plots indicates that the assumption of two different types of exchanging cations is a better one than that involving one type. Values of p'/p'', the ratio of fast to slow exchanging cations, are also shown in Table V. These values were calculated from the equation[3]

$$p'/p'' = \alpha/\alpha' - 1/(1 - \alpha) \qquad (4)$$

Just as for X, the values of p'/p'' are highly dependent upon α, especially when α is close to unity. The correlation between p'/p'' and X is not especially good; that is, a solution with a high exchange rate does not necessarily have a high fast-to-slow cation ratio.

TABLE V

COMPARISON OF α' VALUES AND FAST-TO-SLOW EXCHANGING CATION RATIOS

Series	α' From q_A	From q_B	p'/p''
1	0.78	0.78	2.7
2	.69	.74	6.4
3	.48	.49	5.5
7	.14	.14	10.7
8	.09	.12	10.5
9	1.19	1.19	2.8
11	0.89	0.87	2.5
12	0.25	0.20	4.3

One solution investigated, series 5, was found to have a cation exchange rate that was constant with electrolysis time, and in this case the assumption of one type of exchanging cation appears to be a good one. The half-time of exchange was found to be 1.8 minutes for this solution.

From the results available no definite conclusions can be drawn as to the effect of concentration or percentage neutralization upon the exchange rates; apparently these variables do not seem to be of major importance in affecting the exchange rates over the range investigated.

The X values found for the polyacrylic acid–potassium hydroxide and copolymer–sodium hydroxide solutions are similar to those found for polyacrylic acid–sodium hydroxide. The fact that the X values for series 11 are high may be due to a slight inaccuracy in α, since α is quite close to unity for this solution.

Changing the temperature over the range 0 to 42° does not seem to produce a systematic effect upon the cation exchange rate. Taking into account the experimental errors, it appears that the energy of activation for exchange is low. For low times of electrolysis, the X values are less at 25° than at either 0° or 42°, an unexpected behavior for which no reasonable explanation is readily forthcoming. With increasing temperature, the X values tend to become less dependent on time of electrolysis. These appear to be the only generalizations that can be drawn from the data of Table III.

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[CONTRIBUTION FROM THE RESEARCH DIVISION, ARMOUR AND COMPANY]

Light Scattering in Solutions of a Linear Polyelectrolyte

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Solutions of arabic acid have been investigated by the light scattering technique. The molecular weight for a standard preparation was found to be $1.00 \pm 0.05 \times 10^6$ in contrast to the 300,000 value determined by earlier osmotic pressure measurements. The molecule appears to be a stiff coil due to side branching, varying in extension from 1050 Å. at zero charge to 2400 Å. at maximum charge. Viscosity measurements are in essential agreement with the scattering data. The scattering function, Kc/R_{90}, increases with increasing polyion charge at a given value of the concentration, c. It decreases with increasing ionic strength to a limiting value of that in un-ionized systems. The scattering function is third order at high values of the charge. The dissymmetry, z, exhibits a distinct minimum at $c = 0.75 \times 10^{-3}$ g./cc. for all values of μ for the ionized acid and rises at higher c to a maximum value. The maximum is lower as μ increases and occurs at lower values of c. Some models are described which may explain the free energy relationships giving rise to the above-mentioned Kc/R_{90} *vs.* c and z *vs.* c data.

The behavior of random-coil type, high molecular weight polyelectrolytes in solution has been discussed frequently. In spite of gratifying agreement on some points, several discrepancies still exist between the theoretical behavior of model systems and the observed experimental facts. Investigations of such systems[1-3] by light scattering techniques have yielded much interesting information. The work reported here extends this type of information to a higher molecular weight system. Several details of the behavior of these systems have not been observed in lower weight systems; other details are more pronounced and more accurately measured.

The polyelectrolyte investigated was arabic acid, the acidic carbohydrate structure of gum arabic. It has been studied extensively in several ways: osmotic pressure[4-6]; dissociation constants[6-9,12,13]; conductance[7,9,10,14]; and viscosity.[11,15-17,18] Its

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well known behavior thus lends itself to correlation with the light-scattering data.

