umns in the table are identical with those in the previous tables. The values of the energy and excess entropy of mixing used in this table are those calculated in the preceding paper[5c] and combine the vapor pressure data of Scatchard, Wood and Mochel with the heat of mixing data of Scatchard. The results for this system are very similar to those in the other two systems and tend to indicate that the energy of mixing at constant volume and the excess entropy of mixing at constant volume are relatively independent of temperature when referred to the same constant volume but are dependent upon the volume at constant temperature.

It is also of interest to compare the cohesive energy densities under these various conditions. The values of a_{11}, a_{22} and a_{12} in cal. per cc. for the three systems studied in this paper are given in Table V.

The second column gives these values at 70° and at the volume at 70° and one atmosphere pressure, the third column gives the values at 70° but at the volume at 25° and one atmosphere pressure while the last column gives the values at 25° and at the volume at 25° and one atmosphere pressure. It is again evident that the effect of volume is relatively large while the effect of the temperature is rather small. These same trends are evident also in the percentage differences of a_{12} and the geometric mean of a_{11} and a_{22}.

Similar calculations have been made for the benzene–methanol and carbon tetrachloride–methanol systems but the effects are too small in comparison to the uncertainties in the reported thermodynamic functions to draw any conclusions.

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Electrochemical Properties of Ion Exchange Resins. I. Donnan Equilibria, Membrane Potentials and Conductivities

BY W. JUDA, N. W. ROSENBERG, J. A. MARINSKY AND A. A. KASPER

Ion-exchange resins have been considered as solid electrolytes. Electrochemical properties of sodium salts, including transport numbers and conductances, have been investigated and correlated with Donnan absorption for two chemically different cross-linked phenolsulfonate resin membranes, PERMIONIC CR-41 and PERMIONIC CR-51. The data are consistent with the assumption that the sodium salt of one of the materials (CR-51) is strongly ionized, whereas the other could be partially associated into ion pairs. Electrical conductivity in the two membranes studied can be considered to be entirely electrolytic in character with a uniform ionic flux across the cross-section.

The recent announcement of homogeneous ion exchange membranes[1] of high exchange capacities, water contents and specific electric conductances has stimulated considerable interest in the electrochemistry of ion exchange resins because the membrane form is well suited for theoretical and applied electrochemical work. A correlation of membrane potentials and conductances with Donnan electrolyte diffusion into the membrane phase is of importance in all cells transferring ions from one solution to another through a membrane. Although each of these properties has been investigated[2] separately on different materials, including ion exchange granules and insulating membranes made of collodion, clay and polystyrene bonded ion exchange granules, it was impractical to carry out experimental studies of all three either on the same granular exchanger or on the same insulating membrane; it is difficult to make reliable potential and conductance measurements with the granular exchanger and Donnan determinations are not easily obtained with the insulating type membrane.

(1) W. Juda and W. A. McRae, THIS JOURNAL, **72**, 1044 (1950). See also T. R. E. Kressman, *Nature*, **165**, 568 (1950).

(2) W. C. Bauman and J. Eichorn, THIS JOURNAL, **69**, 2820 (1947); H. Jenny, T. R. Nielsen, N. T. Coleman and D. E. Williams, *Science*, **112**, 164 (1950); K. Sollner, *J. Electrochem. Soc.*, **97**, 139C (1950) and preceding papers: S. K. Mukherjee and C. E. Marshall, *J. Phys. Chem.*, **55**, 61 (1951) and preceding papers; M. R. J. Wyllie and H. W. Patnode, *ibid.*, **54**, 204 (1950); M. R. J. Wyllie, *Science*, **108**, 684 (1948); E. Heymann and I. J. O'Donnell, *J. Colloid Sci.*, **4**, 405 (1949); W. S. Albrink and R. M. Fuoss, *J. Gen. Physiol.*, **32**, 453 (1949).

In this paper, systems involving the sodium salts of two chemically different cross-linked polyphenolsulfonic acids, identified as Permionic CR-41 and Permionic CR-51, in equilibrium with sodium chloride solutions, were chosen for transport, conductance, and Donnan studies. A univalent cation for which simple theoretical concepts may be tested is required for this initial investigation; sodium ion was selected because of its relatively low mobility (compared to hydrogen or potassium, for example), a property which enhances the sensitivity of membrane potentials to the presence of the mobile counterions (chloride ions) in the solid phase.

