

results obtained were: $v_2(180^\circ) = 0.288$; $dv_2/dT = 2.9 (\pm 0.2) \times 10^{-4} \text{ deg.}^{-1}$.

According to theory

$$(v_1\nu/V^*)(\langle r^2 \rangle_i^*/\langle r^2 \rangle_0)[v_2^{1/3} - (v_2/2)\langle r^2 \rangle_0/\langle r^2 \rangle_i^*] = -[\ln(1 - v_2) + v_2 + \chi_1 v_2^2] \quad (4)$$

where ν is the number of moles of network chains in volume V^* and $\langle r^2 \rangle_i^*$ is the mean-square chain displacement length in the dry state of this volume. Taking $\chi_1 = 0 \pm 0.1$, $d\ln\langle r^2 \rangle_0/dT = -1.3 (\pm 0.2) \times 10^{-3} \text{ deg.}^{-1}$ and $dv_2/dT = 2.9 (\pm 0.2) \times 10^{-4} \text{ deg.}^{-1}$, we calculated from eq. 4 that $d\chi_1/dT = 1.5 (\pm 2.5) \times 10^{-4}$, with full allowance for the stated uncertainties in the quantities involved. Even if the extreme value -4×10^{-4} were used for $d\chi_1/dT$ instead of zero, the value of $-d\ln\langle r^2 \rangle_0/dT$ calculated from eq. 3 would be altered only by about $+0.2 \times 10^{-3}$.

The close similarity between the viscosity-temperature coefficients in *n*-hexadecane and in the higher hydrocarbon solvents offers independent assurance that enthalpies of dilution make no significant contribution to the results. If this were not so, their effect should be more prominent in the former than in the latter and therefore apparent in the results.

Conclusions

The average of the values of $-d \ln \langle r^2 \rangle_0/dT$ given in Table III is $1.21 \times 10^{-3} \text{ deg.}^{-1}$. As already noted, use of $\gamma = 3$ instead of 2.5 would increase the result somewhat. On the other hand, incorporation of the suggestion of Stockmayer¹² according to which the numerical factor in eq. 2 should be reduced by one half, reduces α^2 by about 15% and $-d \ln \langle r^2 \rangle_0/dT$ by about 10%. Considering these various sources of uncertainty in the present method, we conclude that $-d \ln \langle r^2 \rangle_0/dT = 1.2 (\pm 0.2) \times 10^{-3}$.

The results of stress-temperature studies on polyethylene networks swollen by *n*-triacontane and *n*-dotriacontane presented in the preceding paper yield $-d \ln \langle r^2 \rangle_0/dT = 1.16 (\pm 0.10) \times 10^{-3}$. The gratifying agreement between results obtained by these unrelated methods lends substantial support to the assumption that the molecular conformation in the amorphous state is not appreciably affected by interactions between neighboring chains. The related assumption² that the chains of a cross-linked network contribute additively to its elastic free energy likewise is validated.

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A Study of the Ionization of Polystyrene Sulfonic Acid by Proton Magnetic Resonance^{1a}

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RECEIVED SEPTEMBER 23, 1960

The chemical shift of the proton magnetic resonance in aqueous solutions of polystyrene sulfonic acid as a function of acid concentration has been measured. The magnitude of the slope of the straight line obtained in the customary plot of the chemical shift (in parts per million) vs. the stoichiometric mole fraction of acidic hydrogen is found to be 11.5 ± 0.3 . This result is interpreted as indicating that the acid is completely ionized.

I. Introduction

It is well known that the thermodynamic properties of linear polyelectrolytes, such as counterion activity²⁻⁷ and osmotic pressure,^{8,9} show values considerably smaller than those of the corresponding ideal solutions. This phenomenon has often been explained on the assumption that most or part of the counterions are associated in some manner with the polyion. In explaining other phenomena, such as conductivity,^{4b,8,10-12} trans-

ference numbers,^{13,14} electrophoresis,^{15,16} Donnan membrane equilibrium,¹⁷⁻¹⁹ potentiometric titration,²⁰ viscosity^{17,20,21} and light scattering,²²⁻²⁴ the idea of counterion binding also has been found useful. Unfortunately, the definition of the term ion binding (*e.g.*, association, fixation) is not

(1) (a) This research was supported jointly by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF49 (638)-694, and by the National Institutes of Health. (b) On leave from the Department of Applied Chemistry, Nagoya University, Nagoya, Japan.

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unique in practice. Ion binding sometimes refers to "true" association such as occurs in an undissociated simple acid or complex molecule (*i.e.*, a chemical bond exists) whereas the term also is used to describe ionic association due to electrostatic forces such as that of the ion pair²⁵ and that of the counterions trapped within the polyion domain.²⁶ Moreover, in addition to the promiscuous use of the term ion binding, some theories do not take ion association of any kind into account.²⁷ Therefore, it is of interest and importance to determine whether any form of ionic association takes place, on the one hand, and if it is found to occur, whether the binding is what we have referred to above as "true" association or one or more of the alternative descriptions of electrostatic interaction.

