$

$$E_5 = E_{cal} + E_j''' - E_{cal} + E_j'' + E_m$$

$$E_6 = E_{g1}^0 - 0.0591 \log a_{H^+}''' - E_{g1}^0 + 0.0591 \log a_{H^+}'' - E_m$$

As reported in most physical chemistry texts, E_j at a reference

electrode-solution interface is negligibly small (< 2 millivolts). Because of this, $E_j'''(\text{KCl})$ and $E_j'''(\text{NH}_4\text{NO}_3)$ will be neglected and we shall refer to E_j'' as E_j .

The suspension effect is defined by the difference between E_1 and E_2 . $E_1 - E_2 = E_j(\text{KCl}) - 0.0591 \log a_{\text{H}^+}''' / a_{\text{H}^+}''$. Now if the $E_j(\text{NH}_4\text{NO}_3) = E_j(\text{KCl})$, then $E_1 - E_2 = E_3 - E_4$.

$$E_3 - E_4 = E_j(\text{NH}_4\text{NO}_3) + 0.0591 \log a_{\text{Cl}^-}''' / a_{\text{Cl}^-}''$$

$$E_5 \text{ represents } E_{\text{cal}} = E_j(\text{KCl}) + E_m$$

$$E_6 = -0.0591 \log a_{\text{H}^+}'' - E_m$$

If $a_{\text{H}^+}''' \times a_{\text{Cl}^-}'' = a_{\text{H}^+}'' \times a_{\text{Cl}^-}'''$, as expected from the Donnan theory (14) and since, $E_m = 0.0591 \log a_{\text{H}^+}'' = 0.0591 \log a_{\text{Cl}^-}''' / a_{\text{Cl}^-}''$, the above expressions become

$$E_1 - E_2 = E_j(\text{KCl}) + E_m$$

$$E_3 - E_4 = E_j(\text{NH}_4\text{NO}_3) + E_m$$

$$E_5 = E_j(\text{KCl}) + E_m$$

$$E_6 = 0$$

The existing literature indicates that there are two schools of thought on the explanation of the suspension effect. One school is of the opinion that E_j is negligibly small (< 2 mv.) (4)(23)(24)(25) and the other is of the opinion that E_j may be large enough to constitute a serious error (as great as 240 mv.) (2)(3)(5)(6)(26)(27). Some feel that E_j accounts for the entire suspension effect (20).

In this section of the thesis, it was proposed that the size of E_j

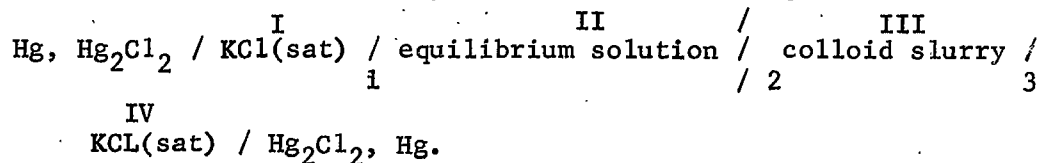
be quantitatively determined for Dowex-50 - water systems. To do this, as previously mentioned, we have studied the distribution of HCl^{36} throughout the system by two independent means. The actual distribution is considered to be the distribution as determined by Cl^{36} . The potentiometric measurements are taken as measures of the apparent distribution. The difference between the apparent and the actual distribution makes possible a calculation of E_j . In order to consider the radiological data as the actual distribution, the assumption is made that the activity coefficient for Cl^- is the same in all phases. The assumption that the activity coefficient of the adsorbed cation and that of the cation in solution were the same has previously been suggested as being valid (13) (3). The assumption made for the Cl^- activity coefficients is equally reasonable. The assumption that the radiological data represents the actual distribution enables us to calculate a value for E_m .

The assumption of activity coefficient of Cl^- being the same in all phases means that the activity coefficient is one for dilute solutions, i.e. in the order of 10^{-3}M . This assumption appears to be consistent with the "bound water" theory. If the "bound water" distribution holds, then $[\text{Cl}^-]''' = [\text{Cl}^-]'' = [\text{Cl}^-]'$. If the solutions are dilute, then $[\text{Cl}^-] = a_{\text{Cl}^-}$. Therefore $a_{\text{Cl}^-}''' = a_{\text{Cl}^-}'' = a_{\text{Cl}^-}'$ and since $a_{\text{Cl}^-} = \gamma_- [\text{Cl}^-]$ then $\gamma_-''' = \gamma_-'' = \gamma_-'$.

Using the above expression given for E_m , these assumptions indicate that $E_m = 0$. From the radiological data it is seen that E_m as calculated has a maximum value of approximately 7 millivolts.

Overbeek's Treatment (26)

Overbeek theoretically treated the following cell:



The e.m.f., E , of the cell is given by

$$-EF = \int_I^{IV} \sum_i \frac{t_i}{Z_i} d\mu_i \quad (17)$$

By manipulation of this equation in order to avoid single ion activities

and including the membrane potential, Overbeek obtained the equation (18)

$$E = \frac{1}{F} \left[\underbrace{- \int_{III}^{IV} \sum_i t_i \frac{d\mu_i}{Z_i}}_A + \underbrace{\frac{\mu_R^{II} - \mu_R^{III}}{Z_R}}_B - \underbrace{\int_I^{II} \sum_i t_i \frac{d\mu_i}{Z_i}}_C \right]$$

Equation (18) now includes

$E = E_j(1) + E_m(2) + E_j(3)$; and as shown by Overbeek, the potential may be expressed approximately by the following equation:

$$E_D = \frac{RT}{F} \ln \frac{\text{conductance of suspension}}{\text{conductance of equilibrium solution}} \quad (19)$$

Table I provides some interesting facts that show merit in equation (19). The strong acid exchangers have a much greater suspension effect than weak acid exchangers. The strong base exchangers have a much greater negative suspension effect than the weak base exchangers. This is as expected according to equation (19), since the conductance of the double layer of a strong acid or base exchanger is much greater than that of the weak acid or base exchanger (see Table I, page 19 and figure 2, page 18).

The conductance of the double layer of the colloid particles does not increase significantly with increasing concentration of equilibrium electrolyte. Thus one would expect from equation (19) that the conductance of the equilibrium electrolyte, as its concentration was increased, would become equal to that of the slurry. This observation was made by Peech et al. (27), Bower (5) (6) for clay-water systems and by the present investigators for Dowex-50 - water systems. (See Figure 5, page 38).

A number of resin samples were equilibrated with solutions of NaCl for twenty-four hours. The concentration of the solutions varied from 0.0005 N to 0.2 N. The ΔpH or ΔE_{cal} of each sample was determined and the value plotted versus concentration of NaCl. Some conductance studies made on clay-water systems (35) are also included. These conductance values were used to calculate E_{Donnan} by equation (19). These values of E_{Donnan} and E_{cal} were compared. These comparisons are depicted by Figures 6, 7, 8, and 9. A similar study was made by the present investigators for Dowex-50, Dowex-50W and Dowex-1. These results are listed in Table VI.

