Salts, as such, have a definite salting out effect, although the present method is usually too insensitive to show the influence of only a few per cent. of either salt or detergent. A small amount of electrolyte may have an enormous effect upon the viscosity of such a detergent as potassium oleate without altering its solubilizing power very noticeably. 15% detergent usually increases the solubility many fold, the highest value in Table I being 18.7 for potassium oleate. Even this is only a small fraction of the amount of propylene which would dissolve in equal weight of a similar pure organic solvent.

In contradistinction to the detergents, the addition of 15% of a good organic solvent has a comparatively negligible result. Thus 15% diethyl carbitol increases the solubility of propylene by only 10% of that of water alone. This again illustrates the difference between solubilizing by detergents which can be appreciable with only a few tenths of a per cent., whereas in hydrotropy with the addition of a good miscible solvent, very high concentrations are required to get a comparable result. The difference is that in the mixed solvent the added molecules are separate and are submerged in the excess of first solvent whereas with the detergent or colloidal electrolyte the solute is segregated in colloidal particles, which themselves incorporate the solubilized material.

Summary

A further study of the effect of added substances upon the solubility of propylene in water is to show that all the detergents tested greatly increase the amount of propylene dissolved, in spite of any salting out action which they may otherwise possess. This solubilizing effect is shown by anion active, cation active, and non-electrolytic detergents.

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The Effect of Temperature and Solvent Type on the Intrinsic Viscosity of High Polymer Solutions

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According to hydrodynamics, the specific viscosity of a Newtonian liquid containing a small amount of dissolved material should depend in first approximation only upon the volume concentration and the shapes of the suspended particles. By suitable application of such hydrodynamical considerations to solutions of long chain molecules, it is possible in a rough fashion to derive the Staudinger–Kraemer equation, denoting proportionality between specific or intrinsic viscosity and molecular weight. It is an experimental fact, however, that the proportionality constant, K_m, is dependent not only upon the type of polymer concerned, but also upon the temperature and the nature of the solvent. Even in the dilute range, where specific viscosity is linear with concentration, these variations are often quite considerable. This paper tries to treat such variations in a systematic fashion, and to advance for them an explanation which is based upon changes in the average geometrical shape of the particles. A relationship between intermolecular and intra-molecular agglomeration tendency is presented.

Theoretical Considerations.—According to Burk,[1a] Eyring,[2] Flory,[3] Guth,[4] Huggins,[5] Kuhn,[6] Mark,[7] and Meyer,[8] a long chain hydrocarbon molecule in solution takes on a somewhat kinked or curled shape, intermediate between a tightly rolled up mass and the rigid linear configuration assumed by Staudinger.[9] Presumably all possible degrees of curling are represented, owing to the internal Brownian movement of the flexible chains, but the configurations of intermediate extension predominate statistically. The average or effec-

(1) This paper was presented in October, 1941, at the meeting of the Society of Rheology in New York City.

(1a) R. E. Burk and L. Laskowsky, J. Chem. Phys., 7, 465 (1939).

(2) H. Eyring, R. E. Powell and W. E. Roseveare, THIS JOURNAL, 60, 3113 (1940); Ind. Eng. Chem., 33, 430 (1941).

(3) P. J. Flory, THIS JOURNAL, 61, 3334 (1939); 62, 1057 (1940).

(4) E. Guth and H. Mark, Monatsh., 65, 94 (1934); E. Guth and H. M. James, Ind. Eng. Chem., 33, 624 (1941).

(5) M. L. Huggins, J. Phys. Chem., 42, 911 (1938); 43, 439 (1939); J. Appl. Phys., 10, 700 (1939).

(6) W. Kuhn, Koll. Z., 68, 2 (1934); 76, 258 (1936); 87, 3 (1939); Z. physik. Chem., A161, 427 (1932).

(7) H. Mark and E. Valko, Kautschuk, 6, 210 (1930); H. Mark, Koll. Z., 53, 32 (1930).

(8) K. H. Meyer, G. V. Susich and E. Valko, ibid., 59, 208 (1932); K. H. Meyer, ibid., 95, 70 (1941).

