

Electrometric Determination of the Fixed-Charge Density of Colloid Surfaces: Further Confirmation of the Method

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Abstract □ Experiments directed toward investigating the verity of an electrometric method, which is applicable to the determination of the net density of fixed charge residing on *in vitro* and *in vivo* tissue surfaces, were performed. The fixed sulfonate-anion charge capacity of a cation-exchange resin material was computed from measured electrical potentials and corroborated with the same result obtained independently employing atomic absorption spectrophotometry.

Keyphrases □ Colloid fixed-charge density, cation-exchange resin—electrometric determination, compared to atomic absorption spectrophotometry □ Cation-exchange resin—electrometric determination of fixed-charge density, compared to atomic absorption spectrophotometry □ Electrometric determination—fixed-charge density of cation-exchange resins, compared to atomic absorption spectrophotometry

Plants and animals are living examples of polyphasic colloidal systems. A colloid system may be broadly considered as one in which interfacial properties must be taken into account in order to describe the system's behavior. The net density of fixed charge on colloid surfaces and the manner in which it is affected by interacting substances are of particular interest with respect to such fundamental biological phenomena as excitation, pinocytosis, permeability, antigenicity, thrombogenicity, cell and tissue adhesion, drug action, *etc.* When the epidermis is of interest, such phenomena as moisture sorption and emolliency, dermal toxicity, percutaneous absorption, and the substantive behavior of skin antibacterials are related to its fixed-charge density.

The fixed-charge density of a colloid surface arises from the dissociation of ionogenic groups covalently bonded to the surface or adsorbed onto neutral surface sites.

Previous reports (1-6) described and implemented an electrometric method which allows the *in vitro* or *in vivo* determination of the fixed-charge density of colloid surfaces without causing any injury. It permits tissue surfaces to be studied under normal physiological or product use conditions. It has been applied to the elucidation of the electronic mechanisms of drug tissue interactions (3-5) and their characterization in terms of thermodynamic and kinetic parameters (1-7); it is useful for the determination of equilibrium sorption isotherms (5, 7) and the study of the kinetics of solute sorption and desorption from *in vivo* tissue surfaces (7). When experimentally feasible, electrometric results were confirmed by more conventional techniques (5-7). Generally, however, the electrometric method provides the only means by which such results can be obtained *in vivo*. It is, therefore, important that as much con-

fidence as possible be obtained with respect to the validity of the results provided.

The presently described *in vitro* experiment was performed as a direct means of further confirming the verity of electrical potentials, measured analogously to the manner that they are recorded *in vivo*, in providing computed values of the net fixed-charge density of colloidal materials. This was approached through a comparison of electrometrically determined magnitudes of fixed-charge density on a cation-exchange membrane with the value of its cation-exchange capacity which was more directly determined by atomic absorption spectrophotometry.

EXPERIMENTAL

Materials—The charged colloidal material consisted of a C-310 cation-exchange membrane¹. It is composed of a polymeric, cross-linked, fluorocarbon with affixed sulfonate groups. The dimensions of the membranes used in the study were, approximately, 5 cm. long, 0.5 cm. wide, and 0.11 cm. thick. Each strip was washed with distilled water and allowed to soak in relatively large volume solutions of 0.015 and 0.15 M NaCl for approximately 12 months prior

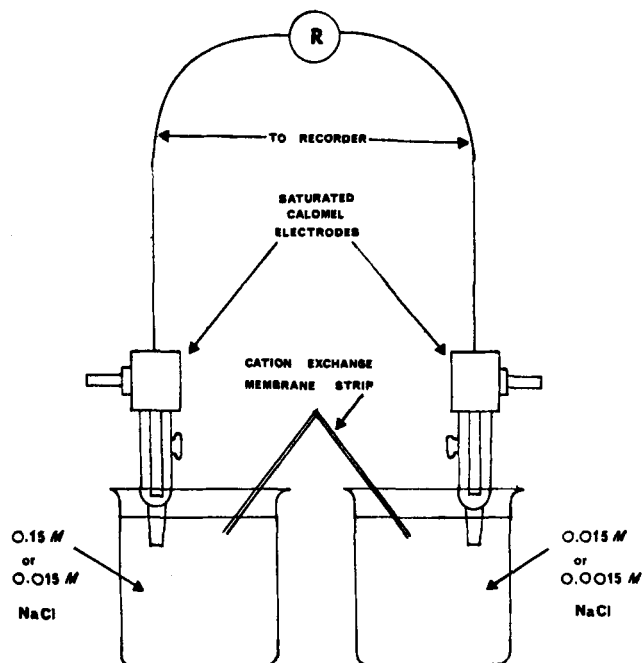


Figure 1—Experimental arrangement for the measurement of dilution (liquid-junction) potentials used to compute the fixed-charge density of a cation-exchange membrane material.

¹ Supplied by American Machine and Foundry Co., Springdale, Conn.