TABLE VI
Comparison of ΔE_{cal} and E_{Donnan}

	<u>E_{cal}</u>	<u>E_{Donnan}</u>
Dowex-50	125 mv.	80
Dowex-50W	160 mv.	79
Dowex-1	74 mv.	68

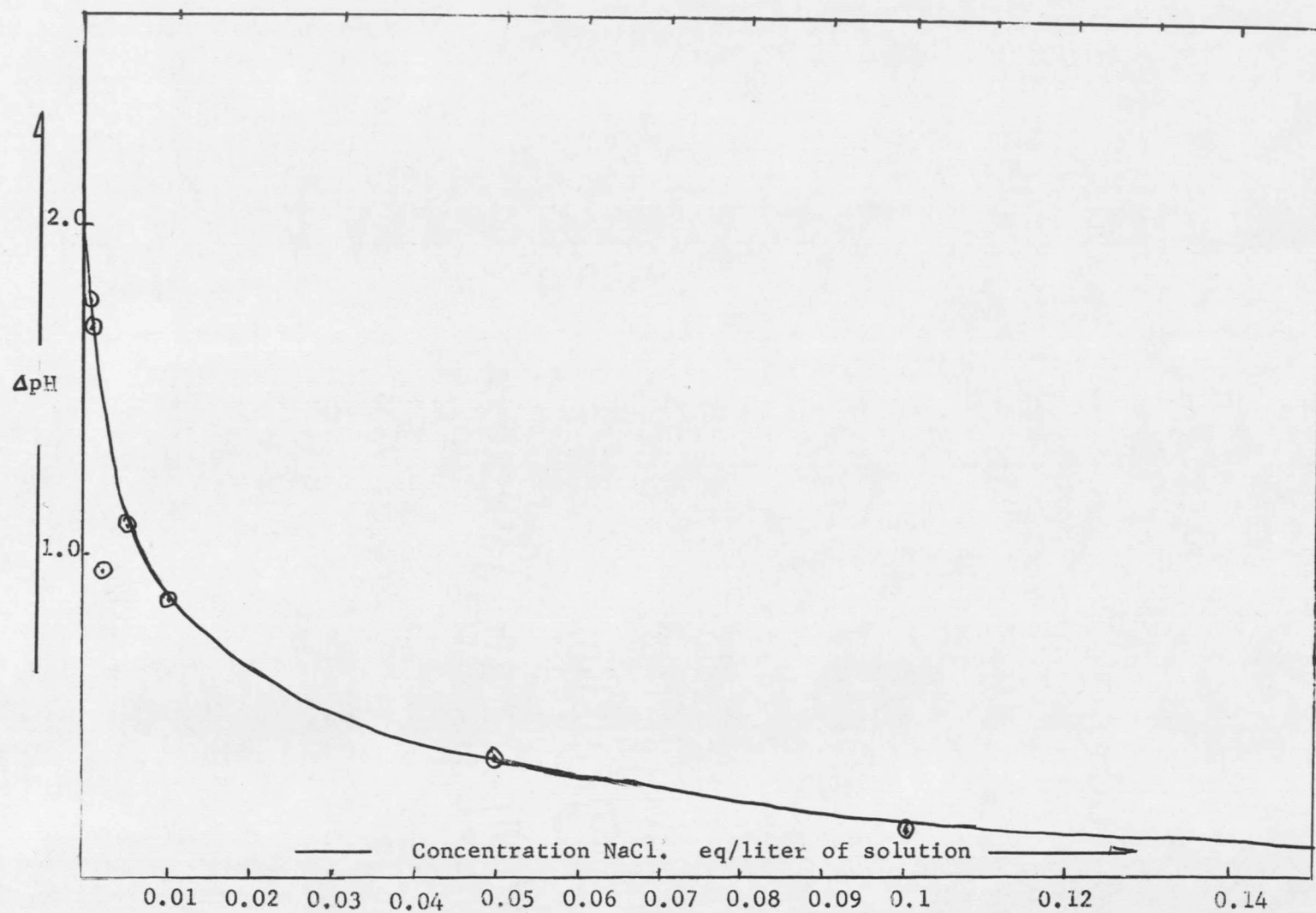


Figure 5. Salt Concentration vs. pH

