A plot log $R_i'/2[\text{Cat}]$ *vs.* $1/T$ is presented in Fig. 3. On this same scale are also shown data obtained for k_d by Raley, Rust and Vaughan[8] at higher temperatures in three different solvents. A very satisfactory correlation exists between the two sets of data, and the equation which gives the best fit to all the data in solution is

$$R_i'/2[\text{Cat}] = k_d = 2.8 \times 10^{14} \exp(-35.0\ \text{kcal.}/RT) \quad (4)$$

The excellent agreement between the data of Raley, Rust and Vaughan with our results for styrene, taken in conjunction with the unity value obtained for $f(1 + x)$ in styrene indicate the equivalence of $R_i'/2[\text{Cat}]$ with k_d in solution. With methyl methacrylate, the situation is not so clean cut for the reasons outlined above.

Figure 4 presents a composite of all results obtained both in the gas phase and in solution. The solution values of Raley, Rust and Vaughan are shown as an average of the values for *t*-butyl benzene and cumene. The line drawn through the gas phase points is that of Lossing and Tickner.[6] If this line be accepted as correct, then our values would be substantially above the gas phase values, extrapolated to our working temperatures, by a factor of three. Since all solution points lie on the same line, however, a more direct comparison can be made between the solution data of Raley, Rust and Vaughan at higher temperatures and the gas phase line. Here the discrepancy is only a factor of 1.6. This divergence is, of course, caused by the lower activation energy which we found, of 35.0 kcal., as compared with the over-all activation energy in the gas phase, which has been cited by Lossing and Tickner as 38 kcal. The difference of 3.0 kcal. appears to be within the range of variation of activation energy obtained in the gas phase by different investigators, although we consider our values to be correct within 1.0 kcal. If more weight be placed on Szwarc's data in drawing the gas phase line, then the divergence is not nearly so great. On the basis of theoretical considerations[25] a cage recombination of primary radicals in solution might be expected to reverse the discrepancy, and cause higher rates in the gas phase, instead of in solution.

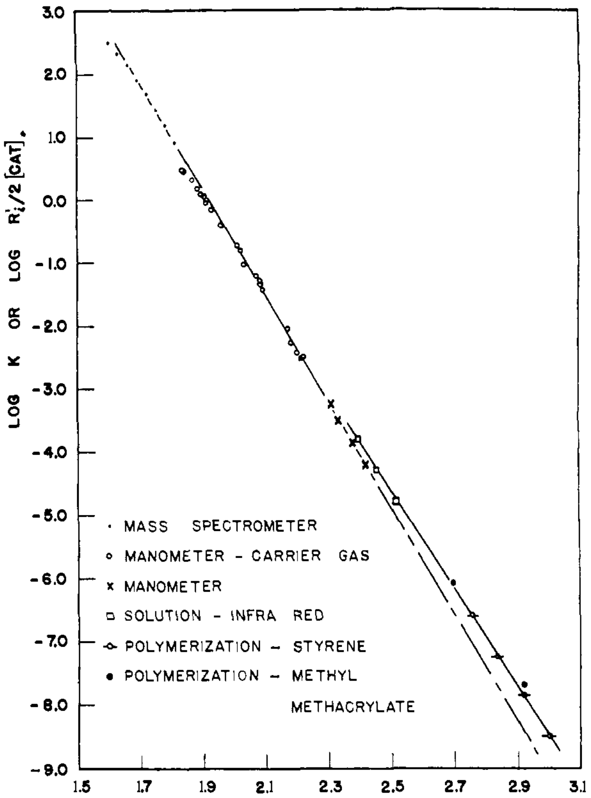

Fig. 5.—Decomposition of di-*t*-butyl peroxide.

A recent series of studies of Szwarc and coworkers has been published on the decomposition rates of diacetyl peroxide in various solvents as well as in the gas phase.[26-28] In contrast to our results with DTBP, higher activation energies and lower rate constants were found in solutions, although both media showed a first-order decomposition.

(25) J. Franck and E. Rabinowitsch, *Trans. Faraday Soc.*, **30**, 120 (1934).

(26) A. Rembaum and M. Szwarc, THIS JOURNAL, **76**, 5975 (1954)-

(27) M. Levy, M. Steinberg and M. Szwarc, *ibid.*, **76**, 5978 (1954).

(28) M. Levy and M. Szwarc, *ibid.*, **76**, 5981 (1954).

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BOSTON UNIVERSITY]

Light Scattering Studies of Poly-soap Solutions[1]

BY SISIR K. SINHA AND A. I. MEDALIA[2] with the technical assistance of DOROTHY P. HARRINGTON

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A new type of poly-soap is described. This is a copolymer of styrene with potassium styrylundecanoate, and thus contains base units with terminal carboxylate groups. Dye solubilization data and solubility behavior of the poly-soap and poly-acid are reported. Light scattering measurements have been made of poly-soaps prepared from poly-acids of known molecular weight. In pure aqueous solution, the apparent molecular weight of the poly-soaps was found to be from one-fifth to one-half of the actual molecular weight. In the presence of added electrolyte (KCl, 0.01–0.1 *N*), values fairly close to the actual molecular weights were obtained. In more concentrated salt solutions, the poly-soap showed evidence of aggregation.

