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Technical Report No. 5

ELECTRICAL CONDUCTIVITY OF
ION EXCHANGE RESINS

by

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ELECTRICAL CONDUCTIVITY OF ION EXCHANGE RESINS

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Introduction

A number of important separation processes utilize an electric field as the driving force to achieve partition of solution components across a membrane. Electrodialysis is an example of such a process in which the membrane consists of an ion exchange resin. As an additional driving force a pressure gradient can be applied, which is done in forced flow electrophoresis.

Electrical conductivity studies of ion exchange and other electroconductive resins which have been reported (1) have generally been restricted to verification of Ohm's Law relationship without identifying the current-carrying species. In an earlier study (2) of polymer membranes containing dissolved quaternary ammonium salts, used in coated wire and other ion selective electrodes, the determination of the pressure dependency of the conductivity of the membrane, gave strong evidence of an ionic conduction mechanism. It was felt that parallel studies of ion exchange resin membranes could provide a useful, simplified model in interpreting our earlier data, inasmuch as only one ion of the pair is mobile, and capable of carrying charge.

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Experimental

Approximately 10 g of Dowex-1 (Dow Chemical) anionic exchange resin, present as the chloride form was converted to the desired anionic form by vigorously shaking it with three successive 30 ml portions of the appropriate 1 M sodium salt. Resins were then thoroughly washed with distilled, deionized water and partially dried by lightly pressing them between sheets of filter paper.

A few grams of the resin, in a KBr-type dye, were pressed a force of 8500 kg/cm^2 , producing a "jelly-like" product found to be water-soluble. Films of the resins were prepared by coating glass slides with aqueous resin mixtures and allowing the water to evaporate. Circular samples (15 mm X 1 mm) were cut from the air-dried master-films then vacuum-dried at room temperature for 48 hours.

Using this technique it has been possible to prepare the Cl^- , Br^- , I^- , and NO_3^- anionic forms of the resin from which uniform, pliable films could be cast.

Electrical conductivity of the films was determined using the previously described techniques and apparatus (2).

Results and Discussion

Electrical conductivity of the films prepared from the ion exchange resins was found to obey the operational semiconductor relationship

$$\sigma = \sigma_0 \exp (\Delta G^\ddagger / RT)$$

where σ is the observed volume resistivity, and $\Delta G^\ddagger$ the molar free energy of activation for the conduction process, analogous to that

for chemical rate processes. The preexponential factor, σ_0 , is dependent on geometric factors and includes a term representing the initial concentration of the charge-carrying species.

Similar Arrhenius-type relationships have been used to characterize the electrical conductivity in a variety of materials, including polymers (3), electrolytic glasses (4), and many organic semiconducting materials (5). While such expressions provide an adequate description of the observed conductivity in these materials it does not, however, distinguish between the types of charge carriers which may be electronic, or ionic. Fortunately one can determine, without prior knowledge of the conduction mechanism, the rather definitive parameter of activation volume for conduction, $\Delta V^\ddagger$, through application of the following quasi-thermodynamic expressions

$$\Delta V^\ddagger = \left(\frac{\partial \Delta G^\ddagger}{\partial P} \right)_T = -RT \left(\frac{\partial \ln \sigma}{\partial P} \right)_T$$

with the assumption that the sample geometry remains relatively invariant throughout the pressure range utilized in this study.

Data gathered from such high pressure - conductivity experiments, when plotted ($\ln \sigma$ vs. P) was linear with a negative slope and was used to calculate the values of $\Delta V^\ddagger$ shown in Table I. Molar volumes, V_m , for the anions presented in this table were calculated using $V_m = 4/3 N_0 \pi r^3$, where N_0 is Avogadro's number of atoms and r is the Pauling ionic radius (6).

The magnitude of the activation volume for conduction obtained from this approach has been previously demonstrated (3, 7) to be a

most useful parameter in distinguishing amongst the several possible charge-carrying particles responsible for electrical conduction. If the conduction process was electronic, then one would expect negative $\Delta V^\ddagger$ values resulting from increased orbital overlaps between adjacent negative molecules during compression (7). On the other hand, if the movement of larger ions (or polymeric segments (8)) was the predominant mode of electrical conduction, this should be reflected through the relatively much larger activation volumes required for ion migration.

In a study describing electrolytic conduction in ionic glasses, Hamman (4) demonstrated that an excellent correlation existed between the experimentally measured $\Delta V^\ddagger$ and the calculated V_m of the mobile, cationic charge carriers. In a similar manner, Sasabe, et al (8) determined activation volumes for conduction which suggested that segmental motion in polymers was responsible for transport of electrical current through polyvinylacetate films.

As the values listed in Table I show, good correlation exists between conduction activation volumes and the molar volume of the respective anion calculated from crystallographic data. One may therefore conclude that the charge is anionically transported through the bulk resin by the anion with the experimentally measured $\Delta V^\ddagger$ corresponding to a process in which compression retards ion migration by decreasing vibrational and oscillatory motions of polymer segments resulting in an increased local viscosity. Since the cationic resin species is immobilized, it probably does not contribute to the observed conductivity.

In an earlier study of polyvinylchloride films doped with the quaternary ammonium salt, methyltricaprylammonium chloride, pressure-conductivity measurements yielded corrected $\Delta V^\ddagger$ values of $34 \pm 2 \text{ cm}^3/\text{mole}$. In contrast to the ion exchange materials, the cation in this system is not chemically bonded to the polymer and despite its relatively low mobility, should be expected to contribute to the electrical conduction process.

One could very roughly estimate the contribution such an additional charge carrier would make to the calculated activation volume by taking the summation of individual molar volumes multiplied by their respective, weighted transport numbers (assumed to be proportional to the reciprocal of the molar volume). As a limit of relative ion sizes (cation volume $\gg$ anion volume) such a calculation would give a value of twice that of the anion volume. While this approximation is admittedly rather crude, it nonetheless suggests the earlier results are reasonable in view of this present study.

The conduction process in both the $\text{PVC/R}_4\text{NX}$ system and the ion exchange resins resembles that in liquids where activation volumes for self-diffusion are generally one molar volume or greater (9, 10). In solids and crystalline materials, it is usual to find $\Delta V^\ddagger < V_m$. A theory (11) based on defect formation in solids suggests that $\Delta V^\ddagger \approx 1/2 V_m$ would be reasonable.

Acknowledgement. This work was supported by a grant from the Office of Naval Research.

TABLE I

Activation Volume for Electrical Conduction for Various
Forms of Dowex-1^(R) Ion Exchange Resin

<u>Resin form</u>	$V^{\ddagger a}$ (cm ³ /mole)	$\bar{r}$ (Å)	V_m (cm ³ /mole)
Cl ⁻	19	1.81	15.0
Br ⁻	22	1.95	18.7
NO ₃ ⁻	23	1.93 ^b	18.1
I ⁻	30	2.16	25.4

^a $\Delta V^{\ddagger}$ values have a r.s.d. of 10%

^b represents the distance from the center of N to end of O

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