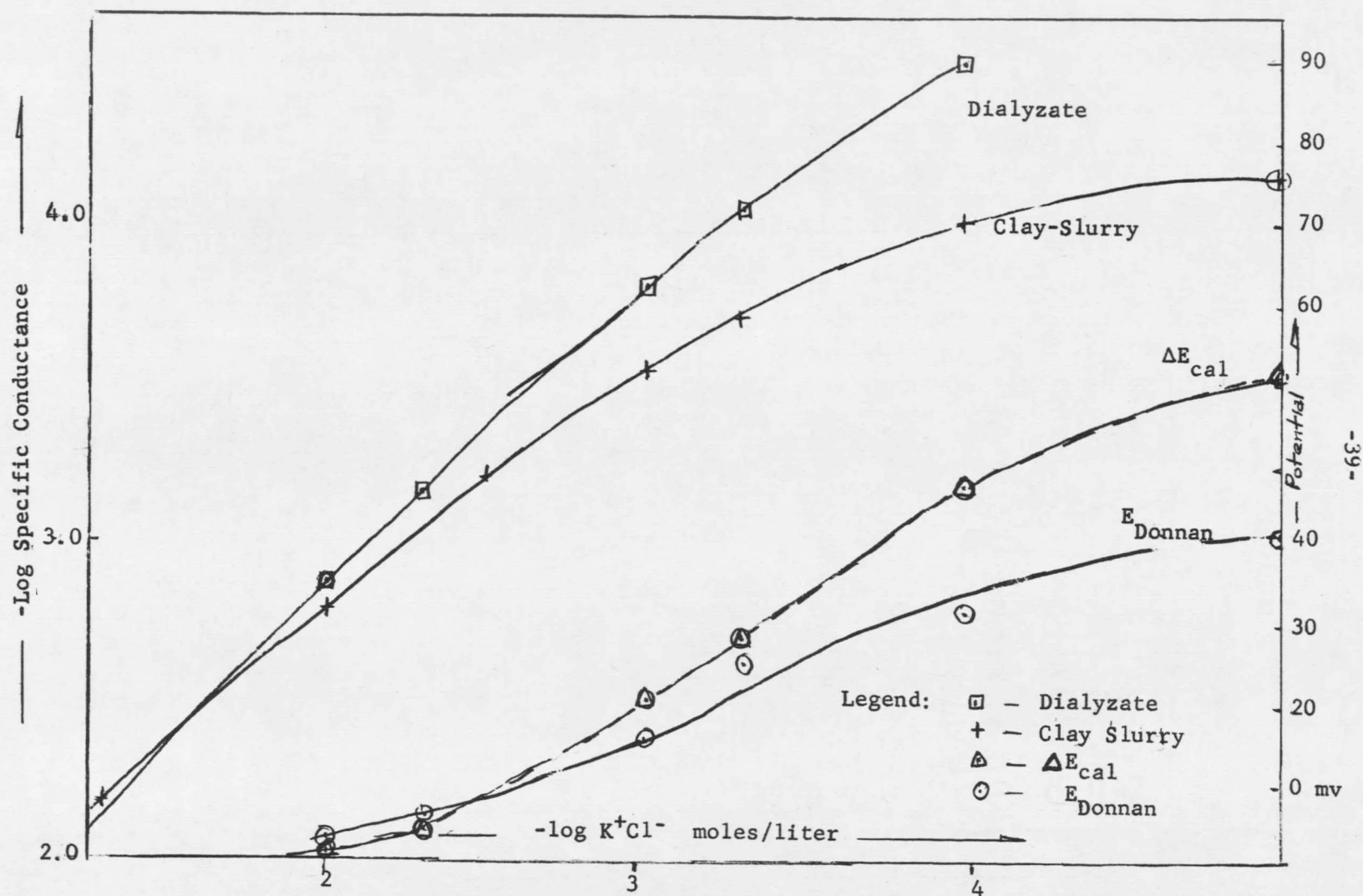


Figure 6. Comparison of ΔE_{cal} with E_{Donnan} using 2.42% H^+ Montmorillonite

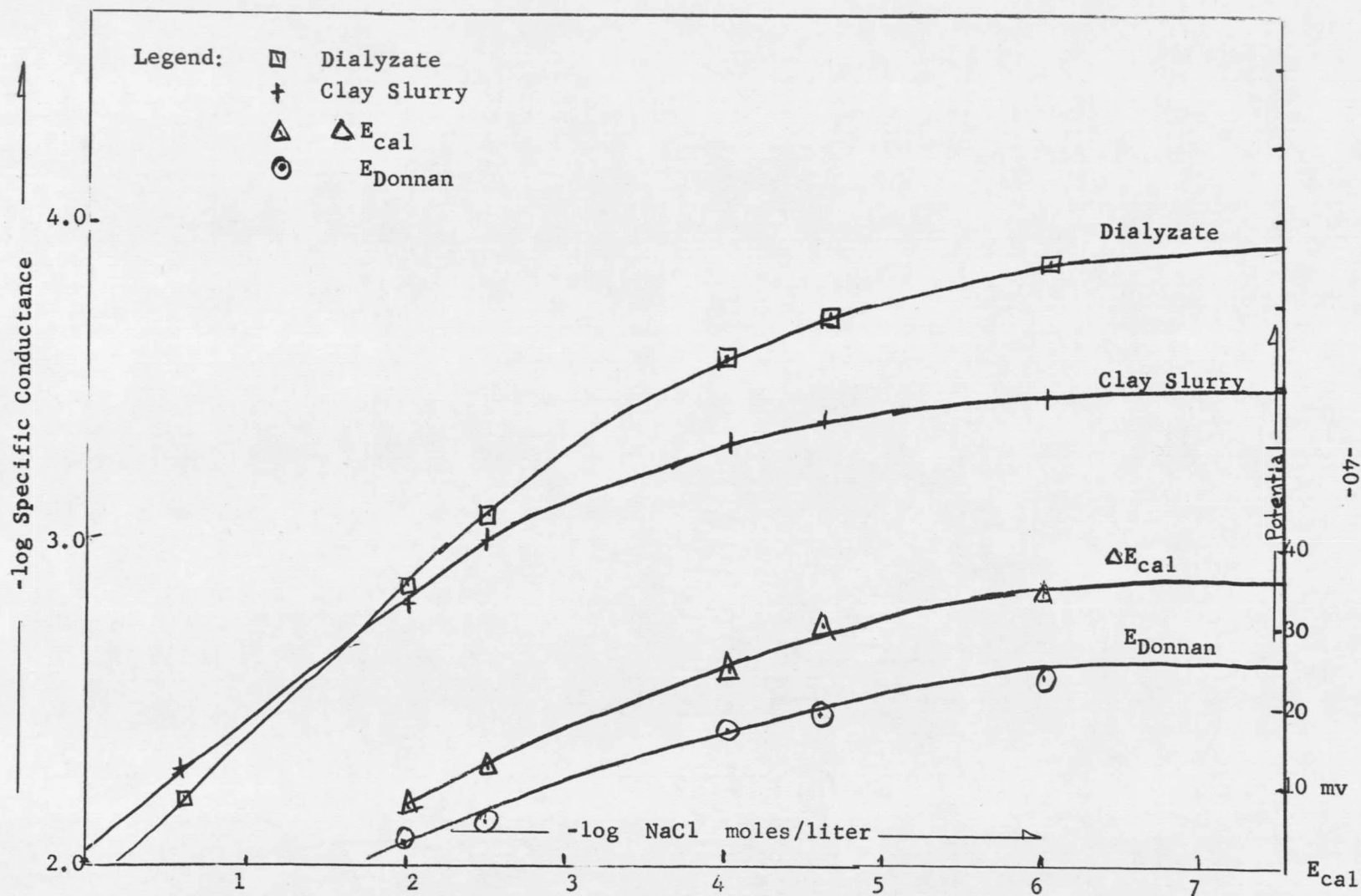


Figure 7. Comparison of ΔE_{cal} with E_{Donnan} using 2.42% Na^+ Montmorillonite