Table I—Electrometric Results of Determination of Fixed-Charge Density of Cation-Exchange Resin Strips Equilibrated in 0.15 and 0.015 M NaCl Solutions

Dilution Potentials, mv.	Fixed-Charge ^a Density, meq./l.	
	0.15 M	0.015 M
27.4	47.6	-189
35.4	39.0	-228
30.8	47.5	-205
Averages 31.2	44.7	-207

^a The fixed-charge densities were computed using Eq. 1 and E_d^0 values of 11.4 and 11.9 mv. for the 0.15 and 0.015 M NaCl equilibrated strips, respectively.

to measurement; this ensured a thorough equilibration of Na⁺ exchange and distribution in the resin. All chemicals used were of reagent grade.

Electrometric Determination of Fixed-Charge Density of the Membrane—Details of the dilution potential method for the determination of the fixed-charge density of colloid surfaces were previously reported (1-6). The *in vitro* measurements were performed in a manner analogous to the *in vivo* procedure. The experimental arrangement is diagrammed in Fig. 1; it simply consisted of two 50-ml. beakers, filled with either 0.15 and 0.015 M NaCl or 0.015 and 0.0015 M NaCl, respectively, with a miniature calomel electrode² inserted into each. The electrodes were connected through a recorder³, which was used to measure the developed potentials.

Prior to the measurement of dilution potentials, the recorder was precalibrated to zero with the membrane placed between beakers, both containing the same concentration of sodium chloride solution equal to that with which the membrane had been equilibrated. Liquid junction potentials, equivalent to the dilution potentials obtained in *in vivo* studies, were recorded immediately upon the completion of the internal circuit by bridging between the beakers, with one containing a sodium chloride solution and the other its 10-fold dilution, with the membrane strips. Strips that had been equilibrated with 0.15 and 0.015 N NaCl solutions were used with the 0.15/0.015 and 0.015/0.0015 M NaCl solution pairs, respectively. The fixed-charge density of the strips equilibrated with the two concentrations of sodium chloride was computed from the measured potentials using previously reported mathematical relations (1, 2).

Equation 1 provides the expression that is specifically appropriate to the present case. The fixed-charge density and measured dilution potential are denoted by f and E_d , respectively:

$$f = \frac{E_d^0 - E_d}{0.206} \quad (\text{Eq. 1})$$

The E_d^0 represents the values of the dilution potentials developed between each sodium chloride solution-10-fold dilution pair at zero net density of fixed charge on the strip of cation-exchange material.

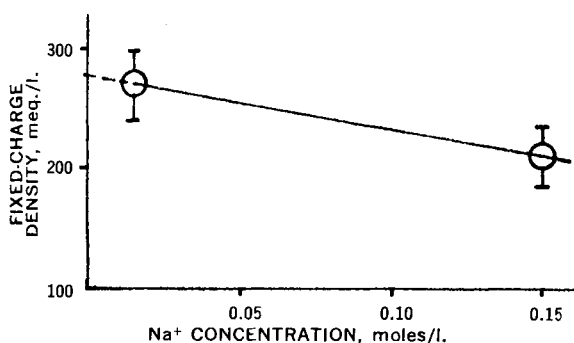


Figure 2—Relationship of the electrometrically determined fixed-charge density of a cation-exchange resin material to the concentration of the sodium chloride solution in which it was equilibrated. The standard deviations of each point are indicated.

² Beckman No. 41239.

³ Sargent model SR.

Table II—Sodium Content of Cation-Exchange Resin Material Determined by Atomic Absorption Spectrophotometry

Treatment	Sodium Content, meq./l. Water ^a
Na ⁺ loaded resin	637
	605
	Average 621 ± 16^b
0.15 M NaCl equilibration	622
0.015 M NaCl equilibration	563

^a Computed using a true density of water equal to 0.997 at 25°.

^b The literature (8) reported value is 700 ± 200 meq./l.

The values of E_d^0 were obtained experimentally through the measurement of liquid junction potentials developed at a boundary formed between the solutions within a Y-tube. Two arms of the Y-tube were inserted into the beakers of sodium chloride solution in place of the membrane strip. A hypodermic syringe was attached to the third arm. The syringe was used to draw simultaneously both sodium chloride solutions sufficiently high into the Y to form a liquid junction between the solutions. The E_d^0 values determined for the 0.15/0.015 and 0.015/0.0015 NaCl solution dilution pairs were 11.4 and 11.9 mv., respectively. The theoretical value of E_d^0 , computed on the assumption of ideal solution behavior, is 12.4 mv. This value may be expected to be approached in the limit as the concentrations of the solutions are progressively diminished to infinite dilution.

Spectrophotometric Determination of Sodium-Ion Content of the Membrane—The sodium present in the membrane strips, previously equilibrated with 0.15 and 0.015 M NaCl solutions, was eluted into 2 N HCl. The eluates were appropriately diluted and assayed for sodium concentration using an atomic absorption spectrophotometer⁴. The strips were fully loaded with sodium by prolonged immersion for approximately 6 days in 1 M NaOH and then rinsed with deionized water; their sodium content was similarly determined.