Soaps are known to form aggregates, called micelles, in aqueous solution above a certain concentration (the critical micelle concentration, or c.m.c.). Despite extensive study,[3] there remains considerable disagreement at present concerning the size of the micelle and its dependence on con-

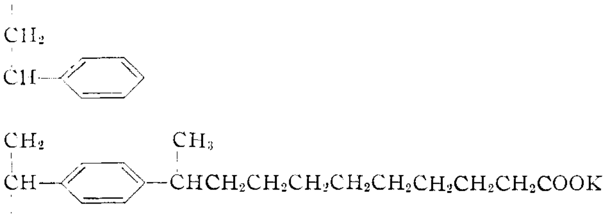
(1) Presented at 128th National Meeting of American Chemical Society, Minneapolis, Sept. 15, 1955.

(2) Godfrey L. Cabot, Inc., Research and Development Department, Cambridge, Massachusetts.

(3) M. E. L. McBain and E. Hutchinson, "Solubilization," Academic Press, New York, N. Y., 1955.

centration of added materials such as electrolytes. This uncertainty regarding micelle size obscures the interpretation of many of the properties of soaps. It therefore seemed desirable to study the properties of a soap of fixed micelle size.

As an approach to this problem, we have prepared a poly-soap, *i.e.*, a polymer composed of soap-like monomer units ("base units"). The poly-soap with which the present studies were carried out is essentially a copolymer of styrene and potassium styrylundecanoate, in 1:1 mole ratio. It is believed that these two monomers alternate fairly regularly along the chain, so that this poly-soap may be regarded as composed of base units of the structure



Since the base unit is styryl–styrylundecanoate the poly-soap is referred to as poly-K-SSU.

A poly-soap of this structure, of molecular weight approximately 300,000, is currently being offered for evaluation by the General Latex and Chemical Corporation of Cambridge, Massachusetts, under the trade name of AK-534. The preparation of this poly-soap will be described in detail in another publication. The structure shown is confirmed both by the method of preparation and by infrared analysis.

Other materials belonging to the same general class of "poly-detergents" have been prepared by Strauss, *et al.*[4] The base units of these materials are dodecyl vinylpyridinium bromide molecules, which differ from soaps in being cationic rather than anionic, and in having the hydrophilic group in a central rather than a terminal position in the molecule. Although it is thus not strictly correct to refer to these materials as poly-soaps, this terminology has been used by Strauss, *et al.*,[4] and has gained acceptance.[3] Solubilization and other interesting properties of these so-called poly-soaps have been studied by Strauss, *et al.*,[4] but we are unaware of any previous publication of light scattering studies.

The plan followed in the present work was to first prepare fractionated samples of the poly-acid, from which poly-soaps of known molecular weight were then prepared. The light-scattering behavior of these poly-soaps was then studied in water and in aqueous salt solutions. Additional measurements, including light scattering, solubilization and conductivity, were made on unfractionated poly-soap solutions.

Experimental

Materials.—Materials were of reagent grade unless otherwise specified. *n*-Heptane and isoöctane (2,2,4-trimethylpentane): both Matheson and Eastman Kodak Co. products were used, both specified as of at least 99% purity. Butanone for light scattering studies was distilled through a 30″ helix-packed column, rejecting the first fraction which was an azeotrope with water. Methanol used in light scattering studies was distilled over magnesium turnings to remove water. The water used in light scattering studies was distilled in a Pyrex still.

Preparation of Poly-acid from Poly-soap.—The poly-acid (poly-SSU) was prepared by pouring a 10% aqueous solution of poly-K-SSU into 10 volumes of cold water containing a 100% excess of hydrochloric acid. The poly-acid separated as porous crumbs which were separated readily from the supernatant liquid. On heating the poly-acid to 50°, it sintered; it was then cooled, ground and vacuum dried, reducing the water content to 10–20%.

Preparation of Poly-soap from Poly-acid.—Of several procedures which were tried for converting the poly-acid to the poly-soap, the following was found most satisfactory for poly-acids of molecular weight above 100,000. The poly-acid is dissolved in acetone as a 10% solution, and this is poured into 3 volumes of either water or methanol containing a 50% excess of potassium hydroxide; water is satisfactory for the lower molecular weight polymers, and methanol is preferable for the highest molecular weight polymer. The poly-soap thus formed is re-precipitated twice by pouring into 10 volumes of isopropyl alcohol.

To prepare a methanol solution of the poly-soap, the re-precipitated poly-soap is allowed to air-dry for 48 hours, thus losing all traces of isopropyl alcohol and becoming a fine dry powder, which is dissolved readily in warm methanol. The dry powder does not, however, dissolve directly in water, apparently owing to failure of the water to wet the polymer and thus reach the hydrophilic carboxylate groups. To prepare an aqueous solution of the poly-soap, the methanol solution may be poured into water, and then the methanol may be removed by fractional distillation. Alternatively, the freshly reprecipitated poly-soap, still wet with the isopropyl alcohol and residual solvent, may be dissolved in hot water, from which the organic solvents are removed by fractional distillation.

Poly-acids of molecular weight below 100,000 may be dissolved directly in the equivalent amount of aqueous alkali.

Light Scattering Apparatus and Technique.—Light scattering measurements were made with a Phoenix–Brice Light Scattering Photometer[5] No. 1270B.

A hand-blown conical cell was used, as described by Doty and Bunce,[6] in order to minimize reflection corrections and permit measurements over an angular envelope. This cell was cemented to a metal plate in a position which gave optical symmetry within 2% as tested by measurement of the angular envelope of a dilute fluorescein solution, the scattering intensity of which was about 3 times background. Optical effects inherent in the use of a narrow slit and curved sloping cell walls were determined by comparison of the readings with this system and with the conventional wide slit and straight cell walls (pentagonal cell), using Ludox solutions poured back and forth between the two cells. The calibration of the instrument was based on a standard opal glass diffusor supplied by the manufacturer.