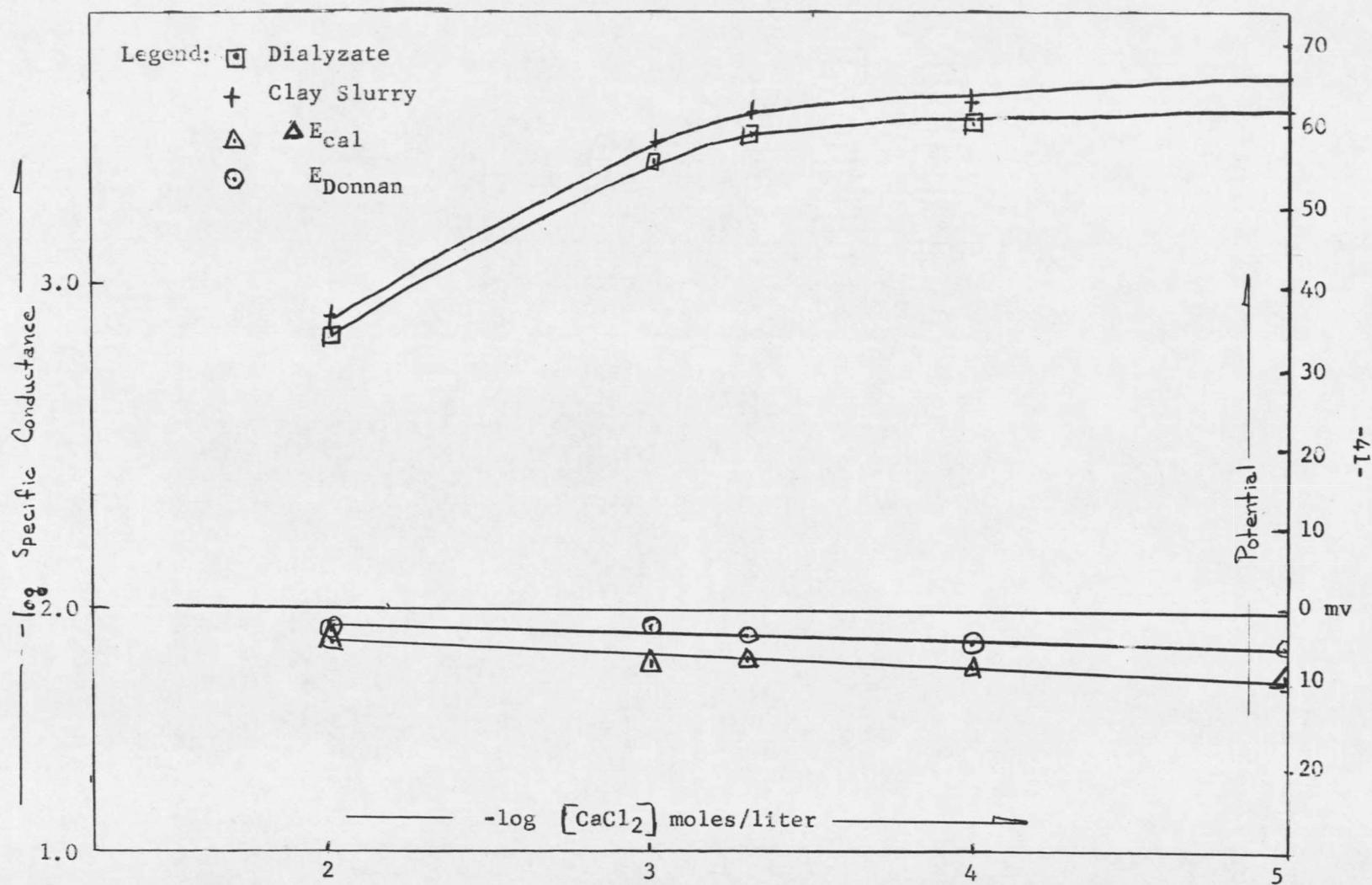


Figure 8. Comparison of ΔE_{cal} with E_{Donnan} using 5.86% Ca^{++} Fort Collins Clay

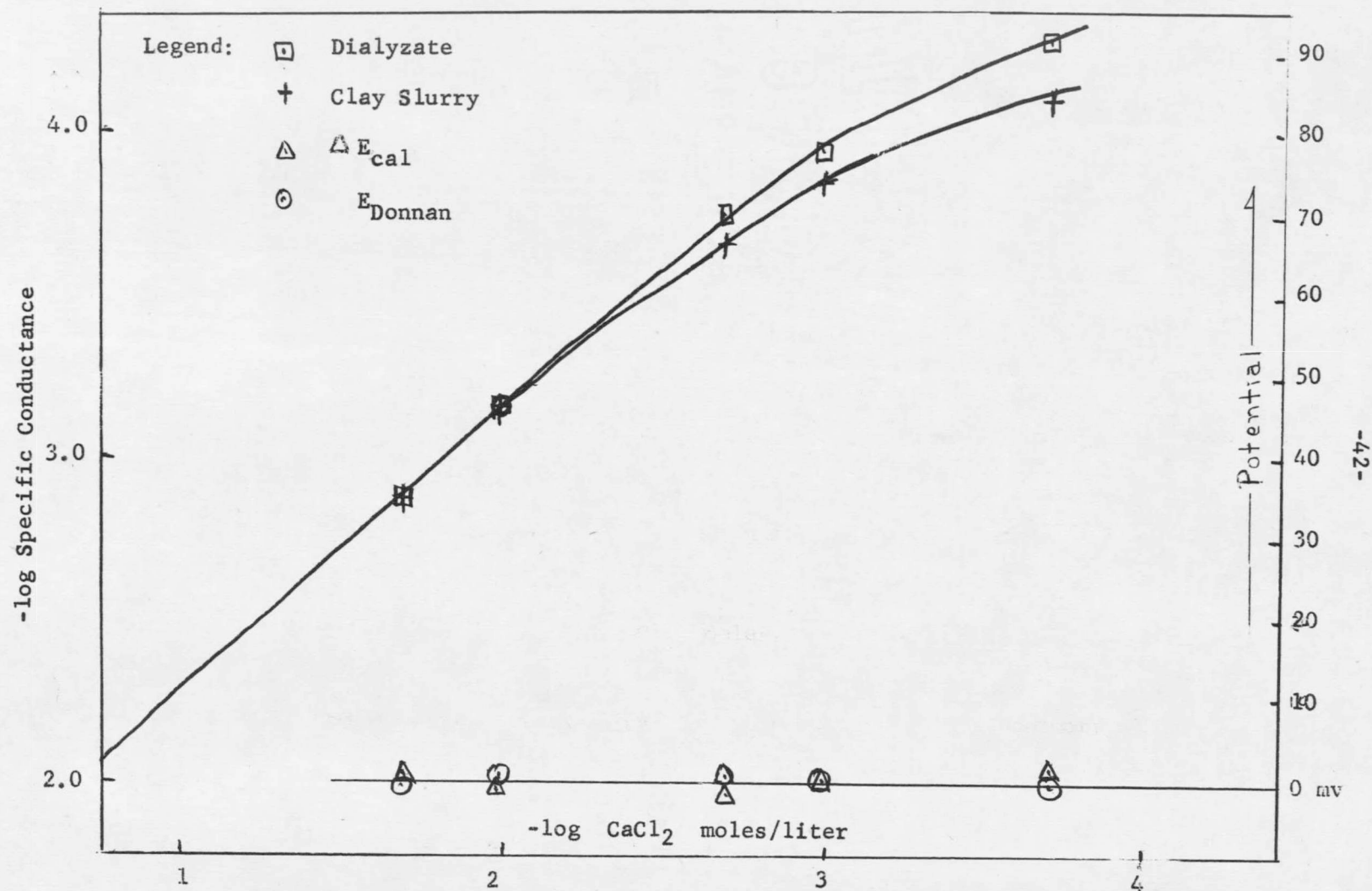


Figure 9. Comparison of ΔE_{cal} with E_{Donnan} using 2.42% Ca^{++} Montmorillonite

The results obtained qualitatively support Overbeek's theory although the values are not in good quantitative agreement. The same conclusion was reached by Bloksma (2) and more quantitative substantiation was obtained by Bower (6).

