Comparison of Electrical Transport Properties of Anionic Polyelectrolytes and Polysoaps[1]

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Two polysoap and three polyelectrolyte samples, prepared by the hydrolysis of copolymers of maleic anhydride with decyl vinyl ether and methyl vinyl ether, respectively, were compared by electrical transport studies at 0°. Conductometric titrations in aqueous saltless solutions gave the following results: (1) the equivalent conductance was smaller for the polysoap than for the polyelectrolyte samples and (2) while the equivalent conductance was independent of the degree of polymerization for the polyelectrolytes, it decreased with increasing degree of polymerization for the polysoaps. In 0.2 *N* LiBr solution, the polysoap conductance was again smaller than that of the polyelectrolytes. On the other hand, the electrophoretic mobility was identical for polysoaps and polyelectrolytes at each given LiBr concentration of the aqueous solvent medium and decreased as the LiBr normality increased from 0.04 to 0.8. The same invariance of the electrophoretic mobility to large changes in macroion configuration had previously been observed for cationic polyelectrolytes and polysoaps and thus appears to be a general phenomenon.

In a previous study[4] it was observed that the electrophoretic mobility of polyelectrolytes and polysoaps, derived from poly(4-vinylpyridine) by quaternization with alkyl bromides, was controlled only by the nature and the concentration of the simple electrolyte in the aqueous solvent medium. Specifically, the mobility was independent of the compactness of the polymer chain; *i.e.*, in any given electrolyte solution, polyelectrolytes and polysoaps whose intrinsic viscosities differed by more than an order of magnitude did not differ in their electrophoretic mobilities. These findings suggested similar experiments with other polyelectrolyte–polysoap systems in order to explore the generality of the observed phenomenon. The copolymers of vinyl alkyl ethers and maleic anhydride appeared especially promising for this purpose. The hydrolyzed polyacids act as typical polyelectrolytes when the alkyl group of the vinyl ether is short[5,6] and as typical polysoaps when the alkyl group is long.[7] Furthermore, the polyacids are alternating 1–1 copolymers. Thus their structure is known, and the backbones to which the fixed electrolyte groups are attached have the required identity for polyelectrolyte and polysoap.

Since very little is known concerning electrical transport properties of polysoaps, it was decided to supplement the electrophoresis with exploratory electrical-conductance studies. Hydrolyzed copolymers of maleic anhydride with vinyl methyl ether and with vinyl decyl ether were used as our polyelectrolyte and polysoap, respectively.

Experimental Section

Materials. Three 1–1 copolymers of vinyl methyl ether and maleic anhydride (VME–MA, our samples G119, G139, and G169) were obtained from General Aniline and Film Corp. Each of the three compounds was purified several times by precipitation from dilute dimethylformamide solution into an excess of ethyl ether at room temperature. The products were dried *in vacuo*, first at room temperature, then at 100° for 24 hr, and were finally stored in a dry atmosphere. The absence of residual monomer and other low molecular weight material was verified by dialysis of small samples in an aqueous environment using Visking cellophane membranes. According to the supplier, the ranges of specific viscosities of 1% solutions in 2-butanone at 25° were 0.1–0.5, 1.0–1.4, and 2.6–3.5 for the low (G119), medium (G139), and high (G169) molecular weight samples, respectively. Since for our purposes we only needed to know that the molecular weights differed fairly widely, no attempt to measure the molecular weights of these samples was made.

One of the copolymers of vinyl decyl ether and maleic anhydride (VDE–MA, our sample S616) was prepared by refluxing in benzene under nitrogen an equimolar 7.5% mixture of the monomers with 0.1% azobisisobutyronitrile. After 4 hr of refluxing, the reaction

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mixture was poured into five volumes of petroleum ether (bp 40–60°); the precipitated copolymer was dissolved in a minimum amount of tetrahydrofuran and was reprecipitated into pentane. After several reprecipitations, the product was dried *in vacuo* using the same procedure as for the VME–MA copolymers.

A higher molecular weight VDE–MA copolymer (our sample S703) was prepared by refluxing an equimolar 20% mixture of the monomers in benzene with 0.05% azobisisobutyronitrile at 63° for 5 hr. By a method similar to that used for the VME–MA copolymers, it was verified that copolymers S616 and S703 contained no remaining low molecular weight substances.

The weight-average degrees of polymerization, P_w, of VDE–MA copolymers S616 and S703 were determined from their intrinsic viscosity values in tetrahydrofuran at 30° by using the relation of Ito, *et al.*[7,8] These values were as follows: for VDE–MA S616, $[\eta] = 0.493$ dl/g and $P_w = 340$; for VDE–MA S703, $[\eta] = 3.30$ dl/g and $P_w = 9200$.

