

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Adsorption Isotherms from Double Layer Capacity Measurements¹

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The instantaneous differential double layer capacity of a dropping mercury electrode has been determined as a function of concentration for a number of organic compounds. Equilibrium has been shown to be reached at least near the end of drop life. Langmuir adsorption isotherm expressions have been found to be obeyed for all compounds studied. From the dependence of adsorption on electrode potential, implications are discussed concerning the possibility of an adsorption step in the reduction mechanism.

Measurements of the differential capacity of the electrical double layer have been found useful in the elucidation of the kinetics of adsorption and desorption, particularly at a mercury-solution interface.^{2,3} Hansen, Minturn and Hickson⁴ extended the theory of Frumkin⁵ on the effect of adsorbed substances on the electrocapillary curves to give a relationship between the differential capacity, the electrode polarization and the fraction of the surface covered in a monolayer process. A detailed study of pentanoic acid was made at a stationary mercury surface to verify the predicted relationship.

In the present investigation, emphasis was placed on the measurement of instantaneous double layer capacity during the formation of mercury drops at a dropping mercury electrode. At sufficiently high concentrations of adsorbable material, equilibrium was shown to be reached before the end of the drop formation.

A simple Langmuir adsorption isotherm expression was found to express the differential double layer capacity or the fraction of surface covered as a function of the concentration in solution. At the potential corresponding to maximum adsorption, where the variation of adsorption with electrode polarization can be neglected, the fraction of surface covered, θ , is related to the differential double layer capacity per unit area C_{dl} by the equation⁴

$$\theta = \frac{C_{dl}^0 - C_{dl}}{C_{dl}^0 - C_{dl, \text{sat}}} \quad (1)$$

where C_{dl}^0 is the value of C_{dl} at the same potential in the absence of surface active agent, and $C_{dl, \text{sat}}$ is the value corresponding to a saturated monolayer. At other potentials, θ is replaced by θ_{app} , the apparent fraction covered. Equation 1 assumes a linear dependence of differential double layer capacity on the fraction of surface covered. This assumption corresponds to an equivalent electrical circuit of a capacitor composed of a clean mercury surface of area $(1 - \theta)$ connected in parallel with a mercury surface of area θ covered with a monolayer of adsorbed material.

The value of $C_{dl, \text{sat}}$ can, in principle, be determined by measuring the complete adsorption iso-

therm. However, if complete surface saturation is not reached in the available concentration range, it is convenient to determine $C_{dl, \text{sat}}$ by means of the empirical equation which is a form of the Langmuir isotherm. By plotting $1/C_{dl}$ versus $1/C$, a straight

$$C_{dl} + \frac{aC}{1 + bC} \quad (2)$$

line was obtained for all the compounds investigated. The value of a/b (reciprocal of the intercept) represents the limiting value, $C_{dl, \text{sat}}$. Now calculating θ from eq. 1, the Langmuir isotherm can be written

$$\theta = \frac{\beta C}{1 + \beta C} \quad (3)$$

where the value of β is given by the reciprocal of the slope of the plot of $1/\theta$ versus $1/C$. From eq. 3, β is the slope of the limiting linear isotherm at low concentrations. The value of β is a measure of the adsorbability of a substance, and may be called the "adsorption index."

Experimental

The impedance bridge used for the capacitance measurements was essentially the same as that previously described,⁵ except that provision was made for mechanical detachment of the mercury drops and for timing the instant of bridge balance by the method of Randles.⁷ A Du Mont Model 304 H oscilloscope was used as a null indicator. A cylindrical cell was used with a large mercury pool serving as the working electrode. The top of the cell was constructed of a standard taper joint to receive a reference electrode provided with a fritted glass junction. The reference electrode, consisting of a saturated sodium chloride calomel electrode, was connected by means of a sodium perchlorate salt bridge to the cell solution.