(9) H. Staudinger and collaborators, Ber., 68, 707 (1935); ibid., 70, 1565 (1937); Melleand, 18, 681 (1937); 20, 693 (1939).

tive value of any shape-dependent molecular property (such as hydrodynamical influences) may be obtained by summing this property over all configurational states, after each state has been given a proper weight factor. If the long chain molecule is surrounded by a continuous, energetically indifferent solvent, then the weight factor for a particular configuration is determined only by internal parameters—potential energy function for restricted rotation, prohibition of segment interpenetration, etc. The mean value of any molecular property in such ani ndifferent (and perhaps hypothetical) solvent might be called the "unbiased" statistical mean for the property.

If the solvent is energetically unfavorable, so that the dissolving of the high polymer is an endothermic process, then the polymer segments will attract each other in solution and squeeze out the solvent between them. The curling forces in such a case will be similar to those postulated in the Mack[10] theory of rubber elasticity. Those molecular configurations which involve many contacts of the molecule with itself will be weighted more heavily than in an indifferent solvent, and the mean value of any molecular property will represent a more curled and contracted shape than the unbiased mean. On the other hand, if a solvent is energetically more favorable than the indifferent solvent as previously defined, then in solution the long chain molecule will be surrounded by a solvated hull which tends to prevent polymer–polymer contacts. Uncurled configurations will be favored, and the mean value of any property will represent a more extended shape than the unbiased mean. Since an extended or uncurled configuration is associated with a high intrinsic viscosity, and *vice versa*, the first prediction as to effect of solvent type upon viscosity is the following.

Other conditions being equal, a given high polymeric material made up of flexible molecules will exhibit a high intrinsic viscosity in an energetically favorable solvent, and a low intrinsic viscosity in an energetically unfavorable solvent. This of course holds only for very diluted systems. At higher concentrations (around or above 5% by weight) an energetically unfavorable solvent will favor polymer–polymer contacts between different chains and hence lead to the danger of gelation, while an energetically favorable solvent will stand a higher concentration of the polymer and yet give

(10) E. Mack, *J. Phys. Chem.*, **41**, 231 (1937).

a fluid, stable solution. Solvents are often classified as "good" or "bad" on the basis of the viscosity of concentrated solutions.

If a good solvent is mixed with a precipitating agent, the resulting mixture can be expected to be energetically less favorable to a long chain molecule than is the pure solvent. A dilute solution of high polymer in a solvent–non-solvent mixture should, therefore, exhibit a lower intrinsic viscosity than a solution of the same polymer in the pure solvent. It will be shown that a series of high polymer solutions of given polymer concentration, in mixtures of increasing non-solvent content, shows a regular decrease in specific viscosity until the precipitation point is reached.

We have interpreted variations in the intrinsic viscosity of a given high polymeric material as being due to changes in the degree of *intramolecular* agglomeration. If this interpretation is correct, there should be also a close connection between the intrinsic viscosity of a high polymer solution and the degree of *intermolecular* agglomeration. Exactly the same solvent characteristics which determine the mean geometrical properties of an isolated long chain molecule should also determine the amount of association of different solute molecules into aggregates. When a non-solvent is added to a high polymer solution, the point at which precipitation begins represents a certain definite agglomeration tendency for chain segments of different molecules. To a first approximation, therefore, it should represent a certain definite mean value for any shape-dependent *internal* property. That solvent composition which is critical from the standpoint of solubility should correspond to a certain intrinsic viscosity, no matter what the solvent and what the non-solvent. One would therefore conclude the following: The intrinsic viscosities of a series of solutions of a given polymer in solvent–non-solvent mixtures of increasing non-solvent content, should decrease to a final value at the limit of solubility. This final value should be in first approximation the same in all solvent–non-solvent systems.

All of these effects should be more pronounced for polymer molecules of high flexibility than for more rigid chains. A paraffin chain should exhibit greater shape changes than a cellulose derivative.

The effect of temperature upon intrinsic viscosity should depend strongly upon the nature of the solvent. In a poor solvent, the effective molecular shape is more compact and curled than the un-

biased statistical mean. An increase of temperature should increase the relative importance of entropy factors over energetic factors, and result in an uncurling of the molecule. In such a solvent, a temperature increase should result in an increase of intrinsic viscosity. In a very good solvent, the energetic weighting factors favor the more extended configurations; here a temperature increase should result in a downward approach to the unbiased statistical mean shape. In a very good solvent, therefore, a temperature increase should cause a decrease in intrinsic viscosity. There should be an intermediate case in which the intrinsic viscosity is independent of temperature over a limited range.