Experimental

Arabic acid was prepared in the usual manner[6,9] by repeated precipitation with alcohol from an acidified gum arabic solution. The final precipitate was air-dried to remove the alcohol, dissolved in distilled water and electrodialyzed. The electrodialyzed solution was freeze-dried to yield a white, crystalline arabic acid. Arabic acid prepared in this manner does not vary in properties from sample to sample to any great extent.[7,17] The acid is readily soluble in water at any *p*H at room temperature.

The instrument used for measuring scattered light was similar to that of Hadow, Sheffer and Hyde[19] in circuitry. The entire unit except the light source and galvanometer was built into a standard 9 × 11 × 12″ metal cabinet and has a sensitivity better than 1×10^{-5} cm.$^{-1}$ (turbidity)/mm. (galvanometer deflection). Octagonal cells were used for measurements at 45°, 90° and 135°. The detector slit covered a range of 3° from the scattering center.

Benzene was used as a scattering standard. The values $R_{90,4360} = 48.5 \times 10^{-6}$ [20] and $R_{90,5460} = 16.4 \times 10^{-6}$ [21] were used for the two wave lengths.

The refractive index increments of arabic acid in water and in hydrochloric acid solution were determined by direct measurements with a Rayleigh interferometer calibrated at the wave lengths used in the light-scattering measurements.

The solutions were filtered through fine sintered-glass filters directly into the scattering cell. After preliminary trials, it was found that satisfactory reproducibility was obtained if dilutions were made directly in the scattering cells when clean pipets and pre-filtered water or salt solutions were used. Net scattering readings were obtained bv subtracting the blank solvent scattering from the arabic acid solution readings.

Results

I. Undissociated Arabic Acid Systems.—Osmotic pressure data[5] indicated that ionization of the acid was effectively suppressed in 0.02 *N* hydrochloric acid. The measurements made to determine the size and weight of arabic acid in the absence of any electrical effects were made in hydrochloric acid solutions of this normality. The data, shown in Table I, have been computed in terms suitable for comparison with Zimm's[22] basic scattering equation

$$\frac{Kc}{R_\theta}\,[P(\theta)] = \frac{1}{M} + 2BP(\theta)c \qquad (1)$$

where

c = grams polyelectrolyte/cc. of solution

R_θ = reduced intensity of the scattered light at scattering angle θ

B = interaction constant

M = molecular weight

$P(\theta)$ is the correction factor for internal interference, which for random coils is[23]

$$P(\theta) = \frac{2}{u^2}\,[e^{-u} - (1 - u)] \qquad (2)$$

where

$$u = 2\left(2 \sin \frac{\theta}{2}\right)^2 L^2/6\lambda$$

L = root-mean-square of the distance between ends of the random coil

λ = wave length of the incident light

TABLE I

SCATTERING DATA ON ARABIC ACID IN 0.02 *N* HCl

$(dn/dc)_{25°, 4356} = 0.152$; $(dn/dc)_{25°, 5460} = 0.150$; HCl = 0.01992 *N*; $K_{4356} = 3.77 \times 10^{-7}$; $K_{5460} = 1.47 \times 10^{-7}$. From plot of Kc/R_{90} *vs.* c, one finds $M = (1.00 \pm 0.05) \times 10^6$, assuming rod, monodisperse coil or polydisperse coil; $B = 4.24 \times 10^{-5}$ cc. mole/g.^{2}; D', the equivalent diameter of a hard sphere, calculated from B, is 323 Å. so that $L_{\text{H.S.}}$ = 307 Å.