It is interesting to note the values obtained for the Ca^{++} -Montmorillonite and the Ca^{++} -Fort Collins clays. A negative ΔE_{cal} (27) is observed and a negative Donnan is calculated by equation (19). Comparison of the mobilities and the conductances of H^+ , K^+ , Na^+ and Ca^{++} reveals no apparent reason for the change in sign of the potential. The suspension effect apparently cannot be a function of conductance alone, but other factors must be involved.

Calculation of E_j

To calculate E_j the following equation was used:

$$\Delta E_{\text{cal}} = E_j + E_m$$

where $E_m = 59.1 \log \frac{a_{\text{Cl}^-}'''}{a_{\text{Cl}^-}''}$ and ΔE_{cal} was determined as in cells No. 1 and No. 2. The data for E_m were taken from Table III. It was pointed out previously that if the "bound water" theory held then E_m would equal zero. Thus the values calculated for E_m would be a maximum value and therefore the value obtained for E_j by the above expression would be a minimum. $\Delta E_{\text{ref.}}$ was also used. The values were determined by cells like No. 3 and No. 4. Another electrode combination used was an Ag,AgCl in conjunction with a saturated calomel electrode. The Ag,AgCl electrode was prepared by the method of Brown (11). All of these data are listed in Table VII, page 44, see also figure 10, page 45.

It should be noted that the values of E_j are all negative.

It should be noted that ΔE_{ref} and the potential as measured by the Ag,AgCl-saturated calomel pair differ in that the reference electrodes are different and the salt bridge solutions are different concentrations. The former having a more dilute bridge solution. The difference obtained in E_j is attributed to two factors: (a) the mobilities of the NH_4^+ and NO_3^- are more nearly equal than those of K^+ and Cl^- , and (b) the different concentrations of salt bridge solution (3).

TABLE VII

Comparison of Values for E_j with Different Electrode Pairs

Sample	ΔE_{cal}	E_m	E_j	ΔE_{ref}	E_j	$(E_{\text{Ag,AgCl}} - E_{\text{cal}})$	E_j
1a	98.0*	8.6	89.4			102	93.4
2a	100.0	6.1	93.9			103	96.9
3a	112.0	7.4	105.6			108	100.6
4a	95.8	7.3	88.5	82	74.7		
5a	88.6	8.0	80.6	77	69.0		
1b	77.5	6.6	70.9	82	75.4		
2b	84.0	6.2	77.8	81	75.8		
3b	97.5	8.0	89.5	79	71.0		
4b	118.2	8.0	110.2	80	72.0		
5b	124.0	6.8	117.2	83	76.2		
6b	101.5	9.1	92.4				

*All readings are in millivolts

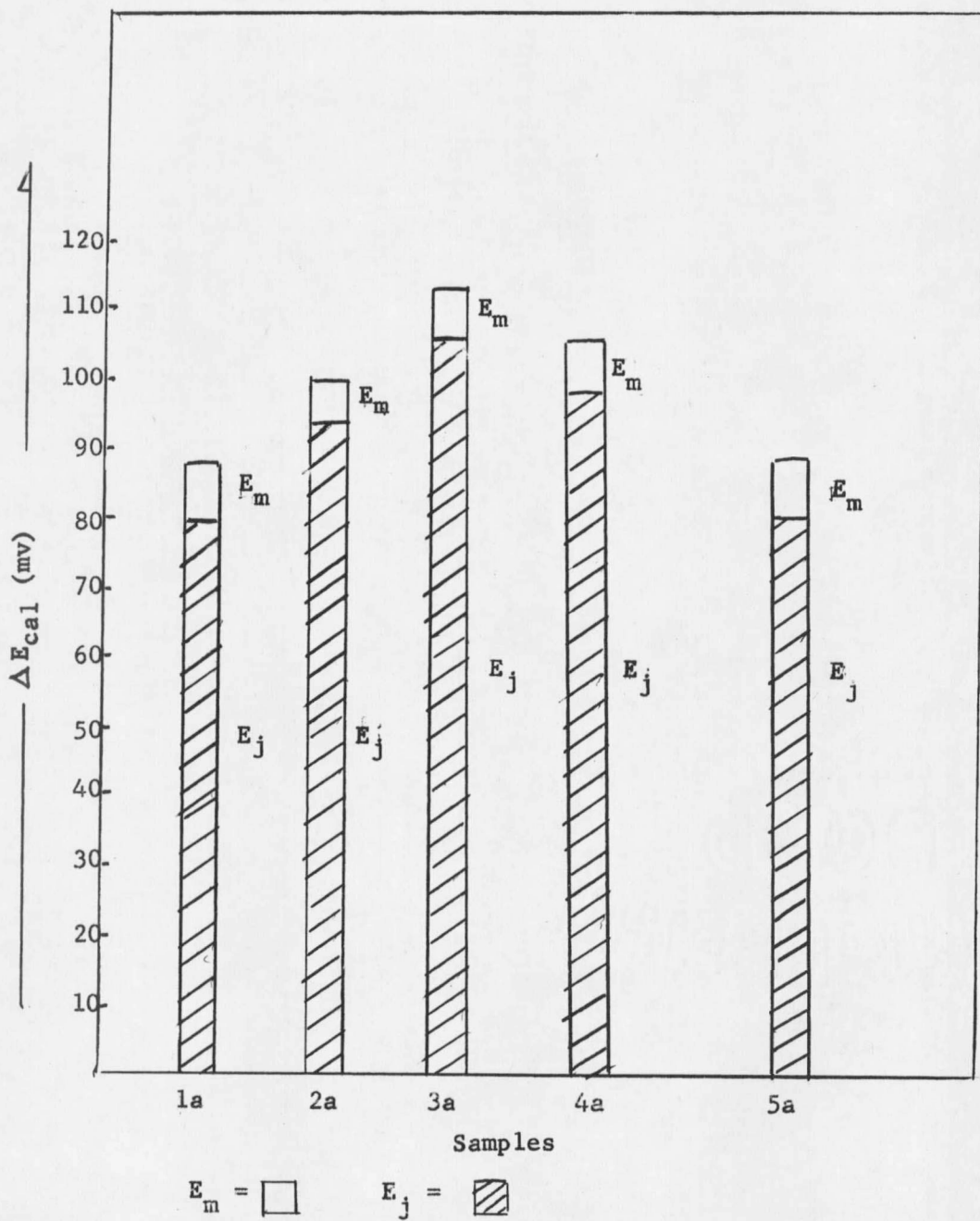


Figure 10. Composition of ΔE_{cal} of Dowex-50 - Water System

SUMMARY AND CONCLUSIONS

The distribution of HCl in a Dowex-50 - water system received attention in this investigation. The distribution could be adequately described, within limits of experimental error, by the so-called "bound water" theory. According to this theory, the resin particles are coated with a thin film of "bound water" (1). This water has a characterized, relatively low density and is presumed to have structural characteristics similar to ice. This theory demands that free ions be excluded from this "bound water", which accounts for negative adsorption of anions (15). Data obtained in this investigation is consistent with, and provides some supporting evidence for the "bound water" theory. The electrical double layer at the resin surface is therefore visualized as a distinct rather than a diffuse layer. The solution in the Dowex-50 - water system beyond the "bound water" film is accordingly considered to be homogeneous.