Experimental

Conversion to Sodium Form.—A membrane sample, 7.5 cm. long, 1.9 cm. wide and 0.9 mm. thick, in the hydrogen form and in equilibrium with sulfuric acid (sp. gr. 1.30) was immersed in about 100 times its volume of distilled water. After 7 minutes of rapid stirring, this leaching procedure was repeated with fresh portions of distilled water until the water was neutral to methyl orange. (Five washes were sufficient to bring the membranes to the leached hydrogen form.) The sample of membrane was then converted to the sodium form with 4 N sodium chloride solution. A 7-minute contact time, with agitation, of five successive portions of this solution effected complete conversion as evidenced by pH measurements of each spent portion. The volume of each portion provided roughly a forty-fold stoichiometric excess over the total equivalents of membrane capacity. The sample was finally leached free from diffused salt by successive washes with distilled water, as described above, until two successive leach waters were free from chloride (silver nitrate test).

Moisture Determination.—A two-gram sample of leached sodium membrane was wiped surface dry, weighed to the

nearest 0.01 g., heated at 110° for 16 hours, and reweighed. Expressed as grams per 100 surface-dry grams of leached sodium form resin, the water content, found to be constant and independent of equilibrating solution to ±2%, is 66.6 ± 1 for CR-41 and 55.3 ± 1 for CR-51.

Capacity Determination.—Two-gram samples in the leached hydrogen form, wiped surface-dry and weighed to the nearest 0.01 g., were converted to the sodium form as described above, except that the hydrogen ion released from the membrane into the leach portions was analyzed by titration. Each sample was then reconverted to the leached hydrogen form (with 2 N sulfuric acid) and the capacity determination was repeated. The capacities, expressed in normalities, i.e., meq./ml. leached Na-form resin, are 0.575 ± 0.010 for CR-41 and 1.26 ± 0.02 for CR-51.

Density Determination.—In preparation for the moisture and capacity determinations, a surface-dry membrane sample, 7.5 cm. × 1.9 cm. × 0.09 cm., in the desired ionic form, was weighed to the nearest 0.01 g. The dimensions of the sample were obtained by direct measurement, the thickness being determined with a micrometer to ±0.0005 cm. The density of CR-41 is 1.15 ± 0.01, that of CR-51, 1.33 ± 0.01.

Donnan Absorption Data.—Five-gram samples of membrane material were converted to the leached sodium form and were equilibrated with sodium chloride solution of the normality under investigation. Seven 10-minute equilibrations were employed for each Donnan absorption measurement. The membrane sample was then wiped surface-dry, and weighed to the nearest 0.01 g. In some cases, the volume was redetermined after equilibration and it was found that volume changes were sufficiently small to be neglected as a first approximation (less than 2%). The sample was then leached for 5-minute periods with successive portions of distilled water, each of about 20 cc., until two successive leach waters were chloride-free (to silver nitrate). The combined leachings were titrated for chloride by the Mohr Method.

In Fig. 1, the Donnan absorption data obtained for Permionic CR-41 and Permionic CR-51 are presented with the ratio of absorbed to solution chloride normalities A/N, as the ordinate and the solution normality, N, as the abscissa.
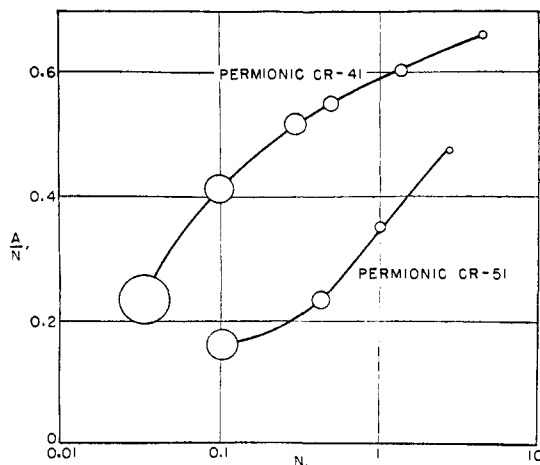

Fig. 1.—Donnan diffusion of sodium chloride into Permionic membranes.

Membrane Potential Measurements.—A Lucite cell, consisting of two identical chambers, 1.3 cm. thick and 1.3 cm. in diameter (3 ml. capacity), was fitted with Ag/AgCl electrodes. This cell was designed to permit the continuous flow of solution past the membrane surfaces. All measurements were made with two different solutions of NaCl, the ratio of their normalities, N_1/N_2, being always equal to 2. In preparation for a measurement a membrane sample, 0.9 mm. thick and 2 cm. in diameter was equilibrated with the solution of concentration N_1, wiped dry, and inserted in the cell. The solutions were then flowed past the membrane surfaces at the rate of about 6 ml./min.; steady potential readings were then obtained after about 10 minutes.

The potentials were measured by means of a Leeds & Northrup Type K-2 potentiometer. Temperature control to ±1° was provided by immersing the cell, protected by a polyethylene container, in a water-bath maintained at 25°. The probable error of these measurements was ±1 millivolt (mv.), corresponding to ±0.03 in the transport number. The reproducibility of the potentials measured for the same membrane material manufactured separately is within 3%.