In order to investigate the nature of ion binding, one can make no use of the thermodynamic or ordinary electrochemical methods so far employed in this direction. These techniques cannot distinguish whether an observed abnormality of a thermodynamic property arises from "true" association or from electrostatic interaction. They may only measure an apparent degree of binding or association. On the other hand, the techniques of nuclear magnetic resonance and Raman spectroscopy which have been used to determine the ionization constants of simple strong acids such as sulfuric and nitric acids by Hood and his co-workers²⁸⁻³² and by Young³³ are suitable for this purpose since they measure the "true" ionization constant. The chemical shift of proton resonance absorption is related to variations of the electronic distributions in the bonds connected to the protons concerned. If the proton is not chemically bonded to its anion, no variation of the chemical shift will be observed. Hence, the effects of electrostatic ion binding in solutions of low concentrations do not manifest themselves in the nuclear resonance method.

In this paper, the "true" degree of ionization of polystyrene sulfonic acid is determined by means of the proton magnetic resonance technique. It is compared with the apparent degree of ionization determined by *pH* measurements.

The *pH* measurements of Mock and Marshall⁴ have shown that solutions of polystyrene sulfonic acid have very low degrees of ionization. They have found a degree of ionization of 0.38 which is independent of concentration. However, polystyrene sulfonic acid is a typical strong acid and it is therefore most unlikely that there are truly undissociated sulfonic acid groups in pure water solutions. The low apparent degree of ionization is therefore assumed to arise from the electrostatic

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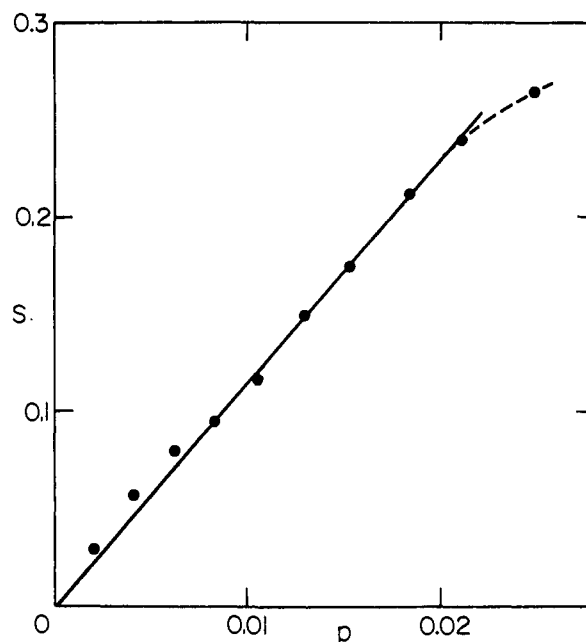


Fig. 1.—Chemical shifts of aqueous solutions of polystyrene sulfonic acid.

interaction between the hydrogen ions and the polyion. However, there has until now been no direct experimental evidence to support this view.

II. Experimental

(1) **Preparation of Sample Solutions.**—The polystyrene sulfonic acid was kindly provided in the form of the sodium salt by Drs. Mock and Vanderkooi of the Dow Chemical Company. The sodium salt was purified by repeated precipitation from aqueous solution by methyl alcohol and subsequent transformation to the acid form by means of an ion exchange resin, Amberlite IR-120. Ten samples, ranging in concentration from 0.0744 to 0.759 base moles of acid per 1000 grams of solution, were prepared under a nitrogen atmosphere since it was observed that oxygen dissolved or trapped in the samples necessitates a rather large magnetic susceptibility correction for the measured chemical shifts. According to Dr. Vanderkooi, the molecular weight of our sample is approximately one million.

(2) **The apparent degree of ionization** was determined by means of a Beckmann Model GS *pH* meter at room temperature. Since a precise measurement of the *pH* of polystyrene sulfonic acid solutions already has been carried out by Mock and Marshall,⁴ we measured the *pH* of only six aqueous solutions from 0.001 to 0.15 *N* and confirmed that the latter's results hold for our solutions too. Therefore, it is certain that the apparent degree of ionization of our samples is less than 0.5 over the experimental range. We may add that it is usually observed that the degree of ionization is almost independent of the degree of polymerization.

(3) **Proton Magnetic Resonance Measurements.**—The chemical shifts of 10 sample solutions were measured with a Varian Model 4300B spectrometer equipped with a super-stabilizer and operating at a frequency of 40 megacycles per second. The samples were spun in the inner cylinder of the standard two concentric cylindrical tube sample assembly obtained from the Wilmad Glass Co. of Landisville, New Jersey. The outer annulus contained pure benzene. The shifts of the solutions with respect to pure water then were obtained by comparison of the chemical shift between water and benzene.