In an equilibrated Dowex-50 - water system, the potentiometrically measured pH of the slurry was found to differ from the corresponding pH of the supernatant solution by as much as 3.26 pH units. This so-called suspension effect is commonly attributed either to an actual difference in a_{H^+} in the system or to the existence of a liquid junction potential (E_j) at the reference electrode - resin interface. In this investigation, a comparison was made between the actual distribution of Cl^- in the system, as determined by Cl^{36} , and the apparent distribution of Cl^- in the system as determined potentiometrically. The results indicated an E_j which could be as high as 93 millivolts, depending upon

certain chemical characteristics of the system. This E_j constitutes a potential source of error in potentiometric determinations made in exchanger-water systems which may be large enough to completely invalidate the results.

Data obtained relative to E_j are qualitatively consistent with the theoretical treatment of Overbeek (26). Both cation and anion exchange resins exhibit the suspension effect: the former being positive in sign and the latter being negative in sign. The E_j was a sensitive function of electrolyte content, approaching zero apparently as a limit as the electrolyte content approached 0.2 N.

SUGGESTION FOR FUTURE RESEARCH

It seems that information regarding the fundamental cause(s) of liquid junction potentials in colloidal-water systems would be desirable. If the cause(s) were known, then one would presumably be able to predict which system would give rise to liquid junction potentials.

Studies could be made comparing the effect on the magnitude of E_j resulting from resin saturated with different cations. From these studies possibly correlations could be made concerning the magnitude of E_j as a function of such factors as, ionic radii, hydration radii and valence.

APPENDIX A

I. Definitions and Symbolism

1. Suspension Effect--the observed difference between the dialyzate pH and the suspension pH.
2. E_j --liquid junction potential--the potential created at the diffusion boundary of a reference electrode.
3. E_m --membrane potential--work required to bring a point charge from one side of the membrane to the other. $E = (\psi_i''' - \psi_i'')$
4. ψ --electrical potential
5. μ --chemical potential
6. $\bar{\mu}$ --the electro chemical potential. This is the sum of the electrical and chemical potentials.

$$\bar{\mu}_i = \mu_0 + RT \ln a_i + ZF \psi_i$$

where R--universal gas constant

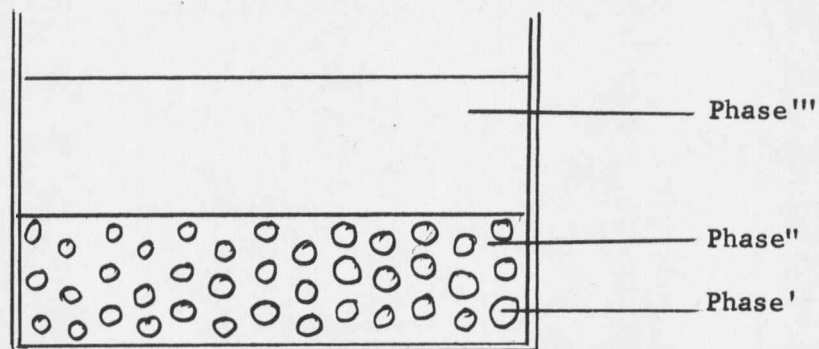
T--temperature absolute

a_i --activity

Z--valence of ion species

F--Faradays

APPENDIX B



Phase''' is the dialyzate.

Phase'' is the interstitial electrolyte.

Phase' is the solvent or solution taken up by the colloid particles.

Figure 11: Three Phase System

APPENDIX C

Membrane Potential and Donnan Equilibrium

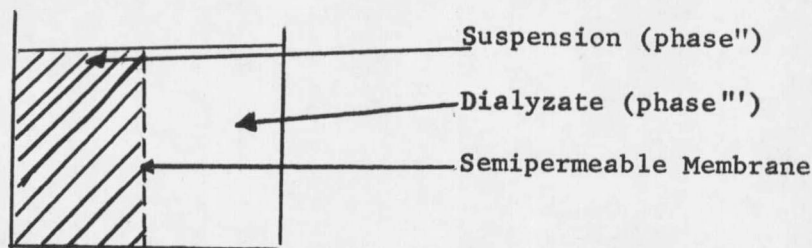


Figure 12: Donnan System

At equilibrium $\bar{\mu}_i'' = \bar{\mu}_i'''$ for a univalent cation

$$1. \mu_0 + RT \ln a_{H^+}'' + ZF\psi'' = \mu_0 + RT \ln a_{H^+}''' + ZF\psi'''$$

upon rearranging

$$2. RT \ln \frac{a_{H^+}''}{a_{H^+}'''} = ZF(\psi''' - \psi'') \text{ and by definition } E_m = (\psi''' - \psi'')$$

$$3. E_m = \frac{RT}{ZF} \ln \frac{a_{H^+}''}{a_{H^+}'''}$$

going back now to equation 1. and writing the expression for an anion and rearranging

$$4. \mu_0 + RT \ln a_{-}'' - ZF\psi'' = \mu_0 + RT \ln a_{-}''' - ZF\psi'''$$

$$5. \frac{-RT}{ZF} \ln \frac{a_{-}''}{a_{-}'''} = (\psi'' - \psi''') \text{ or}$$

$$6. \frac{RT}{ZF} \ln \frac{a_{-}'''}{a_{-}''} = (\psi''' - \psi'') \text{ Now equating 2. and 6.}$$

$$\ln \frac{a_{-}'''}{a_{-}''} = \ln \frac{a_{H^+}''}{a_{H^+}'''}$$

$$\frac{a_{-}'''}{a_{-}''} = \frac{a_{H^+}''}{a_{H^+}'''}$$

This is the expression derived by Donnan (14) which relates the activities of univalent ions in the two phases.

APPENDIX D

Water Content Determination

The method of Gregor et al. (17) was used to determine the water content of the resins. The resin was equilibrated with excess water first, then placed in a sintered glass filter funnel, under suction, for little more than three minutes. As was shown by Gregor et al., after three minutes, the resin maintained a relative constant weight. This is believed to indicate that the interstitial water had been removed, and that any additional loss of weight, after this time, would be due to air drying.