As a check on the entire calibration, measurements were made (a) of the turbidity of benzene, and (b) of the molecular weight of polystyrene, in both cases using the conical cell and the same details of technique as in the ensuing experiments with poly-soaps. The turbidity of redistilled benzene was found to be 79.0×10^{-5} cm.$^{-2}$, using blue light; this compared with values of 81.1 and 83.3×10^{-5} cm.$^{-2}$ previously reported.[5,7] A sample of polystyrene was prepared by emulsion polymerization and fractionated with MEK–methanol. Intrinsic viscosities were determined in toluene. The viscosity-average molecular weight of the center fraction was 281,000, based on the constants previously determined.[8] Light scattering measurements in benzene gave the same value.

Determinations of the refractive index increment, $\partial n/\partial c$, were made with a Phoenix differential refractometer, cali-

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[4] U. P. Strauss and E. G. Jackson, *J. Polymer Sci.*, **6**, 649 (1951); U. P. Strauss, S. J. Assony, E. G. Jackson and L. H. Layton, *ibid.*, **9**, 509 (1952).

[5] B. A. Brice, M. Halwer and R. Speiser, *J. Opt. Soc. Am.*, **40**, 768 (1950).

[6] P. Doty and B. H. Bunce, This Journal, **74**, 5029 (1952).

[7] S. H. Maron and R. L. M. Lou, *J. Polymer Sci.*, **14**, 273 (1954).

[8] P. Outer, C. I. Carr and B. H. Zimm, *J. Chem. Phys.*, **18**, 830 (1950).

brated with standard KCl solutions. We are indebted to Professor Paul Doty of Harvard University for permission to use this instrument.

In all light scattering work, the thorough removal of dust or other solid particles is of prime importance and difficulty. Various techniques have been tried in the present work. Solutions of medium molecular weight poly-acid (up to 400,000) in solvents of moderately low vapor pressure (benzene, butanone) were filtered by suction through an ultrafine Pyrex filter (Corning 36060 UF). With methanol solutions, this technique led to evaporation of much of the methanol in the filtrate; so, instead, the solutions were filtered by pressure through a similar filter (Corning 33992). Aqueous solutions of poly-soaps also could not be filtered by suction since even slight boiling of the aqueous solutions caused precipitation of the poly-soap as a scum which did not redissolve. Pressure filtration of the aqueous solutions gave satisfactory results with poly-soap preparations (both fractionated and unfractionated) of molecular weight up to 400,000.

In another series of experiments (*vide infra*), the aqueous solutions were centrifuged at 25,000 × *g* in 50-ml. stainless tubes in a Servall Centrifuge, Model SS1, inside a refrigerated chamber. After a first centrifuging for 24 hours, the upper $^2/_3$ of the solution was removed and again centrifuged for 24 hours. The upper $^2/_3$ of this solution was removed and used directly for light scattering studies.

Solutions of very high molecular weight poly-acid (in butanone) and poly-soap (in water) could not be filtered through the sintered glass pressure filter, as virtually all the polymer was retained in and above the upper third of the sintered glass plate. It is not certain whether this retention is due to adsorption or to other causes. Solutions of these polymers were clarified by twice centrifuging, as just described.

The completeness of removal of dust was estimated by visual inspection of the contents of the cell at a low angle, using a Mikrarc illuminator (Model C, Boone Instrument Company, New York City), and by dissymmetry measurements.

The solutions of poly-soap in aqueous potassium chloride were prepared as follows. The aqueous poly-soap solution was filtered into the cell, and its concentration and weight were determined. The calculated amount of filtered potassium chloride solution was added from a clean pipet to the poly-soap solution, with continuous gentle magnetic stirring. The concentration of the potassium chloride solution used was 0.5 *M* or less, except in the experiment in the second line of Table IV, in which 0.9 *M* potassium chloride was used. Successive dilutions were made with aqueous potassium chloride of the desired concentration. After completing the light scattering measurements on a given solution, a portion was removed and evaporated to dryness for concentration determination, and then fresh solvent or salt solution was filtered directly into the cell, using either suction or pressure filtration as discussed above. In the measurements in more concentrated salt solutions, the concentration determinations were based on the weight of the cell plus solution after each operation, rather than on the weights of evaporated aliquots.

The poly-soap solutions were somewhat colored, and so it was necessary to determine the transmittance of the filtered solutions at 546 mμ. This was done in a 1 cm. cell with the Beckman spectrophotometer. Since the zero angle readings in the light scattering photometer were always made with the cell removed, the absorption correction at any angle was made by multiplying the galvanometer reading at that angle by a factor (I_0/I) calculated from the extinction coefficient, ϵ, the optical path, l (4.65 cm.), and the concentration, c: $\log(I_0/I) = \epsilon lc$.

Study of the Poly-acid

Solubility Behavior of the Polyacid.—In order to determine suitable conditions for fractional precipitation of the poly-acid, it was first necessary to study its solubility behavior in a number of solvents. This was done by tumbling 10 cc. of a solvent with 0.1 g. of polyacid (M_η = 300,000) for 24 hours at room temperature, then noting whether the polymer had dissolved (S), swelled (P), or remained virtually unaffected (I). These observations are reported in Table I, together with data for the poly-soap (*vide infra*).