The VME–MA copolymers were hydrolyzed by heating their aqueous solutions at 80° for 2 hr followed by tumbling at room temperature for 24 hr. The dissolution of the VDE–MA copolymers in water, which proceeded with difficulty at room temperature, was accelerated by heating for 12 hr at 80°. Even then, clear fluid solutions were obtained only for sample S616, while sample S703 formed jellies at its low natural pH and could be brought to complete solution only by raising the pH above 7.

The intrinsic viscosity values of the hydrolyzed copolymers in 0.2 *N* LiBr, brought to pH 7.5 with LiOH, were 1.38 dl/g for VME–MA G119 and 0.042 and 0.20 dl/g for VDE–MA copolymers S616 and S703, respectively. The small intrinsic viscosities of the latter two compounds are typical of polysoaps in aqueous solutions and indicate that the macromolecules reach high degrees of compactness by intramolecular micellization.[9,10] In contrast, the much higher intrinsic viscosity of the vinyl methyl ether copolymer G119 is typical of ordinary polyelectrolytes.

Methods of Measurements. Electrical conductances were determined at 0° with a Shedlovsky-type bridge.[11,12] Resistance values were measured at 4 kcps with an accuracy of about 0.01%. Polarization errors were found to be negligible. All solutions were prepared with conductivity water obtained by passing distilled water through a mixed-bed ion-exchange resin. The specific conductivity of the water was 0.6×10^{-6} mho/cm.

Electrophoretic mobilities were determined at 0° in a Perkin-Elmer Model 38 Tiselius apparatus by the method previously described.[4] Cell currents ranged from 7 to 20 mA from the most dilute (0.04 N) to the most concentrated (0.8 *N*) LiBr solution. Average values of the mobilities of the ascending and descending boundaries are used. Generally, the ascending boundary moved 5% faster than the descending boundary; however, in the 0.04 *N* LiBr solutions, the differences in the velocities of the two boundaries were of the order of 10%.

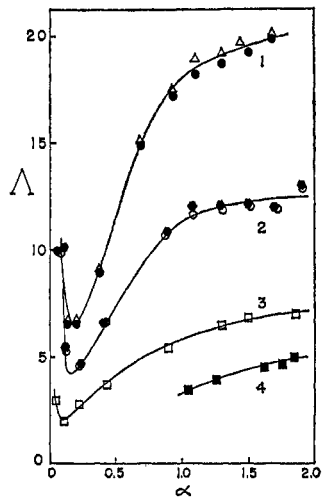

Figure 1. Equivalent conductance in the absence of a simple electrolyte: curve 1, VME–MA neutralized with KOH; ●, G119; △, G139; curve 2, VME–MA neutralized with LiOH; ○, G119; ●, G139; curve 3, VDE–MA neutralized with LiOH; □, S616; curve 4, VDE–MA neutralized with LiOH; ■, S703.

Results and Discussion

Conductometric Titration in Absence of Simple Electrolyte. The effect of added base on the conductivity of aqueous salt-free 0.02 *N* polyacid solutions is shown in Figure 1. The abscissa represents the degree of neutralization, α, defined by the equation

$$\alpha = [(\mathrm{MOH}) + (\mathrm{H}^+) - (\mathrm{OH}^-)]/C_p \qquad (1)$$

where (MOH), (H^+), and (OH^-) are the concentrations of added base, hydrogen ion, and hydroxide ion, respectively, expressed in equivalents per liter, and C_p is the concentration of the polyacid expressed in monomoles per liter. (One monomole contains one maleic acid and one alkyl vinyl ether residue.) The hydrogen and hydroxyl ion concentration terms, which make significant contributions only at low and high pH, were calculated from the pH, the assumption being made that the activity coefficients were unity. With this definition $\alpha = 2$ at complete neutralization of the dibasic acid units. The ordinate represents the equivalent conductance, Λ, defined by the relation

(8) We have neglected a possible small error resulting from the fact that this relation was established for copolymers of maleic anhydride and vinyl dodecyl ether (instead of vinyl decyl ether).

(9) U. P. Strauss and E. G. Jackson, *J. Polym. Sci.*, **6**, 649 (1951).

(10) U. P. Strauss, N. L. Gershfeld, and E. H. Crook, *J. Phys. Chem.*, **60**, 577 (1956).

(11) T. Shedlovsky, *J. Amer. Chem. Soc.*, **52**, 1793 (1930).