The above use of the "unbiased statistical mean" as the shape which is approached as the temperature increases is an oversimplification, since this value itself includes energetic weighting factors, arising from the internal potentials of the molecule. If we consider only the forces which depend upon the solvent, we can make the prediction: In a very good solvent, the intrinsic viscosity of a dilute solution of a flexible polymer should decrease with temperature; in a poor solvent, it should increase.

Experimental

Polystyrene, rubber, and cellulose acetate were used in this investigation. The polystyrene had a weight average molecular weight of 165,000, calculated from viscosity data and using a K_m value of 1.1×10^{-4}. The rubber was smoked crepe, with a weight average molecular weight of 223,000, based upon a K_m value of 2.7×10^{-4}. The cellulose acetate was a fraction with a molecular weight of 35,000, which had been obtained by Harris and Sookne from a sample of commercial cellulose acetate having a weight average molecular weight around 90,000.

Solutions of polystyrene at a concentration of 0.2% by volume in the following solvent–non-solvent systems were investigated: Methyl ethylketone–methanol, toluene–acetone, toluene–methanol, toluene–isoamyl alcohol. Figure 1 shows the variation of specific viscosity with non-solvent content. In each case, the specific viscosity decreases as the mixed solvent becomes less favorable until the coagulation point is reached. For all the solvent–non-solvent systems investigated, the specific viscosity at the solubility limit is in the same range.
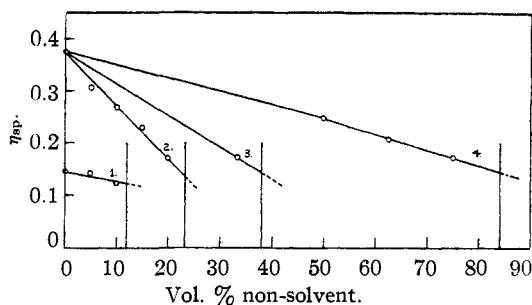

Fig. 1.—Variation of specific viscosity of 0.2% polystyrene solutions with non-solvent content: (1) methyl ethyl ketone–methanol; (2) toluene–methanol; (3) toluene–isoamyl alcohol; (4) toluene–acetone.

Solutions of rubber at a concentration of 0.0468% by volume in the following solvent–non-solvent systems were investigated: toluene–methanol, toluene–acetone, carbon tetrachloride–methanol, carbon tetrachloride-acetone. Figure 2 shows the variation of specific viscosity of these solutions with composition of the mixed solvent. Rubber behaves in the same general way as polystyrene.
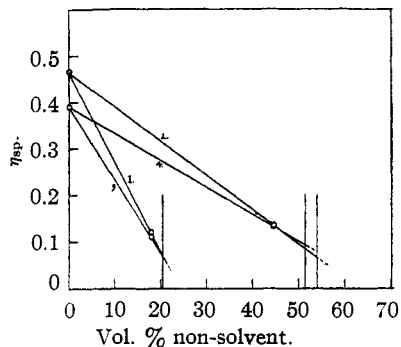

Fig. 2.—Variation of specific viscosity of 0.0468% rubber solutions with non-solvent content: (1) carbon tetrachloride–methanol; (2) carbon tetrachloride–acetone; (3) toluene–methanol; (4) toluene-acetone.

Solutions of cellulose acetate at 0.2% by volume in the following solvent–non-solvent systems were investigated: methylcellosolve–methanol, acetone–methanol, acetone–toluene. The specific viscosities of all solutions were about 0.33. The nature of the solvent medium apparently had no marked effect upon the shape of the cellulose acetate molecule in solution. It is to be expected that the cellulose chain is much less flexible than the rubber and polystyrene molecules.