The poly-acid is soluble in alcohols, ketones and ethers of uitable molecular weight.

TABLE I

SOLUBILITIES OF POLY-ACID AND POLY-SOAP (M_η = 300,000)

S = soluble, P = partially soluble or swollen, I = insoluble

Solvent	Poly-acid Room temp.	Potassium poly-soap Room temp.	Potassium poly-soap B.p. (°C.)
Acetone	S	I	I (56°)
Acetonitrile	I	I	..
n-Butanol	S	I	P (118°)
t-Butyl alcohol	S	I	I (83°)
Butanone	S	I	..
Chloroform	P	I	..
Diethylene glycol monoethyl ether	..	S	S (195°)
Diethylene glycol monobutyl ether	..	I	P (230°)
Dioxane	S	I	..
Ethanol	P	P	S (78°)
Ethyl acetate	I	I	I (77°)
Ethylene glycol monoethyl ether	..	S	S (135°)
Ethyl ether	S	I	..
Methanol	P	S	S (65°)
n-Propylalcohol	S	P	S (98°)
Isopropyl alcohol	S	I	I (82°)
Toluene	P	I	..
Water	I	S[a]	S[a]
Xylene	I	I	I (140°)

[a] Anhydrous poly-soap (M_η = 300,000) does not redissolve in water.

Fractional Precipitation of Poly-acid.—On the basis of the data of Table I, fractional precipitation was carried out using diethyl ether as solvent and *n*-heptane as precipitant, at 30 ± 0.05°. A cumulative precipitation curve was first determined as a guide for the fractional precipitation.[9] A single fractional precipitation was carried out by the usual technique of adding increments of precipitant to the polymer solution (1%) at a temperature somewhat above 30°, then cooling slowly to 30° and keeping at this temperature for 48 hours. This separated the polymer into three main fractions, A, B and C. Each fraction was reprecipitated twice from ether, using a large excess of *n*-heptane, and was then dissolved in dioxane and freeze-dried. These fractions were dissolved in butanone for light scattering measurements, as described below.

In subsequent work, diethyl ether was found unsatisfactory as a solvent, since its boiling point is very close to the convenient fractionation temperature of 30°, and since the poly-acid (poly-SSU) of higher molecular weight is not completely soluble in it even at its boiling point. Subsequent fractional precipitations were carried out at 35° with diethyl ketone (Carbide and Carbon, technical grade) as solvent, and either *n*-heptane or isoöctane as precipitant. The objective in this work was to isolate a "center cut" from a given polymer; the "center cut" fraction was reprecipitated once, dried in the vacuum oven at 50°, and then dissolved in a suitable solvent for light-scattering studies. The same technique was used for poly-SSU of M_η = 300,000 and M_η = 1,600,000; center cut fractions from two different fractional precipitations of the 300,000 polymer are labeled D and E, and that from the 1,600,000 polymer is labeled F. The "center cut" fractions amounted to 26, 22 and 33%, respectively, of the total polymers. The "center cut" procedure is believed to improve the homodispersity of the polymer sufficiently for the desired comparison of viscosity-average and weight-average molecular weights.

Determination of the Relationship between Intrinsic Viscosity and Molecular Weight of the Poly-acid.—Establishment of this relationship is one of the first objectives in the study of a new polymer. The poly-acid was selected for study, rather than the poly-soap, because it is soluble in

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[9] A. I. Medalia and I. M. Kolthoff, *J. Polymer Sci.*, **6**, 433, 447 (1951).

wider range of solvents, and because effects such as ionic dissociation and molecular aggregation should be negligible with the poly-acid. Both intrinsic viscosity and light scattering measurements were carried out with butanone as solvent. Viscosities were measured at 25 ± 0.02° with Cannon viscometers, No. 25, with solvent efflux times of 187.3 and 218.3 seconds. Reduced viscosities measured over at least a threefold range of concentrations extrapolated linearly to zero concentration.

The poly-acid fractions used in this study were those described as A, B, C and F, above. Viscosities were determined both before and after filtration (fractions A, B and C) or centrifuging (fraction F); in each case these viscosities were in exact agreement.

The values of Kc/R_{90} obtained from light scattering were extrapolated linearly; the extrapolated values are given in Table II, together with the intrinsic viscosities of these fractions. The dissymmetries of fractions A, B and C were all negligibly small (less than 1.06). The dissymmetry readings for the highest molecular weight fraction (fraction F) were extrapolated according to the method of Doty and Steiner.[10] The points gave a good fit to the straight line predicted for this type of extrapolation. From the extrapolated dissymmetry (1.735) a correction factor ($1/P(90) = 1.56$) was estimated, based on Table VI of reference 10 for monodisperse coils.

TABLE II

MOLECULAR WEIGHT AND INTRINSIC VISCOSITIES OF POLY-ACIDS IN BUTANONE

$\partial n/\partial c = 0.1840$, $n_0 = 1.376$, $K = 2.35 \times 10^{-7}$, at 546 mμ

Poly-acid	$\left[\frac{Kc}{R_{90}}\right]_{c=0} \times 10^7$	M	$[\eta]$, dl./g.
A	18.7	536,000	0.592
B	29.3	342,000	.472
C	83.4	120,000	.249
F	9.45	1,660,000[a]	1.10
P	133	74,600	0.1630
Q	92.7	108,000	.223
R	27.3	366,000	.513

[a] This value is corrected for dissymmetry.