	λ = 4360 Å.				λ = 5460 Å.		
$c \times 10^3$, g./cc.	$Kc/R_{90} \times 10^6$	Z	L/λ', Å.	L, Å.	$Kc/R_{90} \times 10^6$	Z	L/λ', Å.
5.94	1.96	1.65	0.32	1049	1.95	1.79	0.35
4.44	1.79	1.67	.32	1049	1.99	2.00	.39
2.89	1.70	1.66	.32	1049	1.71	1.70	.33
1.65	1.56	1.63	.32	1049	1.59	1.86	.38
0.743	1.53	1.66	.32	1049	1.60	2.2	.44
.283	1.41	1.77	.34	1113	1.34	2.6	.51
.087	1.20	2.6	.51	1670	1.10	4.5	1.0

The dissymmetry, z, was determined from the ratio R_{45}/R_{135}. Since z is equivalent to $P(45)/P(135)$, L/λ' was readily evaluated with the use of equation 2. The dissymmetry at $c = 0$ was found upon extrapolation to be 1.65 for λ = 4356, neglecting the abrupt rise in z at extreme dilution. This rise may have been due to dust, or some ionization at extreme dilution. The extrapolated value of z was used to correct the extrapolated value of Kc/R_{90} for internal scattering.

The weight average value of M obtained here is much higher than the 300,000 number average value determined from Oakley's osmotic pressure measurements.[5] Absorption and fluorescence effects, checked by the method of Brice, Nutting and Halwer[24] were absent in this system at both wave lengths and could not account for this discrepancy. The molecular weight data may be accounted for in two ways. First, there must be considerable polydispersity in the system with a relatively large number of very large (osmotically inactive) molecules. Secondly, one must take into account the hydrolysis of arabic acid in acid solutions. Subsequent to his determination of M_n, Oakley[25] showed that hydrolysis of the gum did occur in acid to yield small diffusible ($M < 10{,}000$) molecules. The solutions for scattering measurement were made up just prior to examination, whereas the osmotic pressure measurements required at least an overnight period of standing. Therefore one should not be too surprised at finding a very much higher weight-average molecular weight for the acid gum.

The viscosity data of Basu, Dasgupta and Sircar[18] and of Schleif, Higuchi and Busse[17] yield an intrinsic viscosity, $[\eta]$, of 0.329 for the uncharged acid. The Flory–Fox equation[26]

$$(\overline{L^2})^{3/2} = M[\eta]/\Phi \qquad (3)$$

relating the extension of a coil to its molecular weight and intrinsic viscosity, predicts $(\overline{L^2})^{1/2}$ to be 548 Å. as compared with the 1049 Å. estimated from the dissymmetry data. In equation 3 Φ is a universal constant of value 2.0 to 2.5 × 10^{21}

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for coils whose extension ratio $(\overline{L^2}/\overline{L^2}_{\max})^{1/2}$ is less than 0.25. The value of this parameter falls as $(\overline{L^2}/\overline{L^2}_{\max})^{1/2}$ becomes larger.[27] Φ can become as small as 0.5×10^{21} when the extension ratio is near 0.5. The arabic acid chain is irregular due to side branching and is probably somewhat stiffer than most other polyelectrolytes discussed elsewhere.[18] For example, $[\eta]_{0\,\text{charge}}$ and $[\eta]_{\text{max. charge}}$ are 0.33 and 2.2, respectively, for arabic acid while these quantities are 0.1 and 55.0 for a polymethacrylic acid fraction of molecular weight 90,000.[1,18] Thus, the contraction of arabic acid in the uncharged form cannot be too great and the extension ratio must be high. The root-mean-square extension between chain ends computed from equation 3 with $\Phi = 2 \times 10^{21}$ will, therefore, be low. In the light of the above considerations, the dissymmetry and viscosity data are not in serious disagreement.

II. Ionized Arabic Acid.—Viscometric studies[22] of ionized arabic acid indicate typical, though limited, polyelectrolyte behavior in spite of the relative stiffness of the uncharged acid. The light scattering data also reflect this behavior.

The data were compiled for two cases. In the first instance the acid was neutralized with an exactly equivalent amount of sodium hydroxide (equivalent weight = 1200). No salts were added so that the ionic strength, μ, in excess of the polyion contribution was zero. For the other measurements the acid was allowed to assume its equilibrium charge (α, degree of ionization = 0.25). The effect of changes in μ was investigated.