The dropping mercury electrode was introduced through a loosely fitting Tygon sleeve to act as a shock mount and to serve as an exit for nitrogen gas. The latter was used to deaerate the solution prior to the measurements and was passed over the solution during the measurements. A special electrode of unusually long drop time was prepared by sealing a 9-cm. length of Sargent 6 to 12 sec. capillary, i.d. ca. 0.05 mm. to a piece of lead glass tubing. A platinum contact was sealed to the lead glass tubing, the tip of which was drawn out to have an inside diameter of about 0.3 mm. The end surface was polished to give a plane surface as observed under the microscope. With a mercury column height of 67 cm., the natural drop time at the potential of the electrocapillary maximum was about 15 seconds in 0.1 M sodium perchlorate. The rate of flow of mercury was determined before and after each set of measurements by a semi-automatic timing device similar to that described by Lingane.⁸ The instantaneous area was calculated assuming the drop to be spherical. A typical value of the electrode area was 0.0424 cm.² for $m = 1.65$ mg. sec.⁻¹ and $l = 6.85$ sec.

(1) Abstracted from the Ph.D. thesis of B. Mosier, University of Illinois, 1957. Supported by the National Science Foundation under Grants G-750 and G-2420.

(2) A. Frumkin and V. I. Melik-Gaikazyan, *Doklady Akad. Nauk U.S.S.R.*, **77**, 855 (1951).

(3) V. I. Melik-Gaikazyan, *Zhur. Fiz. Khim.*, **26**, 560, 1184 (1952).

(4) R. S. Hansen, R. E. Minturn and D. A. Hickson, *J. Phys. Chem.*, **60**, 1185 (1956).

(5) A. Frumkin, *Z. Physik*, **35**, 792 (1926).

(6) H. A. Laitinen and R. A. Osteryoung, *J. Electrochem. Soc.*, **102**, 598 (1955).

(7) J. E. B. Randles, *Trans. Faraday Soc.*, **50**, 1246 (1954).

(8) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **16**, 329 (1944).

The behavior of the bridge and timing mechanism was checked by measuring the instantaneous double layer capacity as a function of time for the supporting electrolyte of 0.1 *M* sodium perchlorate. The estimated precision of instantaneous double layer capacity measurements is $\pm 1\%$.

All solutions were prepared using demineralized water which was distilled from an alkaline permanganate solution in an all glass apparatus.

For an experimental test, acetophenone pinacol was chosen. It represents a relatively unfavorable case for rapid attainment of equilibrium because the diffusion coefficient is lower than that of most compounds studied here. The results (Fig. 1) clearly show the lack of equilibrium for drop

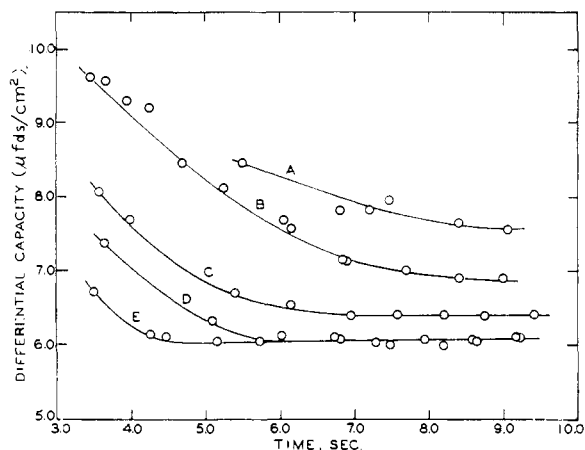


Fig. 1.—Time dependence of differential double layer capacity of acetophenone pinacol in 0.1 *M* NaClO₄ at -0.7 v. vs. SCE: curve A, 1×10^{-4} ; curve B, 1.2×10^{-4} *M*; curve C, 1.4×10^{-4} *M*; curve D, 1.5×10^{-4} *M*; curve E, 1.7×10^{-4} *M*.

times shorter than 5 sec. for all concentrations below 1.7×10^{-4} *M*, which corresponds to $C = 3.7a$ (Table I). For $t = 9$ sec., on the other hand, all curves have flattened out. Attempts to fit the data to a Langmuir isotherm were unsuccessful for $t = 6$ sec., but a satisfactory fit was obtained for $t = 9$ sec. A plot of $1/\theta$ against $1/C$ is shown in Fig. 2.

It appears that equilibrium must be achieved at least to within a few per cent. and that in any case the β -values are useful for comparative purposes.

For most of the substances studied, equilibrium was attained earlier in drop life than for acetophenone pinacol. In each case, the time independence was verified in the later stages of drop life before the isotherm was evaluated.