Extrapolated values of Kc/R_{90} for unfractionated poly-acid samples, designated as P, Q and R, are also given in Table II. Dissymmetries were negligibly small (less than 1.05). Viscosities were determined as above.

The intrinsic viscosities of both the fractionated and unfractionated samples are plotted logarithmically against the molecular weights in Fig. 1. From the straight line of Fig. 1, the values of the parameters in the well known relationship, $[\eta] = K'M^a$, were established as $K' = 1.61 \times 10^{-4}$, $a = 0.625$.

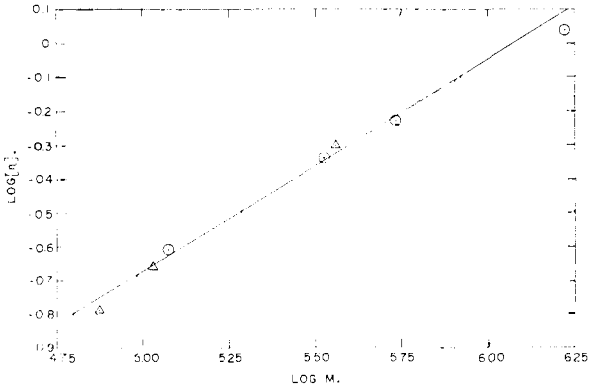

Fig. 1.—Intrinsic viscosity *vs.* molecular weight, for poly-acid in MEK.

Discussion of Poly-acid Data

The above values of K' and a may be compared with those obtained for polystyrene in butanone[8]: $K' = 3.9 \times 10^{-4}$, $a = 0.58$. The slightly higher value of a for the poly-acid indicates that butanone is a slightly "better" solvent for it than polystyrene, probably owing to hydrogen bonding between carboxyl and ketone groups.

From the value of $z = 1.735$, characteristic dimensions of the poly-acid of fraction F were calculated, according to the tabulations of Doty and Steiner.[10] For a monodisperse coil, the root-mean-square end-to-end distance, R, is 1310 Å.; for a polydisperse coil, R is 1180 Å.; and for a rod, the length is 1900 Å. The backbone of the polymer molecule of molecular weight 1,660,000 contains 16,900 carbon atoms; and taking a distance of 2.52 Å. for alternate carbon atoms in a zigzag chain, the fully extended polymer would be 21,300 Å. Evidently the molecule is considerably coiled. It is of interest that Outer, Carr and Zimm[8] have reported a value of R of 900 Å. for a polystyrene of molecular weight 1,320,000, in butanone. The fully extended length of this polystyrene would be 32,000 Å. Thus, the end-to-end distances of the poly-acid with 16,900 backbone atoms is greater than that of the polystyrene with 25,400 backbone atoms. This may be due partly to the increased attraction between poly-acid and butanone, as indicated by the slightly higher value of the viscosity parameter, a; and partly to steric hindrance of the carboxyalkyl groups, tending to stretch the chain.

Properties of Poly-soap Solutions

The solubility of poly-soap ($M_\eta = 300{,}000$) in various solvents was studied by the technique described for the poly-acid, and also by immersing the poly-soap in the refluxing solvent for 15 minutes. The observations are summarized in Table I. Only strongly hydrogen-bonding solvents—water, lower alcohols, etc.—act as solvents for the poly-soap. The solubility behavior of the poly-soap is similar to that of ordinary soaps.

Solubilization of DMAB.—To confirm the soap-like nature of the poly-soap, dye solubilization studies were carried out in the conventional manner.[3,11] Recrystallized *p*-dimethylaminoazobenzene (DMAB) was placed in bottles containing poly-soap solutions of different concentrations, which were shaken for two weeks in a bath at 38°. Aliquots of the solutions were withdrawn into a syringe fitted with a Swinney filter adapter containing 2 discs of fine filter paper (S and S No. 604). The aliquots were diluted in isopropyl alcohol–water (50:50) and the extinctions read at 416 mμ on the Beckman DU spectrophotometer. The results are shown in Fig. 2 and Table III.

Poly-soaps (1) and (2) in Fig. 2 and Table III were samples of poly-K-SSU; their molecular weights are estimated as 500,000 and 100,0000, respectively. Poly-soap (3) was a homopolymer of potassium styrylundecanoate, of molecular weight approximately 1,500,000.

It is evident that the poly-soaps have zero c.m.c., as expected from their structure, since each poly-soap molecule is in effect a preformed micelle. Similar behavior has been reported for the cationic poly-soaps.[4] The solubilizing power for DMAB is

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[10] P. Doty and R. F. Steiner, *J. Chem. Phys.*, **18**, 1211 (1950).

[11] I. M. Kolthoff and W. Stricks, *J. Phys. Colloid Chem.*, **52**, 915 (1948).