(12) D. Edelson and R. M. Fuoss, *J. Chem. Educ.*, **27**, 610 (1950).

$$\Lambda = 1000\kappa_{sp}/2C_p \quad (2)$$

where κ_{sp} is the specific conductance due to the polyelectrolyte, *i.e.*, the difference between the specific conductance values of the solution and of the solvent. The data obtained by neutralizing the VME–MA copolymers G119 and G139 with KOH are given by curve 1; those obtained by neutralizing the same samples with LiOH are given by curve 2. The curves resemble those obtained with other weakly acidic polyelectrolytes, such as poly(acrylic acid) and poly(methacrylic acid),[13,14] and their prominent features, such as the minimum at low α and the plateau at high α, have been discussed previously.[13,14] The observed independence of chain length is also characteristic of polyelectrolytes.[13,15]

Relevant molecular parameters derived from these conductance data are given in Table I. In the absence of a rigorous theory, we have followed the usual procedure of considering part of the counterions bound to and traveling with the macroion and the remainder of the counterions completely free, *i.e.*

Table I: Conductometric Titration Results in the Absence of Simple Salt

α	i(G139)[a]	$10^4 u_p$(G139),[a] cm² V⁻¹ sec⁻¹	Λ(S616)/Λ(G139)	Λ(S703)/Λ(G139)
0.2	0.086[b]	2.3[b]	0.553	...
0.4	0.14	2.5	0.570	...
0.6	0.19	2.5	0.543	...
0.8	0.24	2.5	0.515	...
1.0	0.30	2.1	0.520	...
1.2	0.34	1.7	0.525	0.319
1.4	0.36	1.4	0.550	0.348
1.6	0.37	1.4	0.565	0.372
1.8	0.40	1.2	0.575	0.400

[a] Calculated by means of eq 3 and 4 (see text). [b] See ref 18.

$$\Lambda = i(\mathfrak{F}u_p + \lambda_M) \quad (3)$$

where i is the fraction of ionized carboxylate groups, $\mathfrak{F}$ is the faraday, u_p is the mobility of the polyion, and λ_M is the equivalent conductance of the counterion. In addition we have used the relation

$$i = \frac{\Lambda_{KP} - \Lambda_{LiP}}{\lambda_K - \lambda_{Li}} \quad (4)$$

where Λ_{KP} and Λ_{LiP} refer to the equivalent conductances of the VME–MA polyacids partially neutralized with KOH and LiOH, respectively, to the same value of α. Relation 4 has been derived from eq 3 with the assumption that in the absence of simple electrolyte i and u_p are independent of the alkali metal ion and depend only upon α and C_p, an assumption which is supported by the findings that such a behavior is indeed followed by poly(acrylic acid) and poly(methacrylic acid).[16] For λ_K and λ_{Li} we used the values at infinite dilution, 40.7 and 19.4, respectively.[17,18] The parameters i and u_p for VME–MA polyacid G139, which are given in the second and third columns of Table I as functions of α follow the same trends as observed for other polyacids.[14,19] The polymer charge fraction, i, increases rapidly at first and then more slowly, as with increasing neutralization an increasing number of counterions is attracted to the macroion. The decrease in the mobility, u_p, with increasing charge has been attributed to an increase in the friction coefficient caused by an extension of the molecular dimensions.[14,16] However, an increase in binding of alkali metal ions may also bring abont this result.

Turning our attention now to the polysoaps, the effect on Λ of neutralizing the VDE–MA copolymers S616 and S703 with LiOH is shown by curves 3 and 4, respectively, of Figure 1. The behavior differs from that of the VME–MA polyelectrolytes in two aspects. First, the equivalent conductance of the polysoaps is smaller than that of the polyelectrolytes; second, whereas for typical polyelectrolytes the conductance is independent of chain length, for the polysoaps there appears to be an inverse dependence between the equivalent conductance and the degree of polymerization. The ratios of the equivalent conductance values of the polysoaps S616 and S703 to that of polyelectrolyte G139 are given in columns 4 and 5 of Table I. We note that these ratios show only small variations with changing α. We note further that since the friction coefficients must be smaller for the compact polysoap molecules than for the extended polyelectrolytes, the lower conductance of the polysoaps indicates a higher effective degree of counterion association. We shall discuss these effects further below.

Conductance and Electrophoresis in the Presence of Simple Electrolyte. The equivalent conductance of polyelectrolytes G119, G139, and G169 and polysoap S616 in 0.2 *N* LiBr solution is given as a function of the polymer concentration in Figure 2. Most of the

(13) W. Kern, *Z. Physik. Chem.* (Leipzig), **A181**, 249 (1938).

(14) J. R. Huizenga, P. F. Grieger, and F. T. Wall, *J. Amer. Chem. Soc.*, **72**, 2636 (1950).