Results and Discussion

Attainment of Equilibrium.—Delahay and Trachtenberg^{9a} have calculated the rates of diffusion-controlled adsorption, assuming a linear adsorption isotherm. They concluded that for semi-infinite linear diffusion to a plane electrode, equilibrium is reached very slowly because the concentration gradient decreases rapidly with time. Their measurements with a hanging drop indicated that the final values of differential capacity were reached very slowly.

Delahay and Fike^{9b} recently have carried out computer calculations for the Langmuir isotherm $\theta = C/(a + C)$, in which $a = C_{1/2} = 1/\beta$ in the present notation. The computations were exact for a planar electrode, but neglected drop curvature for the dropping electrode (the expansion of the diffusion layer was considered, but the "wedge

(9) (a) P. Delahay and I. Trachtenberg, *THIS JOURNAL*, **79**, 2355 (1957); (b) P. Delahay and C. T. Fike, *ibid.*, **80**, in press (1958); private communication from P. Delahay.

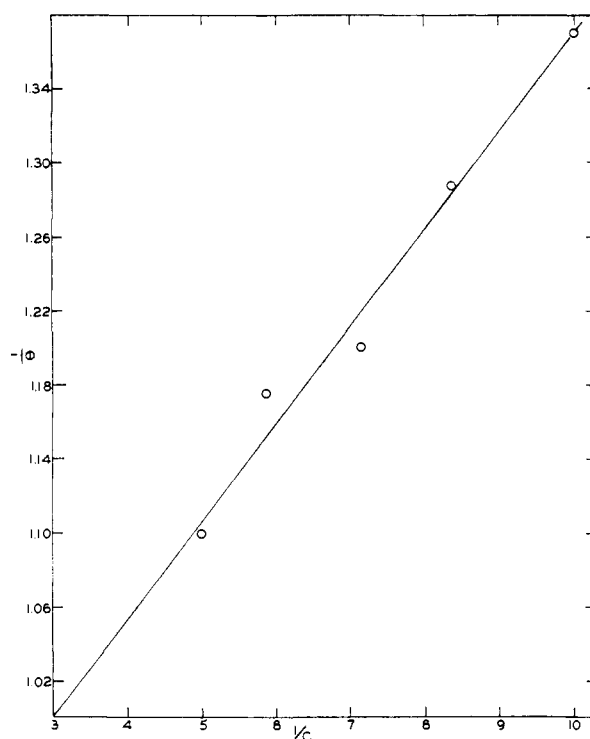


Fig. 2.—Plot of $1/\theta$ vs. $1/C$ for acetophenone pinacol.

effect" for a spherical surface was ignored). They concluded that the condition $C \geq 10a$ represents the order of magnitude of concentration for attainment of equilibrium within 1 sec. For longer time values, the condition is only slightly less stringent, because the calculated curves flatten out rapidly with increasing time. However, under the conditions of the present experiments ($10 \text{ sec.} > t > 5 \text{ sec.}$), the wedge effect should become increasingly important because the diffusion layer thickness increases as $t^{1/2}$, whereas the drop radius increases as $t^{1/3}$.

Adsorption Equilibrium Parameters.—The adsorption behavior of a number of organic compounds was studied in a supporting electrolyte of 0.1 *M* sodium perchlorate as a function of concentration and of electrode potential. For the sake of brevity, the results will not be presented in detail. A summary of the parameters $C_{\text{dl,sat}}$ as obtained from the intercept of a plot of eq. 2, and β as obtained from the slope of eq. 3, is given in Table I for a potential corresponding to a minimum in the double layer capacity curves.

The value of β , the adsorption index, is a measure of the limiting slope of the isotherm at low concentrations and is therefore a measure of the surface activity. The value $C_{1/2}$ is the concentration at which $\theta = 0.5$, which from eq. 3 is given by $1/\beta$.

The value of $C_{\text{dl,sat}}$ is qualitatively a measure of the effective dielectric constant of the double layer and therefore may be interpreted as a measure of the polarity of the adsorbed layer.

The following comparative observations, made on series of closely related compounds, are of interest.