Effect of Temperature.—Viscosities of many of the solutions were determined at two different temperatures, 25 and 60°. Table I shows the relation between the specific viscosity at 60°
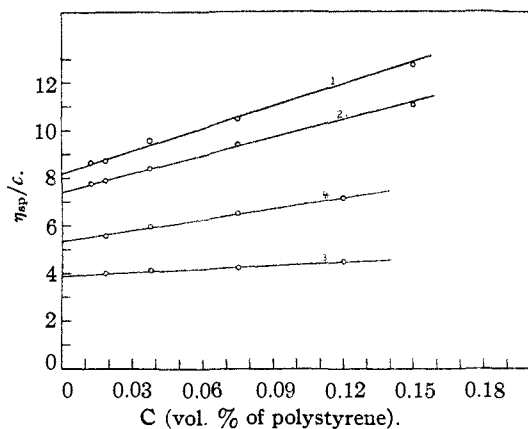
Fig. 3.—Relation between η_{sp}/c and c for polystyrene solutions: (1) toluene, 20°; (2) toluene, 80°; (3) 20% methanol, 80% toluene, 20°; (4) 20% methanol, 80% toluene, 60°.

and that at 25°, as a function of solvent composition, for several systems. In the pure solvents, specific viscosity decreases with temperature, while in the mixtures containing much non-solvent, specific viscosity increases with temperature.

TABLE I

η_{sp} AS A FUNCTION OF TEMPERATURE

Sample	Temperature, °C. 25	60
Rubber in		
Toluene	0.390	0.373
Carbon tetrachloride	.466	.430
Toluene–14% methanol	.205	.243
Polystyrene in		
Toluene	.370	.350
Toluene–10% methanol	.320	.317
Toluene–20% methanol	.160	.185
Toluene–10% amyl alcohol	.336	.340
Toluene–33% amyl alcohol	.170	.210

Effect of Concentration.—The effect of concentration on specific viscosity (in the dilute range) was investigated in both "good" and "poor" solvents, and at different temperatures. A sharp molecular weight fraction of polystyrene (mol. wt. 730,000) was used in this part of the investigation.

If η_{sp} is given by a power series in concentration, there will be a range in which all terms but the first can be neglected ($\eta_{sp} = ac$). Experimentally this range turns out to be very small in the case of a high molecular weight sample. Deviations from the simple linear relation are found at concentrations well below 0.05% by volume. For a somewhat wider range, the first two terms will serve to give the viscosity ($\eta_{sp} = ac + bc^2$). Experimentally, this range proves to be fairly wide,

even for high molecular weight samples. When η_{sp}/c is plotted against c, the slope of the straight line gives the second coefficient, b, and the ordinate intercept gives the first coefficient, a. In Fig. 3, (η_{sp}/c) is plotted against c for polystyrene in toluene, and in a mixture of 80% toluene and 20% methanol. In this way is seen the effect of temperature and solvent type upon both virial coefficients. The presence of the non-solvent not only reduces the linear coefficient (which reflects the shape of individual molecules), but also reduces to an even greater degree the second coefficient (which is determined by the *degree of interaction* among different molecules).

An increase in temperature shifts the whole curve downward in the case of toluene, and upward in the case of the toluene–methanol mixture. In the toluene–methanol mixture, the interaction term, b, is least important at the lowest temperature.

It may be significant that Flory[11] has reported a similar situation in regard to the osmotic pressure–concentration relationship for high polymer solutions. The osmotic pressure is more nearly linear with concentration in "poor" solvents than in "good" solvents.

Summary

1. The specific viscosity of a dilute solution of polystyrene or rubber is strongly dependent upon the nature of the solvent; the specific viscosity is high in a good solvent, and low in a poor solvent or a solvent–non-solvent mixture. This has been interpreted as being due to changes in mean molecular shape. The specific viscosities of cellulose acetate solutions are not so sensitive to the nature of the solvent.

2. The extrapolated specific viscosity at the limit of solubility is in the same range for several different solvent–non-solvent systems.

3. The effect of a temperature increase is to lower the specific viscosity of rubber or polystyrene solutions in a good solvent, but to increase the specific viscosity in a mixture of solvent and non-solvent.

4. The specific viscosity of a dilute polystyrene solution is more nearly linear with concentration in a toluene–methanol mixture than in pure methanol. The quadratic term b in the equation ($\eta_{sp} = ac + bc^2$) is reduced relatively more than the linear term a by the presence of the non-solvent.

(11) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).