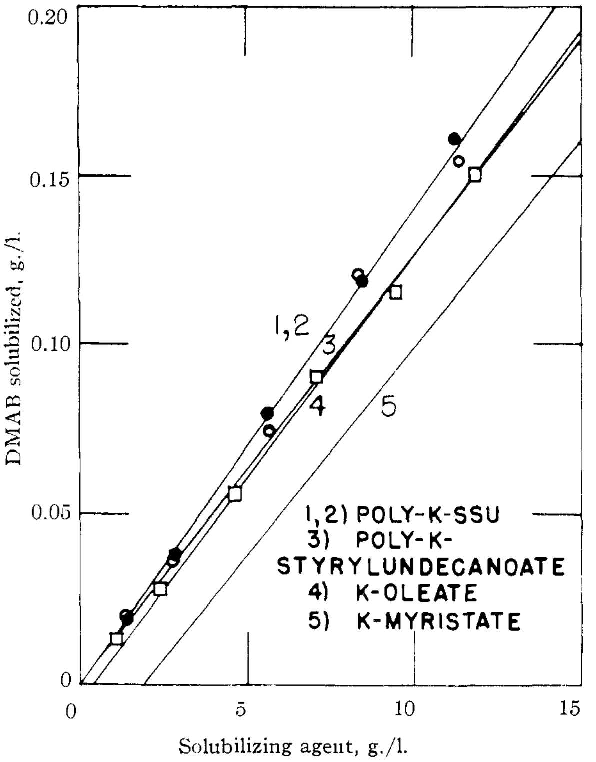

Fig. 2.—Solubilization of DMAB by poly-soaps.

quite comparable for the three poly-soaps and the two ordinary soaps listed, on a weight basis.

TABLE III

SOLUBILIZATION OF DMAB AT 38°

The value of K is defined by the equation g.DMAB/l. = K[(g. soap/l.) − C.M.C.]

Soap	C.m.c. (g./l.)	$K \times 10^3$
Poly-K-SSU (1)	0	13.9
Poly-K-SSU (2)	0	14.1
Poly-K styrylundecanoate	0	12.8
K oleate[a]	0.26	12.0
K myristate[a]	1.9	12.4

[a] Interpolated from date of Kolthoff and Stricks[11] at 30 and 50°.

Conductivity Measurements.—A sample of poly-K-SSU (molecular weight 300,000) was purified by dissolving it in methanol (10% solution) and precipitating in 10 volumes of cold isopropyl alcohol. This procedure was repeated twice in order to free the poly-soap from traces of free alkali. The poly-soap was air-dried and then dissolved in anhydrous methanol. The conductivities of this solution, and of solutions prepared by successive dilutions, were measured with a conductivity bridge (Industrial Instruments Model RClB, 60 cycle) using lightly platinized electrodes. Over a range of concentrations from 10 to 70 meq./l., the equivalent conductance decreased somewhat erratically from 31 to 27 ohm.$^{-1}$ cm.$^{-1}$. This is approximately one-tenth of the equivalent conductivity of KCl in water, and indicates that the poly-soap is very roughly 10% dissociated, at least with regard to the conditions of this measurement.

Light Scattering Studies of Aqueous Solutions of Poly-soaps

Results.—Studies were carried out with three different batches of potassium poly-soaps prepared from fractions D, E and F, described above. The molecular weights of fractions D and E, as determined from intrinsic viscosities in butanone, were 474,000 and 336,000, respectively; that of fraction F was 1,620,000 (see Table III).

The values of Kc/R_{90} obtained from light scattering measurements of aqueous solutions of the three fractionated poly-soaps are shown in Fig. 3. The extrapolated values are given in Table IV. The data are discussed further below.

Potassium chloride was added to aqueous solutions of fractionated poly-soaps to give the concentrations indicated in Table IV. These solutions were diluted successively with aqueous KCl of the normality indicated in Table IV. The light scattering data are also plotted in Fig. 3. The significance of the measurements in 0.4 M KCl is open to some question, since the value of R_{90} increased by about 20% during the first 4 hours after mixing. The rate of increase at that time was very small, so that readings at successive dilutions were taken then. It was noticed that after standing 10 weeks, the solutions in 0.4 M KCl contained a copious precipitate.

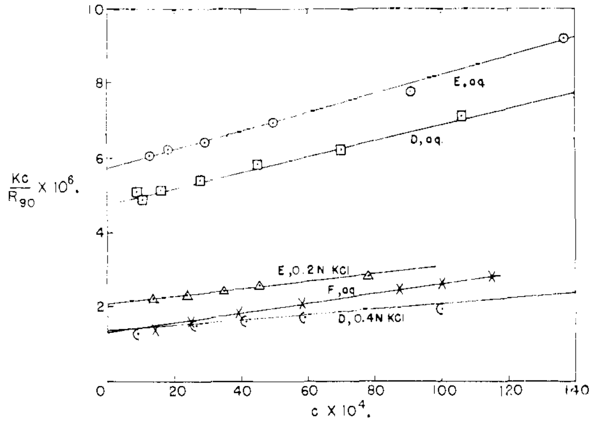

Fig. 3.—Light scattering of fractionated poly-soaps in water and in aqueous potassium chloride.

More extensive studies were carried out with three unfractionated poly-soap samples, prepared from poly-acid samples P, Q and R of Table II. Typical measurements with aqueous solutions, both in the absence of salt and in the presence of potassium chloride of various concentrations, are shown in Fig. 4. The results of these and other measurements are reported in Table IV. After making the light scattering measurements the solutions of higher salt concentration were allowed to stand for over 1 hour and were then remeasured. One such solution, that of sample R in 0.10 N potassium chloride, showed an increase of 20% in 1–1.25 hours; the others remained constant.

Discussion

Several theories have been proposed for the interpretation of light scattering results in solutions of micellized soaps, polyelectrolytes, or other com-

Table IV

Light Scattering Measurements of Aqueous Solutions of Poly-soaps

Water: $\partial n/\partial c = 0.2072$ cc./g., $n_0 = 1.3310$, $K = 2.78 \times 10^{-7}$, at 546 mμ, 0.4 N KCl: $\partial n/\partial c = 0.2120$ cc./g., $n_0 = 1.3359$, $K = 2.96 \times 10^{-7}$, at 546 mμ

Values of $\partial n/\partial c$ and n_0 in salt solutions of intermediate concentrations obtained by interpolation.