Comparing pyridine, quinoline and acridine, the adsorption index increases from 0.013 to 5 to 100

TABLE I
ADSORPTION EQUILIBRIUM PARAMETERS IN 0.1 M NaClO₄
UNLESS OTHERWISE NOTED

Compound	Poten- tial, -E vs. SCE	C _{dl} , μfd. cm. ⁻²	C _{dl} , sat., μfd. cm. ⁻²	C _{1/2} , mmole l. ⁻¹	β, l. mmole ⁻¹
Octyl alcohol	0.6	21.0	4.22	0.027	37
Acetophenone	.7	18.2	8.22	.78	1.3
Acetophenone pinacol	.7	18.2	4.02	.046	22
Acetomesitylene ^a	.7	21.4	5.75	.021	47
Quinuclidine	.6	21.0	4.65	1.95	0.51
Triethylamine	.6	21.0	3.80	0.49	2.0
Pyridine	.8	16.7	7.36	.79	0.013
2,6-Lutidine	.8	16.7	4.43	1.0	1.0
Quinoline	.7	18.2	5.20	0.2	5.0
8-Hydroxyquinoline	.7	18.2	6.77	.034	29
Acridine	.7	18.2	3.50	.01	100
Phenazine	.8	16.7	2.78	.076	13
Aniline	.8	16.7	7.20	7.1	0.14
β-Dimethylamino- ethanol	.7	18.2	5.58	18	0.057
5-Ethyl-2-methyl- piperidine	.6	21.0	5.27	0.40	2.5
1,2-Dimethyl-5- ethylpiperidine	.6	21.0	4.85	.16	6.2
Ethyl benzoate	.6	21.0	6.13	.019	53
Benzyl alcohol	.6	21.0	5.82	3.7	0.27
Di-n-propyl ketone	.7	18.2	5.57	0.23	4.3
Diisopropyl ketone	.7	18.2	3.65	1.6	0.61
Coumarin ^b	.6	22.0	11.4	0.10	10
Thymol	.6	21.0	5.72	.037	27
β-Naphthol ^c	.7	23.9	8.55	.075	13
Iodobenzene	.6	21.0	5.35	.053	19
Benzonitrile	.7	18.2	9.92	1.0	1.0
1,10-Phenanthroline (oxidized)	.7	18.2	7.11	0.025	40
1,10-Phenanthroline (reduced)	1.3	14.9	3.65	.01	100
Alizarin Red S (reduced) ^b	0.7	19.2	13.1	.19	5.3
Phenolphthalein ^d	.7	24.4	8.18	.09	11.0
Methylene blue (reduced) ^b	.6	22.0	10.5	.006	167

^a Clark and Lubs phthalate buffer, pH 4.6. ^b Acetate buffer, 0.1 M sodium acetate, 0.1 M acetic acid. ^c Phthalate buffer, 0.1 M, pH 4.4, with 0.1 M KCl. ^d Clark and Lubs phthalate buffer, pH 4.78.

while $C_{dl,sat}$ decreases from 7.36 to 5.20 to 3.50, indicating increasing surface activity and decreasing polarity. For 8-hydroxyquinoline, the value of β is higher than for quinoline, showing its greater surface activity, while $C_{dl,sat}$ is also higher as expected from the greater polarity. The lower surface activity of phenazine ($\beta = 13$) as compared with acridine ($\beta = 100$) is presumably to be associated with its lower basicity ($pK_a = 1.23$ as compared to 5.6 for acridine).

2,6-Lutidine ($\beta = 1.0$) is a more surface active than pyridine ($\beta = 0.013$), showing that the increased basicity of lutidine is decisive in spite of the possible structural interference of the substituent methyl groups. Similar considerations prevail for 1,2-dimethyl-5-ethylpiperidine, which is more surface active than 5-ethyl-2-methylpiperidine.

Another example in which steric factors appear to be relatively unimportant is that of triethylamine, which is slightly more surface active than quinuclidine.¹⁰ In contrast, quinuclidine forms a much more stable addition compound with trimethylboron than does triethylamine.¹¹

Di-n-propyl ketone is more surface active than di-isopropyl ketone, as might have been expected from structural considerations.