The resin was placed in weighing bottles, weighed and placed in a vacuum dessicator. The samples were weighed periodically until no further loss in weight was shown. This was taken as the dry weight of the resin. By transferring samples to the weighing bottles with timing and care, good precision was obtained. The resin was found to contain 46% water, by weight.

Another method, used by Gregor et al., was centrifugation. The samples were placed in sintered glass funnels which sat in special centrifuge flasks. They were centrifuged for thirty minutes at 1500 g's. This was found to be adequate to extract nearly all of the interstitial water.

The Effect of Percent Resin in Suspension upon the Apparent pH of the Suspension

A series of samples, containing twenty milliliters of distilled water and varying amounts of resin from 1.5 gms. to 5.5 gms. dry weight, were measured for suspension pH. The pH of the resin was plotted versus

the amount of dry weight of resin. (See figure 13.)

It was found that the pH varied but very little, going from 3.6 to 2.9. The relatively high pH values, observed here, are due to the fact that, while measuring the pH, the resin was stirred constantly. Upon settling, the pH of the resin samples was all 1 ± 0.1 pH.

Determination of the Volume Occupied by Wet Resin

A column of resin was prepared in a 50 milliliter buret. The column was thoroughly wetted with water and the water level was above the resin level. Some of the water was allowed to drain down, well below the resin level, and then some of the resin was scooped out and placed in a weighing bottle. The amount of resin that was taken out was always approximately a half inch layer. The buret was refilled with water after the extraction. The difference in resin levels was taken, as the wet resin volume. This method was repeated for several samples. The resin samples were weighed repeatedly, until no further loss of weight was detected with additional drying.

Method of Separation of Phase^{'''}, Phase^{''} and Phase[']

Two methods were used for separation of phase^{'''}. Both gave similar results. Phase^{'''} may be effectively separated either by decanting the dialyzate or by forcing the dialyzate out through a sintered glass funnel. The resin, phase^{''}, and phase['] are left behind.

Considering phase['] and the water content of the wet resin to be identical, the separation of phase^{''} was similar to the experiments for determining the water content. The sintered glass funnel was centrifuged for thirty minutes at 1500 g's to remove phase^{''}. Chlorides in phase['] was

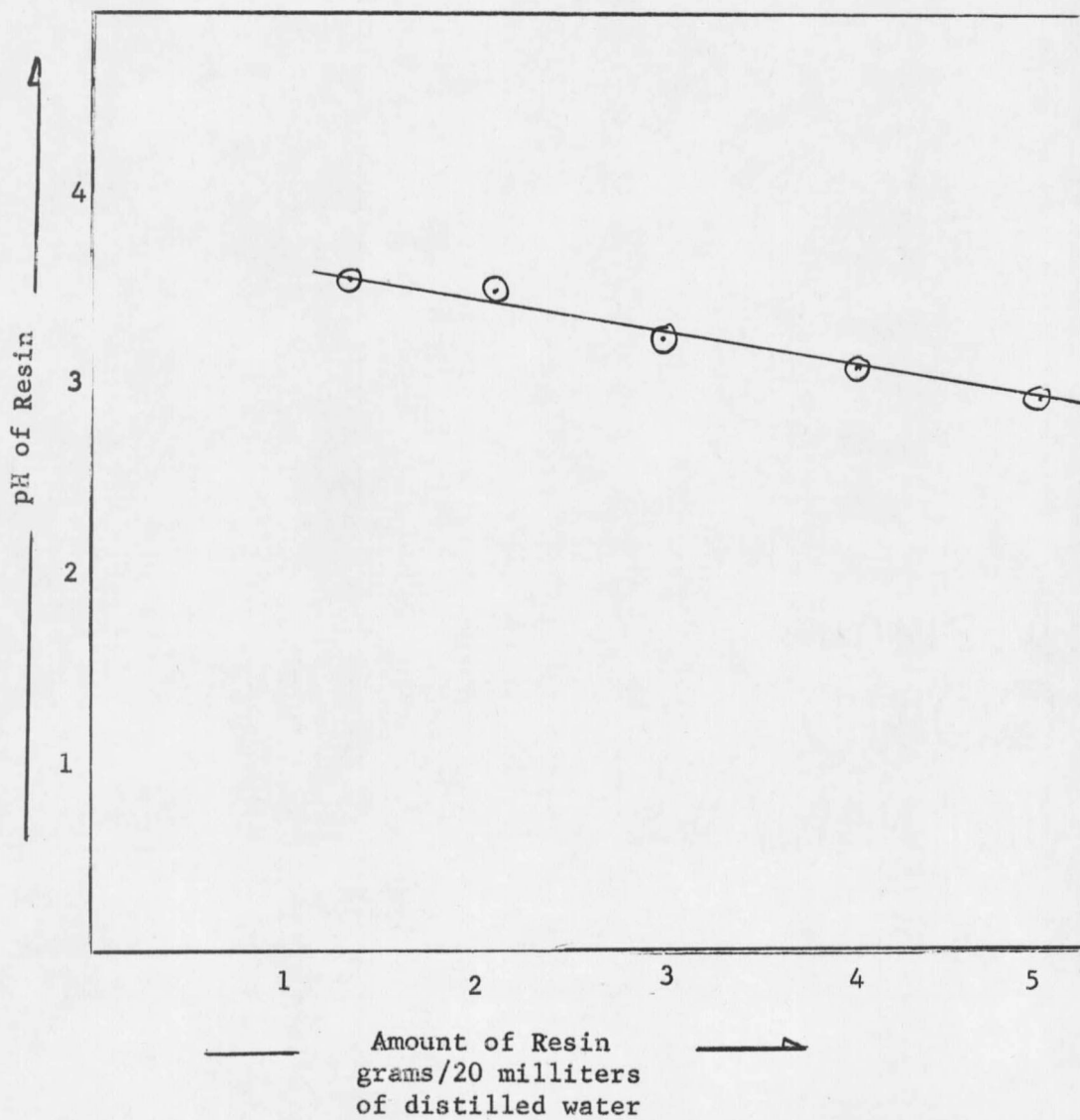


Figure 13. The Effect of % Resin on Suspension Effect

washed out of the resin sample with distilled water.

Determination of the Volume of Phase^{'''}, Phase^{''} and Phase[']

The resin was equilibrated with 11 ml. of distilled water. Phase^{'''} was decanted and placed in a weighing bottle and weighed. From the density of water at 27°C., the volume of phase^{'''} was calculated. The volume of phase['] was calculated from the water content and the density value. The volume of phase^{''} was considered to be the difference of the total volume and the sum of phase^{'''} and phase['].