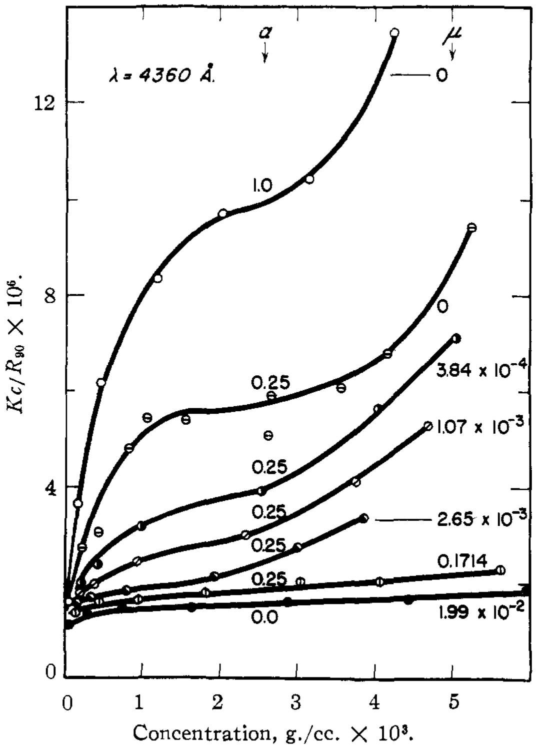

Fig. 1.—Reduced intensity of scattered light from arabic acid as a function of degree of ionization, α, and ionic strength, μ; $dn/dc = 0.152$, $K = 3.77 \times 10^{-7}$. The ionic strength was adjusted with NaCl in each case except the last, which was the run in HCl.

The Kc/R_{90} data are plotted in Fig. 1. As in other polyion systems, the function Kc/R_{90} increases markedly with c, then begins to level off with nearly the same slope as found when the polymer is uncharged. As c is increased further R_{90} falls rapidly and Kc/R_{90} shows a sharp inflection upward. Virial coefficients beyond the usual second one cannot be neglected in this case as the equation for Kc/R_{90} as a function of c is obviously of the third degree. This behavior, not so noticeable for other polyelectrolytes reported in the literature, is perhaps emphasized by any or all of the following special features of the arabic acid structure: (1) the highly polar nature of the carbohydrate main chain, (2) the large extension and stiffness of the chain, and (3) the presence of many bulky polar side chains.

As expected, R_{90} increases as α decreases at constant c; compare the upper two curves of Fig. 1. Along any given curve the degree of ionization does not change appreciably in the small concentration range in question.[7] The lower curves of Fig. 1 reflect changes in R_{90} with varying ionic strength. Increasing μ has the same effect on Kc/R_{90} as decreasing the charge.

The dissymmetry behavior, Fig. 2, is unique. After the expected minimum in z is observed as c is increased from zero a maximum is also evident. The dissymmetries taken at λ = 5460 Å. were similar but all values of z were higher at $C > 1 \times 10^{-3}$, an evidence of external interference.

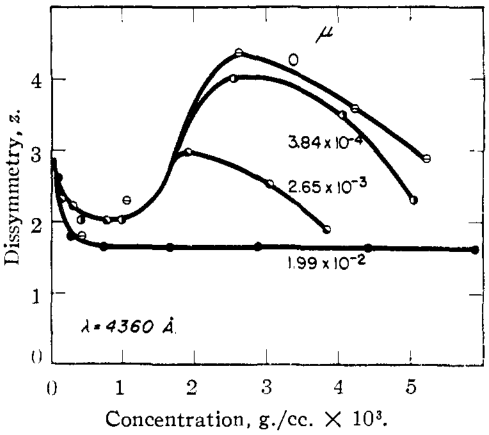

Fig. 2.—Dissymmetry of scattered light from arabic acid as a function of μ and polyion concentration at 25% ionization. The lower curve is the dissymmetry in HCl.

There were no significant differences in the values of z for the completely ionized acid and the 25% ionized acid. Viscosity measurements[18] show that for arabic acid there is a maximum in the function η_{sp}/c as α is increased at constant polyion concentration and that these maxima occur prior to 100% ionization. The intrinsic dissymmetry obtained by extrapolation to infinite dilution, interpreted in terms of polydisperse random coils, gives $(\overline{L^2})^{1/2}$ = 2400 Å. or about twice the average extension calculated for the un-ionized molecule. The dissymmetry data are not sensitive enough in

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the low concentration range to enable one to differentiate between solutions of varying ionic strength. However, it is apparent from a plot of the limiting interaction constant, B, Fig. 3, *vs.* $\mu^{1/2}$ that the effective volume of the polyion increases as the ionic strength is decreased.