Poly-soap sample and mol. wt., M_{Bu}[a]	KCl (M)	Apparent mol. wt. in aqueous soln.	Ratio, M_{aq}/M_{Bu}
D; 523,000	..	212,000	0.41
	0.4	695,000	1.33
E; 380,000	..	177,000	0.47
	.2	474,000	1.25
F; 1,770,000	..	880,000[b]	0.50
P; 82,800	..	46,500	0.56
	.00391	70,400	0.85
	.0156	92,600	1.12
	.100	105,000	1.27
Q; 119,000	..	23,300	0.20
	.00391	71,400	0.60
	.0156	86,200	0.73
	.100	119,000	1.00
	.20	244,000	2.06
R; 402,000	..	137,000	0.34
	.00391	318,000	0.79
	.0156	328,000	0.82
	.100	500,000	1.25

[a] Molecular weight of poly-soap, based on the molecular weight of the poly-acid in butanone. [b] Corrected for dissymmetry; $z = 1.16$, thus $(1/P_{90}) = 1.11$.

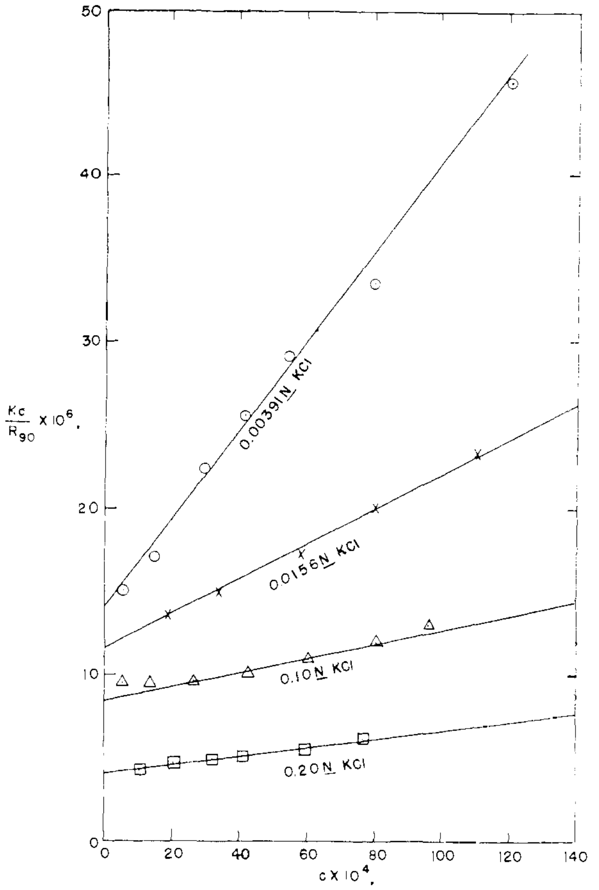

Fig. 4.—Light scattering of poly-soap sample Q in aqueous potassium chloride.

pact macro-ions. Hutchinson and co-workers,[12-14] as well as Doscher and Mysels,[15] have shown that in the absence of added electrolyte, the apparent molecular weight (micelle size) should be smaller than the true molecular weight by a factor $(1 + p)$, where p is the number of "unbound" simple ions of opposite charge associated with each micelle. The present experiments lead to values of p in the range 1 to 4. However, there is no independent method of evaluating p, which may indeed be regarded as simply a parameter defined by the above relationship, so that the present work cannot be regarded as a test of these interpretations.

Mysels[16] and Prins and Hermans[17] have proposed the following expression for the turbidity of colloidal electrolytes in the presence of a single salt having a common ion

$$\frac{Hc}{\tau} = \frac{1}{M}\left[1 + \frac{p}{1 + (2x/z)}\right] \qquad (1)$$

where x and z are the concentrations (equivalents per liter) of the simple salt and of the colloidal electrolyte, respectively. The data obtained in several of the experiments in the more dilute salt solutions have been treated according to eq. 1. The value of M has been taken as equal to M_{Bu} (the molecular weight of the poly-soap calculated from the molecular weight of the poly-acid in butanone), and from the value of Kc/R_{90} ($= Hc/\tau$) at a given concentration, the value of p has been calculated. Values determined at both the lowest and highest experimental concentrations in each run are given in Table V, designated as p_1 and p_2, respectively. In the more concentrated salt solutions, the apparent molecular weights were higher than the nominal molecular weight (M_{Bu}), presumably due to aggregation; application of eq. 1 would yield negative values of p, as in the second line of Table V.

Table V

Values of p from Experiments in Salt Solutions

		Lowest concn. studied		Highest concn. studied		From slope at zero concn.	
Poly-soap	KCl (M)	$c \times 10^4$ (g./cc.)	p_1[a]	$c \times 10^1$ (g./cc.)	p_2[a]	$B_0 \times 10^1$	p_0[b]
P	0.00391	12	0.274	144	0.96	14.5	8.81
P	.0156	4.34	<0	115	4.31	4.57	9.85
Q	.00391	5	5.65	120	5.55	25.4	16.8
Q	.0156	18.9	4.64	111	3.76	10.2	21.2
R	.00391	8.7	2.19	104	2.91	5.24	25.7
R	.0156	5.14	6.88	89.3	2.47	2.24	33.6

[a] From eq. 1. [b] From differential form of eq. 1.