The water content of water-saturated exchange membrane material was determined from the weight loss observed following drying to constant weight (approximately 3 hr. at 60°). The average of four replications of the moisture content was found to be $20.2 \pm 0.26\%$ wet weight, which resembles the literature value of $17.0 \pm 0.04\%$ (8).

RESULTS AND DISCUSSION

Electrometric Determination of Fixed-Charge Density—The observed dilution potentials, E_d , and fixed charge densities, f (given in milliequivalents per liter of membrane water) recorded in three replications on the strips equilibrated in the 0.15 and 0.015 M NaCl solutions are listed in Table I. As discussed, the fixed-charge densities were computed from the dilution potentials using Eq. 1. The average fixed-charge densities of the ion-exchange strips are plotted in Fig. 2 as a function of the sodium chloride concentration in which they were equilibrated. The increase in negative fixed-charge density, which occurs with increased dilution of sodium chloride, is attributable to an increasing dissociation of ion pairs formed between the fixed sulfonate anions and their sodium counterions. Extrapolation to zero sodium chloride concentration gives an ordinal intercept value of -283 meq./l. as the total ion-exchange capacity of the resin material. The standard deviations of the plotted values are indicated in the figure.

Spectrophotometric Determination of Fixed-Charge Density—Table II presents the values of the sodium content of the ion-exchange strips, which were loaded with sodium ion and equilibrated with the 0.15 and 0.015 M NaCl solutions. The sodium concentrations recovered from the fully loaded strips are in fair agreement with themselves and the literature value (8), i.e., 621 ± 16 determined, compared with 700 ± 200 meq./kg. wet weight from the literature.

The sodium recovered from the membrane may be attributed as being, in each case, composed of a relatively constant quantity of

⁴ Perkin-Elmer model 290.

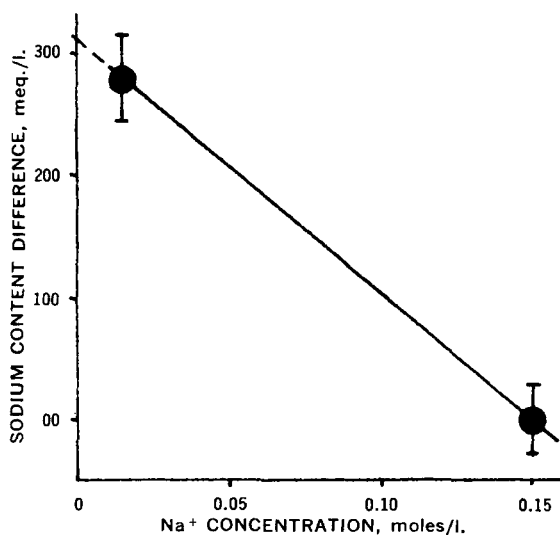


Figure 3—Sodium-ion content differences for a cation-exchange resin material loaded with sodium ion relative to being equilibrated with the concentrations of sodium chloride solutions indicated on the abscissa. The extreme deviations for each point are indicated.

bound and free sodium counterions, which function to compensate electrically the fixed sulfonate anions, and concentration-dependent quantities of Na^+ , which are interstitially sorbed and distributed within the polymeric matrix. The latter can be expected to diminish progressively with decreasing external equilibrium concentrations of sodium chloride; in the limit the quantity of Na^+ not electrically associated with fixed anions can be assumed to extrapolate to zero at infinite dilution. Therefore, the extrapolated value of the difference in sodium content of the fully loaded resin and the content of the resin equilibrated with the lesser concentrations of sodium chloride will provide an estimate of the quantity of sodium chloride occurring in the fully loaded membrane in a form other than sulfonate counterion.

Figure 3 presents a plot of the differences (plotted with the magnitudes of extreme deviations indicated), which provides an ordinal intercept of 315 meq./l. The difference between this value and the concentration of sodium recovered from the fully loaded membrane may be attributed as equal to the sulfonate-anion fixed-charge capacity of the resin material. By using the average determined value of 621 meq./l. for the sodium content of the loaded membrane, a value of 306 meq./l. is obtained for the fixed-charge capacity. Considering the magnitude of the errors inherent in the extrapolations as well as those arising in both experimental methods, this

value can be considered to compare very favorably to the 283 meq./l. fixed-charge capacity determined electrometrically. The difference between the values, of approximately 8%, can readily be reconciled as well within the range of error involved in their determination.

SUMMARY AND CONCLUSIONS

The anionic fixed-charge capacity of a sulfonate cation-exchange material was determined electrometrically and compared to a similar result obtained from independent measurements performed utilizing atomic absorption spectrophotometry. Considering the magnitudes of the errors involved in the necessary means by which the extrapolated values of fixed-charge capacities were obtained, the within 8% agreement between the two independently determined values is considered satisfactory; therefore, this result can be interpreted as providing still further confidence in the application of the electrometric method to the investigation of biological systems where studies of drug tissue interaction kinetics and equilibria, for example, cannot generally be obtained under normal *in vivo* conditions by any other experimental means.

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