Effect of Electrode Potential.—All neutral molecular species are most strongly adsorbed in the region of the electrocapillary maximum and in general undergo desorption at sufficient anodic or cathodic polarization, unless some process such as electroreduction of the adsorbed film or oxidation of the electrode intervenes. The region of desorption is usually characterized by a peak in the curve of apparent double layer capacity plotted against electrode potential. Such peaks (termed "tensammetric waves" by Breyer¹²) are concerned with the kinetics of the adsorption-desorption equilibrium and are strongly frequency dependent. In the potential interval between the peaks, the apparent fraction of surface coverage can be determined as a function of electrode potential and of concentration from the measured capacitance values. The resulting family of curves, illustrated in Fig. 3 for triethylamine, indicates the manner

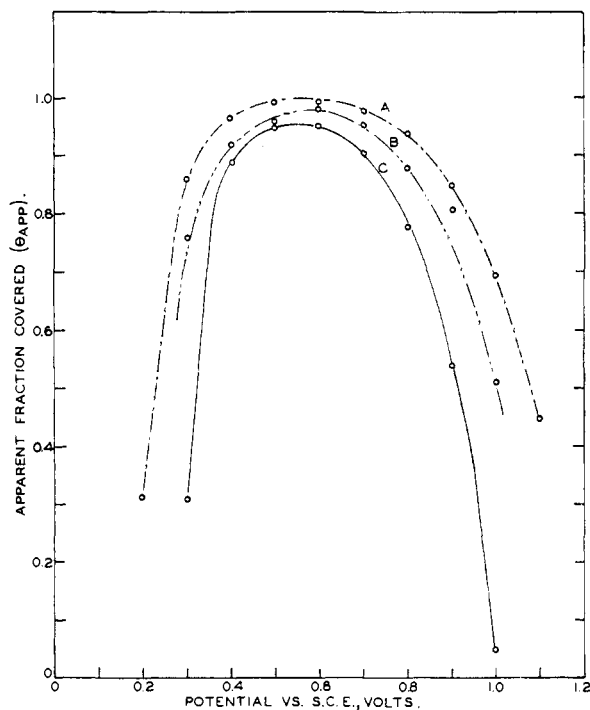


Fig. 3.—Dependence of apparent fraction of surface covered on electrode potential: curve A, 0.05 M; curve B, 0.02 M; curve C, 0.009 M triethylamine in 0.1 M NaClO₄.

in which the tendency for adsorption varies with electrode potential and solution concentration.

(10) A sample of quinuclidine hydrochloride was kindly furnished by Professor H. C. Brown, Purdue University.

(11) H. C. Brown and M. S. Taylor, *THIS JOURNAL*, **69**, 1332 (1947); H. C. Brown and S. Sujishi, *ibid.*, **70**, 2878 (1948).

(12) B. Breyer and S. Hacobian, *Aust. J. Sci. Res.*, **A5**, 500 (1952).

For most of the compounds studied in the present investigation, not enough detailed measurements were made to attempt a more complete interpretation of such curves.⁴ However, some observations on desorption potentials, as determined from the positions of the adsorption-desorption peaks, are of interest in connection with the question of the importance of adsorption as a possible step in electroreduction mechanisms. If the desorption potentials of the original compound and its reduction product are reached at a lower cathode potential than the reduction potentials, it seems clear that adsorption cannot play a role in the reduction mechanism. Thus acetophenone in millimolar concentrations in 0.1 *M* sodium perchlorate is desorbed at a potential of about -1.1 v. (*vs.* S.C.E.), its first reduction product acetophenone pinacol at about -1.3 v., while reduction in a neutral unbuffered solution does not begin until about -1.5 v.¹³ Even in a buffered solution of *pH* 4.6, the half wave potential is -1.35 v.¹⁴ Apparently, adsorption does not play a role in the reduction mechanism.

Likewise, ethyl benzoate and its reduction product benzyl alcohol are desorbed at -1.1 and -1.0 v., respectively, in 0.1 *M* sodium perchlorate, as compared to the half-wave potential of -2.14 v. in 0.05 *N* tetraethylammonium iodide solution in 75% dioxane.¹⁵

Chlorobenzene was not found to exhibit measurable surface active behavior, 10⁻³ *M* bromobenzene barely showed a noticeable effect on the double layer capacity of 0.1 *M* sodium perchlorate, while 10⁻³ *M* iodobenzene gave a saturated monolayer. However, desorption of iodobenzene occurred at about -1.3 v., which is anodic with respect to its

(13) S. Wawzonek and H. A. Laitinen, *THIS JOURNAL*, **63**, 2341 (1941).