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(16) H. Eisenberg, *J. Polym. Sci.*, **30**, 47 (1958).

(17) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press Inc., New York, N. Y., 1955, p 454.

(18) At low pH the hydrogen ion makes a significant contribution to the equivalent conductance, and eq 3 must be modified to $\Lambda = i(\mathfrak{F}u_p + \lambda_M) + i_H(\lambda_H - \lambda_M)$, where $i_H = (H^+)/2C_p$ represents the contribution of the hydrogen ion to i. The left-hand side of eq 4 becomes $i - i_H$ under these circumstances. The magnitude of this contribution can be seen from the fact that without the modification the calculated values of i and u_p at $\alpha = 0.2$ would be 0.080 and 4.2, instead of the correct values given in Table I. The effect of the modification is very slight at $\alpha = 0.4$ and is completely negligible at higher values of α.

(19) F. T. Wall and R. H. Doremus, *J. Amer. Chem. Soc.*, **76**, 1557 (1964).

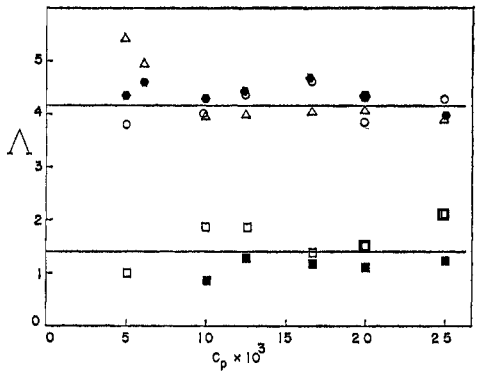

Figure 2. Equivalent conductance in 0.2 N LiBr at pH 7.0: ○, VME-MA G119; ●, VME-MA G139; △, VME-MA G169; □ ■, VDE-MA S616 (two independent dilution runs).

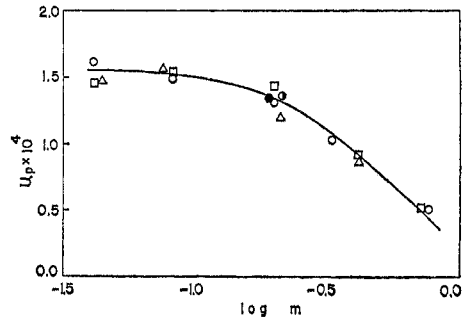

Figure 3. Electrophoretic mobility as a function of LiBr concentration, m, at pH 8.8 (unless otherwise indicated): ○, VME-MA G119; ●, VME-MA G139; □, VDE-MA S616; △, VDE-MA S703; ◑, VDE-MA S703 at pH 7.0.

results were obtained at pH 7.0 where α in this solvent is 1.5 for the polyelectrolyte and 1.2 for the polysoap. However, changes in pH up to 9 had no significant effect on Λ. For both the polyelectrolyte and the polysoap, the equivalent conductance shows no trend with varying polymer concentration, similar to previous findings with polyphosphates.[20] Neither is the influence of molecular weight noticeable for the three polyelectrolytes; however, as was the case in the absence of salt, Λ is significantly smaller for the polysoap than for the polyelectrolytes. (Unfortunately, the supply of polysoap S703 was not sufficient to permit the completion of these measurements and thus the effect of molecular weight on polysoap conductance in 0.2 N LiBr could not be determined.)

The results of the electrophoretic mobility determinations for polyelectrolytes G119 and G139 and for polysoaps S616 and S703 are presented in Figure 3 where the mobility u_p is given as a function of the LiBr concentration. Normally, the data were obtained with $C_p = 0.01$ and at pH 8.8. However, the effect of varying these parameters was also investigated. It is seen that in each given environment the electrophoretic mobility is identical for the extended polyelectrolyte and the compact polysoap molecules. The mobility is also independent of the concentration and the molecular weight of the polyelectrolytes and polysoaps and of the pH over the measured range from pH 7 to 8.8. (Some of the data were omitted from Figure 3 in order to avoid clutter.) In this range the mobility appears to be controlled only by the lithium bromide concentration. Thus we observe here the same type of behavior as has previously been found for the cationic polyelectrolytes and polysoaps derived from poly(4-vinylpyridine).[4]