To obtain the sodium transport number as a function of solution concentration, the observed potential, E (in mv.) was divided by $E_0 = 118 \log a_1/a_2$, where a_1 and a_2 were the known activities of the sodium chloride solutions of concentrations N_1 and N_2. Activity data were taken from Harned and Owen.[3]

The experimental potential, E, corresponding to each pair of concentrations, decreased considerably more rapidly with increasing concentration in the case of CR-41 than in the case of CR-51.

In Fig. 2, the transport numbers are plotted vs. $\bar{N}$ where $\bar{N}$ is the geometric mean of N_1 and N_2.
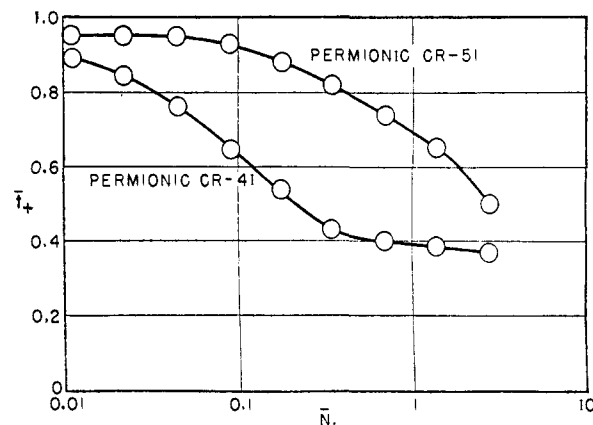

Fig. 2.—Sodium transport numbers across Permionic membranes in chloride solutions.

Rapid Conductivity Determination.—A "Solu-bridge" (Industrial Instrument Company, New Jersey), a simple 60-cycle a.c. bridge circuit without capacitance correction, and a 1000-cycle a.c. bridge (described below), were used to determine the conductances of thin, saran-backed membrane strips of Permionic CR-51. The strips, 7.5 cm. × 1.9 cm. × 0.09 cm., were converted to the Na form, were completely leached, and were then equilibrated with a solution of the desired concentration. Equilibration was carried out in a manner identical with conversion, using solutions of the desired concentration. To measure conductance, the strip, wiped free of adhering solution and protected from moisture loss by a thin latex wrapper, was clamped into place between two copper electrodes, 2 cm. × 0.5 cm., mounted 6 cm. apart on a Lucite block. The bridge reading was then made. The cell constant was obtained by a measurement of the dimensions of the membrane and the electrode spacing.

Concerning the effect of the membrane backing, its specific conductance is at least three orders of magnitude smaller than that of the resin material and hence negligible; a 20% decrease in conductivity of the backed over the unbacked material has been observed. This compares favorably with the 17.1% of backing volume, determined (by weight and density calculations) to constitute the membrane.

Precise Conductivity Determination.—An a.c. system similar to that used in the very accurate conductance researches of Jones[4] on aqueous salt solutions was assembled in an attempt to determine more accurately the conductance of Permionic CR-41 and Permionic Cr-51. This system utilized a Hickock Audio-Frequency Signal Generator—Model 198, coupled with a Leeds–Northrup Jones Bridge for which additional balancing capacity was provided as needed. As null point detector, a General Radio tuned amplifier type GR-430 coupled to a DuMont oscilloscope, Model 224, was

(3) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., 2nd Ed., rev. and enlarged, 1950, p. 360 and p. 557.

(4) G. Jones and R. C. Josephs, This Journal, **50**, 1949 (1928).

used. The system was shown to be in proper operating condition (±0.001 ohm accuracy) by a calibration using direct and alternating current on resistors calibrated by the Bureau of Standards.

An air thermostat was used to control the temperature to ±0.01°. This method avoided the multiple, stray electrical paths expected in a water-bath and the undesirable condition of contacting an aqueous gel phase with oil of an oil-bath. Water evaporation from the membrane edges in the air thermostat was eliminated by covering the joint between the two cell halves by means of a wide rubber band cut from a thin-walled latex tube of one-inch diameter.

The resistance of a sodium chloride solution was measured in a cell composed of two halves; then the resistance was determined with the same solution and with a membrane of known geometry separating the two halves of the cell. By difference the resistance of the membrane was obtained. Despite the precision of individual measurements, it was found that the inherent irreproducibility of re-assembly of any cell composed of two halves, and the small differences between the two resistance values, especially in dilute external solutions, limited the accuracy to ±2%. Because of the lack of reproducibility and the involved procedure, the method has not been used extensively. It has served the valuable function of allowing a calculation of the cell constant of the simpler cell (previous section) by a comparison of the conductances experimentally found in the simple cell with the more accurately determined conductivities.