The chemical shift *s* measured in parts per million is plotted against the stoichiometric mole fraction of acidic protons *p* as shown in Fig. 1. It is assumed in this work that the measured shift with respect to pure water satisfies the equation

$$s/p = \alpha s_{\text{H}_3\text{O}^+} + 1/3(1 - \alpha)s_{\text{HP}} \quad (1)$$

where $\delta_{\text{H}_3\text{O}^+}$ and δ_{HP} are the chemical shifts of the hydronium ion and pure polyacid, respectively, α is the "true" degree of ionization and p is defined by

$$p = 3x/(2 - x) \quad (2)$$

where x is the base mole fraction of acid. The basis for eq. 1 and the underlying assumptions of the method have been thoroughly discussed by Gutowsky and Saika³⁷ and elsewhere.²⁸⁻³²

The slope of the line drawn in Fig. 1 is 11.5 ± 0.3 . The volume magnetic susceptibilities of the samples were determined by means of a Gouy balance and it was found that the measured susceptibilities were rather small and have the effect of lowering the measured slope by not more than 5%. It is therefore observed that the slope lies in the range of limiting slopes found in aqueous solutions of simple acids (e.g., nitric, 11.8; hydrochloric, 11.4; perchloric, 9.2).²⁸

III. Discussion

From the fact that the slope of the line in Fig. 1 lies within the range of the limiting slopes of the simple acid solutions or alternatively, within the range of measured values of the chemical shift of the hydronium ion, it can be safely concluded that the "true" degree of ionization of polystyrene sulfonic acid in the present concentration range is practically unity. That is, since the measured slope agrees with those of simple acids in which α is assumed to be unity, we may expect that α is also equal to unity in the present case. Hence, the low apparent degree of ionization determined by $p\text{H}$ measurements is due to electrostatic interaction. If there were an appreciable amount of "truly" undissociated sulfonic acid groups, say that corresponding to the apparent degree of ionization, we should have obtained a much lower value for the slope, even though we might have found that the points formed a straight line in accord with the finding of Mock and Marshall.^{3,4}

It would be useful to have an estimate of the lower limit of the dissociation constant. This would require that measurements be made on rather viscous solutions of higher concentration and on a pure solid sample of polystyrene sulfonic acid. Unfortunately, however, it is not feasible to make accurate measurements of the chemical shifts of these samples with our present equipment.

This conclusion is supported by our knowledge of the difference in the conductimetric titration curves between polysulfonic^{34,35} and polycarboxylic acids.⁸ It is believed that the hydrogen counterions are bound closely to the acid groups in the polysulfonic acid solutions. If it is assumed that the bind-

ing is purely electrostatic in nature, the bound ions must be more or less mobile. If the bound hydrogen ions are replaced by alkali metal ions by titration of the acid with alkali hydroxide, the conductivity of the solution should decrease, since the mobility of the bound hydrogen is much larger than that of the bound alkali metal ions, even though both may be much lower than the mobilities of the free ions. This behavior is indeed found experimentally. On the other hand, the conductivity of polycarboxylic acids increases by titration with alkali hydroxide. This result is easily consistent with the idea that the hydrogen atoms of the carboxyl groups are "truly" associated (*i.e.*, covalently bound) since these groups should have no mobility while the alkali metal ions of the salt have a finite mobility.

In addition, judging from the result of the present work on hydrogen ion binding, it seems highly probable that the very low activity coefficients of alkali metal ions in polyacid salts^{2,5-7} are also simply due to the electrostatic interaction between the polyion and its counterions.

Finally, we must point out that our conclusion sheds no light on the question of the particular type of electrostatic binding involved. We cannot distinguish between ion pair formation or domain binding, for example. However, it must be asserted that the notion of site binding introduced by Harris and Rice²⁰ into polyelectrolyte theory need not be excluded by our conclusion, for although the sites in polystyrene sulfonic acid are not covalently bound, they may nevertheless involve specific ion pairing. Therefore, the use of the site binding concept in calculating the interaction free energy between a polyion and its counterions may be both useful and realistic, although there is some experimental evidence which suggests that the electrostatic binding takes the form of a "mobile layer" of counterions about the polyion.³⁶ We do know that "true" site binding exists in the case of some combinations of counterions and polyions such as the transition metal or alkaline earth ions with polycarboxylic acids.

It is hoped that the present work has made some progress in clarifying somewhat the character of ion binding of monovalent ions in polyelectrolytes.

Acknowledgments.—The authors wish to thank Drs. Mock and Vanderkooi for supplying samples, and Professor S. A. Rice for his support and encouragement. The generous support of the Air Research and Development Command of the United States Air Force, the U. S. Public Health Service and the National Science Foundation is also gratefully acknowledged.

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