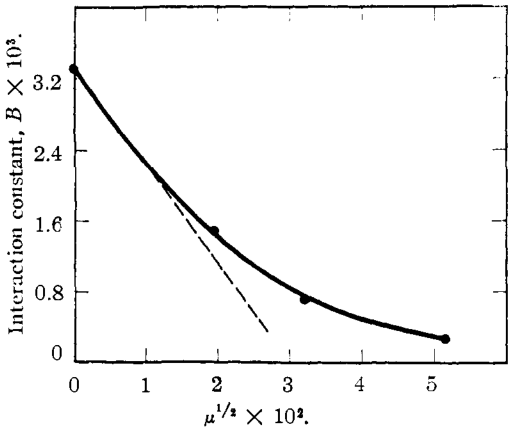

Fig. 3.—Limiting interaction constants for arabic acid as a function of the ionic strength.

Discussion

A rough calculation, utilizing the Debye relationship between the equivalent hydrodynamic radius and the root-mean-square end-to-end extension of a random coil, is sufficient to point out the important effect of excluded volume in these systems. Uncharged arabic acid, L = 1050 Å., has an equivalent radius of 555 Å. or an effective volume of 7.2×10^{-16} cc./molecule. One may estimate that a solution of independent, non-overlapping, minimally extended arabic acid molecules could exist only at concentrations of about 2×10^{-3} g./cc. and lower. Thus, all of the solutions examined must be considered "concentrated" in the range where the minimum in z is observed and intermolecular interactions cannot be disregarded. The dissymmetry curves for the ionized acid at different charges and ionic strengths in the very low concentration range are nearly superimposable rather than clearly separated as in polymethacrylic acid dissymmetry measurements[1] because of the restricted contraction of the stiff, branched molecule.

Randomly-coiled polyelectrolytes are notable for the ease with which they seek to attain configurations of minimum free energy consistent with their environment. One is tempted to speculate on the nature of such changes in the restricted system under discussion. In the most dilute range one assumes as usual that the extended molecule contracts as the concentration increases as long as there is empty solvent space between molecules. As this space is filled, the repulsion between individual polyions is increased. However, contraction into smaller individual units is limited by the bulkiness of the molecule, but this contraction would have led anyway to higher individual coil free energies, neglecting the effect of counterions. With contraction limited, the only other alternative path to minimum free energy is through expansion of each polyion to a rod-like structure of lower individual free energy and probably lower mutual interaction energy[28] as well as a smaller effective volume.

Further increase in polyion concentration would lead to a situation in which no free solvent volume existed. Intermolecular electrostatic repulsive forces would then be shorter range, localized forces of the same nature and quantitative value as the intramolecular repulsions. Segments of different molecules could overlap into the same "effective" volume while the actual polyion extension was little changed. These energy configuration considerations seem to be in general accord with the scattering data and in particular explain the plateau region in the Kc/R_{90} *vs.* c plots for the ionized acid at zero added ionic strength. The subsequent rise in Kc/R_{90} is indicative of the high degree of order built into the system of interpenetrating coils. The maximum in the dissymmetry–concentration plots for the ionized acid (and the linear portion of the z *vs.* c plots for ionized polymethacrylic acid described by Oth and Doth[1] may also be interpreted as an indication that the distance of closest approach of centers of the particles, required in expressing the interparticle potential energy, is not inversely proportional to the cube root of the concentration beyond that concentration at which all of the solution is effectively filled. z will again fall beyond that concentration if it is assumed that the distance of closest approach of centers of the particles is independent of concentration. The addition of small ions will decrease all of these effects. Data on the conductance of low concentrations of small ions in concentrated polyion solutions[9,10,29,30] also support the concept of the existence of uniform electrical distributions in the over-all solution.

A quantitative description of these effects in terms of the free energy of the coil is being undertaken.

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