The invariance of the electrophoretic mobility with macroion configuration thus appears to be a general phenomenon. Apparently, if a contraction of the molecular dimensions causes a decrease in the friction coefficient, such a decrease is compensated by a decrease in the effective electrical charge. It has been shown theoretically that the electrophoretic mobility for microscopic particles depends upon the charge density of their surface and on their ionic atmosphere. The theoretical results are usually represented by an equation of the type

$$u = \frac{\epsilon\zeta}{C\eta} \tag{5}$$

where ϵ and η are the dielectric constant and viscosity of the medium, respectively; C is a parameter ranging from 4π to 6π; and ζ, "zeta potential," is the potential at the surface of shear between the particle and medium.[21-23] It is well-known that, if microscopic particles of various sizes and shapes are coated with a protein, they assume the electrophoretic mobility of the protein.[24,25]

These considerations suggest that the compact polysoap molecules may be viewed as impermeable particles whose electrolytic behavior is determined by their surface. This surface contains the same hydrophilic groups as the chemically related polyelectrolyte; *i.e.*, the polysoap molecules behave as if they were electroneutral particles covered with polyelectrolyte. This hypothesis would account for the fact that the polysoap and the polyelectrolyte have the same mobility and that the polysoap mobility is independent of molecular weight. The observation that the polysoap conductance is smaller than that of the polyelectrolyte would be attributable to the fact that the ionic groups which are buried in the micellar interior would not contribute to the conductance while the ionic groups in the surface contribute the same amount as if they were part of the polyelectrolyte.

(20) U. P. Strauss and S. Bluestone, *J. Amer. Chem. Soc.*, **81**, 5292 (1959).
(21) M. Smoluchowski, *Krak. Anz.*, 182 (1903).
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Table II: Molecular Dimensions and Surface Areas of Polysoap Molecules

Sample	DP	$[\eta]$, dl g^{-1}	ν	J	$\mathring{a}$	$\mathring{b}$	$10^{-3}S$, Å^2	S/DP, Å^2	$(S/DP)_{S616}/(S/DP)_{S703}$
				Case 1: v_{sp} = 1.00 cm^3 g^{-1}					
S616	340	0.042	4.2	3.53	80.0	22.7	18.5	54.5	1.99
S703	9200	0.20	20	12.94	572	44.3	251	27.3	
				Case 2: v_{sp} = 1.68 cm^3 g^{-1}					
S616	340	0.042	2.5	1.00	41.3	41.3	21.4	63.0	1.84
S703	9200	0.20	11.9	8.87	533	60.0	317	34.4	

Thus the equivalent conductance ratios of polysoap to polyelectrolyte in Table I may be interpreted as the fraction of ionic groups in the surface of the polysoap molecules. Finally, the difference in equivalent conductance found for polysoaps S616 and S703 may then be due to a difference in exposed surface areas. To test this hypothesis, let us estimate the ratio of these surface areas from the available viscosity data.

The intrinsic viscosity may be related to the molecular dimensions by the Simha equation[26]

$$[\eta] = 0.01\nu v_{sp} \tag{6}$$

where v_{sp} is the effective specific volume and ν is a shape factor, which for spheres equals 2.5 and which for prolate and oblate ellipsoids has been tabluated[27] as a function of the axial ratio J. It is clear that ν and v_{sp} cannot be uniquely obtained from eq 6. However, if we assume that the molecules of the two polysoaps are prolate ellipsoids with a common value of v_{sp} chosen arbitrarily, but realistically, to account for possible extents of solvent swelling, we find that the desired ratio of specific surface areas is affected only little by the choice of v_{sp}. As examples, the results of the calculations for two values of v_{sp} are given in Table II. Case 1 represents v_{sp} = 1 while case 2 represents v_{sp} = 1.68, the highest possible value consistent with $\nu \geq 2.5$. While the values of the major and minor semiaxes, $\mathring{a}$ and $\mathring{b}$ (expressed in ångström units), respectively, are seen to be quite sensitive to the chosen value of v_{sp}, the surface area, S, of the polysoap molecules is much less sensitive, and the figures in the last column which give the ratio of the specific molecular surface areas of both polysoap samples lie within 8% of one another. These figures represent the predicted value of the equivalent conductance ratio, $\Lambda(S616)/\Lambda(S703)$. The experimental value of this ratio obtained from the data in Figure 1 is 1.6 in the appropriate range of α ($\alpha \sim 1.4$).[28] The rather good agreement lends support to our hypothesis concerning the electrolytic behavior of polysoaps.

Acknowledgment. We wish to thank Mr. Andrew Schultz of this laboratory for his help in the synthesis of the polysoaps used in this work.

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(27) J. W. Mehl, J. L. Oncley, and R. Simha, *Science*, **92**, 132 (1940).

(28) It should be noted that the molecular dimensions were obtained in 0.2 N LiBr, while the conductances were measured in the absence of simple electrolyte. Our procedure thus involves the not unreasonable assumption that the specific surface ratio of the two polysoap samples is insensitive to changes in the salt concentration of the solvent.