(14) R. Pasternak, *Helv. Chim. Acta*, **31**, 753 (1948).

(15) S. Wawzonek, H. A. Laitinen and S. J. Kwiatkowski, *THIS JOURNAL*, **66**, 830 (1944).

reduction potential.¹⁶ Therefore adsorption seems to play no role in the reduction.

Di-*n*-propyl ketone and diisopropyl ketone, which are weakly surface active, are desorbed far below their reduction potentials.

In contrast, the first reduction step of 1,10-phenanthroline occurs at a half-wave potential¹⁷ of -1.23 v., and adsorption occurs on both sides of this potential, indicating that both oxidized and reduced forms are strongly surface active. Not enough is known about the reduction process, however, to make it worth while to speculate about the possible role of adsorption.

Alizarin Red S showed a strong pseudocapacity behavior in the region of its half-wave potential (-0.45 v. in an acetate buffer of *pH* 4.73)¹⁸ and marked capacity minima on both sides of the half-wave potential, a behavior characteristic of a reversible reduction step with adsorption of both oxidized and reduced forms.

A similar pseudocapacity behavior was observed for methylene blue in an acetate buffer. A strong capacity minimum was observed on the cathodic side (-0.6 v.), corresponding to a marked adsorption of the reduced form. Brdicka¹⁹ and Müller²⁰ have clearly demonstrated from polarographic observations that the adsorption prewave is characterized by the formation of a monolayer of adsorbed reduction product. The present result demonstrates unequivocally that an adsorbed layer of reduction product is also formed at more cathodic potentials.

(16) M. von Stackelberg and W. Stracke, *Z. Elektrochem.*, **53**, 118 (1940).

(17) W. W. Braudt and J. M. Kruse, *Anal. Chem.*, **24**, 1306 (1955).

(18) N. H. Furman and K. G. Stone, *THIS JOURNAL*, **70**, 3055 (1948); H. Berg, *Chem. Tech., Berlin*, **6**, 585 (1950).

(19) R. Brdicka, *Z. Elektrochem.*, **48**, 278 (1942); *Coll. Czech. Chem. Commun.*, **12**, 522 (1947).

(20) O. H. Müller, *Trans. Electrochem. Soc.*, **87**, 441 (1941); *J. Biol. Chem.*, **145**, 425 (1942).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS, THE STATE UNIVERSITY]

Molecular Dimensions and Interactions of Long-chain Polyphosphates in Sodium Bromide Solutions¹

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Light scattering and viscosity investigations were carried out in aqueous sodium bromide solutions at 25° on samples of sodium polyphosphate whose molecular weights ranged from 11,000 to 1,250,000. Most of the samples were prepared from potassium Kurrol salts by ion exchange; a few were Graham salts. For molecular weights above 70,000, intrinsic viscosity-molecular weight relationships in 0.35 and 0.415 *M* NaBr were $[\eta] = 0.65 \times 10^{-4} M^{0.69}$ and $[\eta] = 4.94 \times 10^{-4} M^{0.60}$, respectively. At lower chain lengths, the exponent of *M* became smaller in both solvents. From a study of one sample in solutions of several NaBr concentrations, the 0.415 *M* solution was also found to be the one in which the second virial coefficient vanishes. The proportionality of the intrinsic viscosity to the square root of the molecular weight in the same solvent in which the second virial coefficient vanishes is predicted by Flory's theory but apparently has not been demonstrated previously for a polyelectrolyte. The ratio of the molecular dimensions in this theta-solvent to those calculated assuming free rotation about each P-O bond is 1.68 which is close to the corresponding value reported for a silicone but smaller than values obtained with most polymers based on the carbon chain. Theoretical relationships between the second virial coefficient and molecular dimensions are obeyed by sodium polyphosphate to about the same extent as they are by uncharged high polymers. However, the ionic strength dependence of the molecular dimensions could not be fitted to existing theories. The assumptions underlying Flory's equation were examined by an alternate derivation. Other theories could not be applied because of the strong solvent incompatibility of un-ionized NaPO₃ groups, which made extrapolation of the molecular dimensions to infinite ionic strength meaningless.

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pared by P. L. Wineman in 1957 to Rutgers, The State University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.