TABLE VIII

Volumes of the Separate Phases

<u>Phase</u>	<u>1 g. Samples</u>	<u>2 g. Samples</u>
'''	9.23 cc.	7.57 cc.
''	0.90 cc.	1.70 cc.
'	0.87 cc.	1.73 cc.

Determination of Chloride Distribution
by Radiological Methods

For determination of the Cl³⁶ distribution, a resin sample was equilibrated with one milliliter of 0.00769 N HCl³⁶ and ten milliliters of distilled water. The sample was stirred occasionally and then allowed to equilibrate over night. The total equilibration period was at least 24 hours. The pH of the supernatant did not change significantly after this time.

The three phases were separated as described on page 52. The separate portions were neutralized with excess NaOH and then evaporated to dryness in stainless steel planchets.

The samples were counted in a Geiger-Mueller counter. Each sample was counted for a five minute period.

Cl^{36} Self-Absorption

A number of NaCl^{36} solutions were evaporated to dryness in stainless steel planchets in order to ascertain whether or not any self absorption was taking place in the samples used in the study of Cl^- distribution. The amount of salt was varied from 0.2 mg. to 90 mg. and the count rate was determined. From these data a plot was made; the results appear in figure 14. From the graph it is easily seen that self absorption would be of no concern for the samples used in this investigation. The samples used in the investigation weigh approximately 0.2 milligram. According to figure 14 no appreciable absorption takes place for samples of this weight.

Determination of Chloride by Potentiometric Measurement

For determining the chloride activity, a Beckman silver billet combination electrode #39187 was used as a Ag,AgCl electrode. This electrode is designed to be used with the Beckman Model G pH meter. This electrode is two electrodes in one unit, containing an Ag,AgCl electrode and an Ag,AgCl reference electrode in a solution that is saturated with respect to both KCl and AgCl .

Between the reference electrode and the sample solution, there is a reservoir containing a 10% solution of NH_4NO_3 . This bridge solution connects the sample with the reference electrode. This prevents chloride ions from the reference electrode from contaminating the sample. A linen fiber connects the reference electrode to the bridge solution and

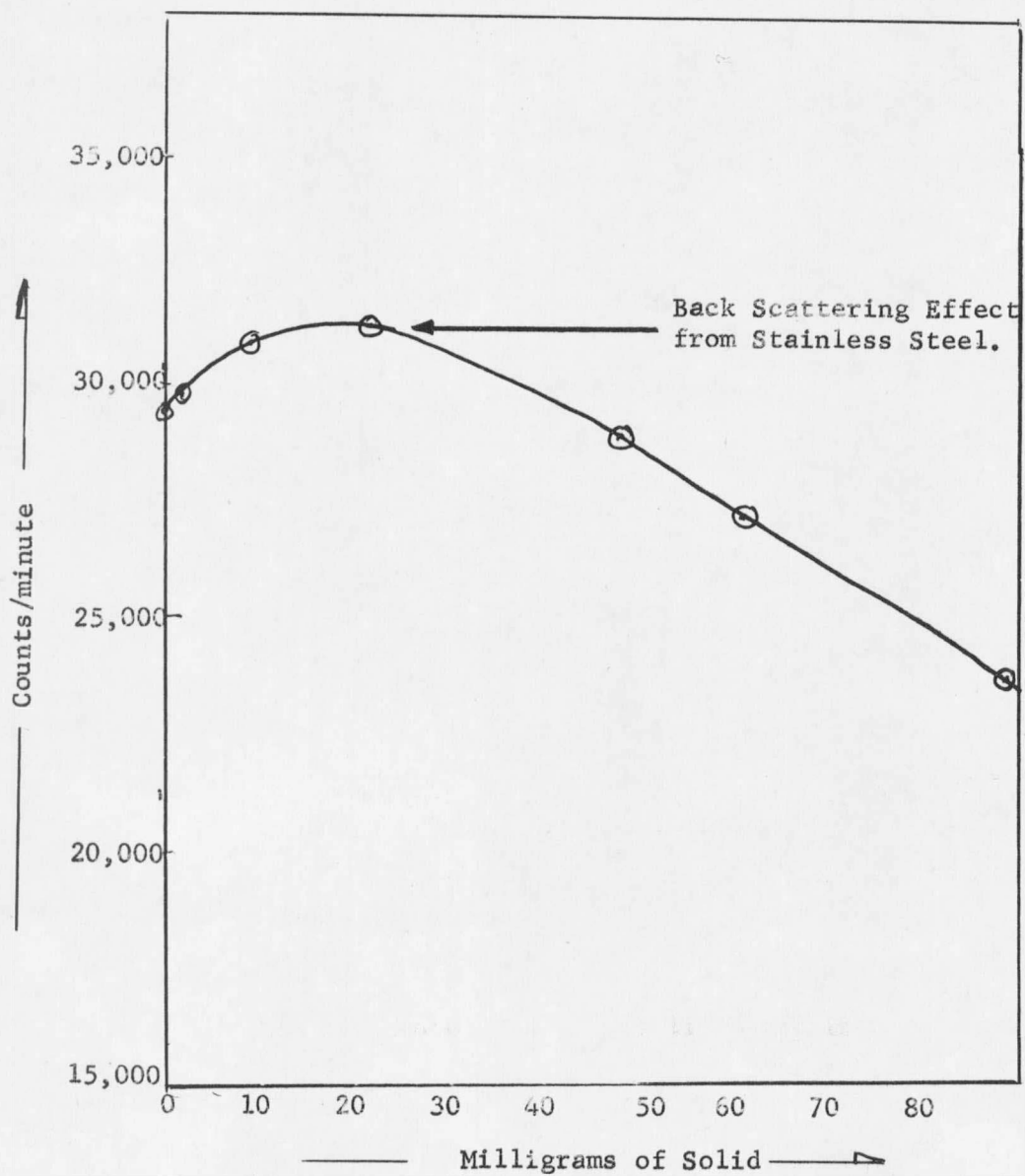


Figure 14: Cl^{36} Self Absorption

the bridge solution to the sample.

Some electrodes, prepared by the method of Brown (11), were also used. These electrodes were used in conjunction with a S.C.E.

An Attempt to Determine a_{H^+} by Rates
of Ester Hydrolysis

The amount of resin to be used for each sample was weighed in a 50 milliliter Erlenmeyer flask. Enough water was added to the system to occupy all of phase' and phase". The amount of acid was comparable in volume. The acid solutions varied from 0.0 to 2.12 in pH. The pH of the resin was measured at a temperature of 35°C. The resin and acid samples were placed in a constant temperature bath, shaken and allowed to reach 35° C. One milliliter of pure methylacetate was added to each sample. The zero time was taken at this point. The reaction was stopped by adding just enough NaOH to titrate the total equivalents of H^+ in the system. The samples were immediately back titrated with a standard HCl solution and phenolphthalein.

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