A logarithmic plot of the conductivities measured with the 1000- and 60-cycle bridges is given in Fig. 3. In this figure, the rapid 60-cycle and 1000-cycle a.c. measurements are represented as square and triangles, respectively; the circles represent the precise measurements made with the "fixed geometry" conductivity cell.
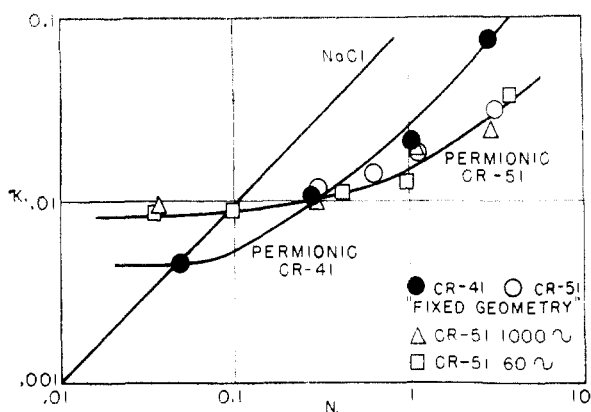

Fig. 3.—Specific conductivity of Permionic membranes CR-51 and CR-41 compared with specific conductivity of sodium chloride.

Discussion

Any quantitative interpretation of the Donnan diffusion data awaits a better knowledge of the activities of ionic species in the membrane phase. The fact that the more permselective membrane, CR-51 (Fig. 2), is considerably more effective in screening the chloride ion (Fig. 1) than CR-41, suggests a lesser tendency toward ion-pair formation in CR-51 than in CR-41. The steeper slope of the A/N vs. N plot of CR-41, indicating increasingly stronger screening effects at the dilute end, is consistent with this assumption.

From consideration of the concentration cell with transference

Ag/AgCl/NaCl (a_1)//Na-membrane//NaCl (a_2)/AgCl/Ag

the transport number of Na^+ in the membrane in equilibrium with a solution at activity $(a_1a_2)^{1/2}$ is given by the usual expression[5] $t_+ = E/E_0$, where

(5) See, for example, K. Sollner, reference 1; also S. Glasstone, "An

E is the cell potential and $E_0 = 2RT/F \ln a_1/a_2$, provided that (1) the membrane is sufficiently thick so that its two faces are in equilibrium with their respective solutions; and (2) the ratio a_1/a_2 is sufficiently small so that the variation in t_+ with log a is essentially linear. For these reasons, 0.9 mm. thick membranes and solution concentration ratios equal to 2 were used throughout this work.

In 1–3 N sodium chloride solutions, t_+ approaches 0.4 at 25°. The value of t_+ in the CR-41 membrane equilibrated in these solutions is about the same (Fig. 2), although its exchange capacity (0.575) is still of the same order of magnitude as the adsorbed salt concentration (Fig. 1). This equality of the t_+ values may be explained by substantial ion-pair formation in CR-41.

In the limit only the mobile Na^+ ion in a leached resin is presumably capable of carrying current; in sodium chloride solutions Donnan diffusion introduces chloride ions and additional sodium ions which contribute to the conductance. This effect is illustrated in Fig. 3 where the sodium chloride conductance line has been plotted for comparison with the measured conductance curves of CR-41 and CR-51. The intersection of this line with the conductance curve of CR-41 or CR-51 may be termed the "isoconducting value" since the membranes have here the same conductivity as the equilibrating solution (0.06 N for CR-41 and 0.1 N for CR-51). The isoconducting values are nearly the same as the leached values for both membranes. The fact that the CR-41 curve crosses the CR-51 curve (Fig. 3) is attributable to the higher Donnan salt diffusion and the poorer selectivity of CR-41 (Figs. 1 and 2). This observation is also consistent with the assumption of stronger ion-pair formation of CR-41.

If the dielectric constant of CR-41 is lower than that of CR-51, a stronger ion-pair formation may result in a manner similar to that of strong electrolytes in dioxane–water mixtures.[6]

The simple concept presented here is as yet inadequate for quantitative use, leaving open such essential questions as dielectric constants, activities, steric considerations and swelling effects. Evidently, a considerable volume of experimental data is required for checking and amplifying the present interpretations. Further work is planned along the lines of obtaining similar data (Donnan transport and conductance) with different ionic species (both cationic and anionic) and dielectric constants in order to accumulate further information on ion-pair formation and on steric effects due to large mobile counterions.

Introduction to Electrochemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1949, pp. 208–209.

(6) For a weight per cent. of 53 (and a dielectric constant of 38) a K value of 2.5 × 10⁻⁷ has been reported for tetraisoamylammonium nitrate in a dioxane–water mixture (reference 3, p. 192).