Phillips and Mysels[18] have used a differential form of eq. 1 to calculate p from the slope, B, of the plot of Kc/R_{90} *vs.* c. (This is of course the only method of determining p if the actual molecular weight of the colloidal electrolyte is not known, as with ordinary soap micelles.) Values of p cal-

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(12) E. Hutchinson, *J. Colloid Sci.*, **9**, 191 (1954).

(13) E. Hutchinson and J. C. Melrose, *Z. physik. Chem.*, **2**, 363 (1954).

(14) Ref. 3, p. 232.

(15) T. M. Doscher and K. J. Mysels, *J. Chem. Phys.*, **19**, 254 (1951).

(16) K. J. Mysels, *J. Phys. Chem.*, **58**, 303 (1954).

(17) W. Prins and J. J. Hermans, *ibid.*, **59**, 576 (1955).

(18) J. N. Phillips and K. J. Mysels, *ibid.*, **59**, 325 (1955).

culated in this manner from the extrapolated slopes at zero concentration of poly-soap are designated as p_0 in Table V.

These values of p_0 in Table V are of the same order of magnitude as the values reported by Phillips and Mysels[18] for sodium lauryl sulfate, based on a similar calculation. However our values of p_0—calculated from the slopes—are much higher than the values of p_1 and p_2 calculated on the basis of eq. 1. This discrepancy cannot be accounted for by assuming that the molecules are aggregated, since this assumption would affect the value of p_0 almost as much as the values of p_1 and p_2. Thus, in the experiment with poly-soap R in 0.00391 M KCl, the assumption of aggregation to the extent of an aggregate weight of 2,000,000 would increase p_0 to 128, while increasing p_1 to only 29.4.

Unfortunately the value of p has no direct significance in terms of measurements other than by light scattering. The internal discrepancy between the values of p calculated from the same data by two different methods must cast some doubt on the validity of the theory on which these calculations were based.

We also have attempted to interpret the present data according to the theory of Doty and Steiner.[19] This theory, however, predicts a dissymmetry coefficient $z_{45} < 1$, while in all our experiments we have found z_{45} between 1.0 and 1.2.

Conclusions

From the theoretical standpoint, it appears that the data obtained in aqueous salt solutions cannot be adequately interpreted by either of the theories considered; while the theories proposed for soap in the absence of salt do not permit direct experimental verification.

From a practical standpoint, the present data indicate that molecular weights of soap micelles, estimated from light scattering measurements in aqueous solutions, may be too low by a factor from 2 to 5.

Insofar as the present data can be applied to ordinary soaps and other micelle-forming substances, the data obtained in dilute salt solutions indicate that in the presence of an electrolyte in the range 0.01–0.1 N, micelle molecular weights within 30% of the correct value will be obtained. Extrapolation to the critical micelle concentration, as recommended by Debye[20] and Mysels[16] should give molecular weights of this order of accuracy, with soaps of fairly high critical concentration such as sodium laurate or sodium lauryl sulfate. However, with soaps of critical concentration much below 0.01 M, this procedure may give somewhat more erroneous results.

The data obtained in salt solutions of higher concentration (0.2–0.4 M) indicate that association of the poly-soap does take place. It is likely that association or enlargement of ordinary soap micelles would also take place at these salt concentrations. However, the addition of salt to bring the total electrolyte concentration (including unmicellized soap) up to 0.01–0.1 M would seem a safe practice.

Any effects arising from hydrolysis of the poly-soaps do not prevent transfer of the conclusions drawn from the poly-soap systems to ordinary soap systems, since hydrolysis should be comparable in both systems. Furthermore, the extent of hydrolysis must be comparatively small, since poly-soap solutions of 0.34–1% concentration (0.008–0.025 M) have a pH of 9.5. The present data should thus have some bearing on the behavior of detergents such as sodium lauryl sulfate, etc. A sulfate ester type of poly-soap has been prepared in this Laboratory, but we have not had the opportunity to study its light scattering behavior.

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[20] P. Debye, *J. Phys. Colloid Chem.*, **53**, 18 (1949); P. Debye and E. W. Anacker, *ibid.*, **55**, 644 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

The Thermodynamic Properties of Ammonium Fluoride: Heat Capacity from 6 to 309°K., the Entropy, Enthalpy and Free Energy Function[1]

BY EDWIN BENJAMINS AND EDGAR F. WESTRUM, JR.

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Measurements of the heat capacity of NH_4F have been made by adiabatic calorimetry over the range 6 to 309°K. In contrast with the reports by others of a hump in the heat capacity near 240°K., no thermal anomaly was found in the entire range of measurement. The molal heat capacity and the derived molal entropy and enthalpy at 298.16°K. are 15.60 ± 0.02 cal./deg., 17.20 ± 0.02 cal./deg., and 2655 ± 3 cal., respectively.

Introduction

Although recent thermodynamic, spectroscopic and diffractional studies have contributed much to the interpretation of the mechanism of the pseudorotational transitions in ammonium chloride, bromide and iodide, the treatment of the fluoride has been less decisive. Simon, Simson and Ruhemann[2] determined the low temperature heat capacities

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[1] Adapted from the dissertation of Edwin Benjamins submitted to the Graduate School of the University of Michigan in partial fulfillment of the requirements of the Ph.D. degree. This work was supported by the U. S. Atomic Energy Commission.

[2] F. Simon, Cl. von Simson and M. Ruhemann, *Z. physik. Chem.* **129**, 339 (1927).