

this was added 0.50 g. of benzhydrol dissolved in 10 ml. of carbon tetrachloride. As soon as the stirred mixture became homogeneous it was poured into 250 g. of ice-water mixture. The solution was extracted with ether, the extract dried, filtered, and the benzhydrol, 0.47 g. (93% of the original weight) melting at 60–65°, was recovered.

When the benzhydryl carbonium ion solution was added to methanol under such conditions that the temperature of the mixture was kept below 25°, no benzhydrol could be recovered from the reaction mixture. These experiments show that the reaction to form methyl benzhydryl ether was not a simple acid-catalyzed etherification.

Reaction of Benzhydryl Carbonium Ion Solution with Glacial Acetic Acid.—The carbonium ion solution was poured into 150 ml. of stirred glacial acetic acid. The red color remained, indicating the presence of carbonium ions. The mixture was poured immediately into 250 g. of ice-water mixture, and instant decolorization resulted. The mixture was extracted immediately with two 150-ml. portions of ether, and the extract treated with sodium carbonate solution. It was then dried, filtered and the solvent evaporated. The residual sirupy liquid was dissolved in 0.5 ml. of petroleum ether and chilled in a methanol-solid carbon dioxide bath. The solid formed was allowed to stand at room temperature until all of the solvent had evaporated. The yield was 0.34 g. (55% calculated as benzhydryl acetate) of a solid melting at 36.5–

40.5°. The recrystallizations from petroleum ether resulted in a melting point of 40.3–41.0. The literature gives a value of 42°.⁹

Saponification of the solid acetate with methanolic sodium hydroxide yielded benzhydrol, identified by melting point and mixed melting point.

Summary

When solid benzhydrol is added to sulfuric acid, solution is slow, and considerable sulfonation apparently takes place. This solution has "i" factors as high as six. A solution of relatively stable benzhydryl carbonium ions can be prepared by dissolving the benzhydrol in carbon tetrachloride, and extracting with sulfuric acid. By pouring the acid solution into water, methanol and glacial acetic acid, dibenzhydryl ether, methyl benzhydryl ether, and benzhydryl acetate, respectively, may be prepared in reasonable yields.

(9) E. Berner and A. Hjulstad, *Ber.*, **71B**, 2053 (1938).

KNOXVILLE, TENNESSEE

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[CONTRIBUTION FROM THE EXPERIMENT STATION, HERCULES POWDER COMPANY]

Bound Metal in Ethyl Cellulose Effect on Dilute Solution Properties

BY EVAN F. EVANS AND HAROLD M. SPURLIN

Introduction

Our knowledge of the behavior of linear high polymers in dilute solution is usually considered fairly complete. When the situation is analyzed, however, it becomes apparent that our information is really good for only the two extremes, ionic polymers in water and simple non-ionic polymers in organic solvents. Recent work by Fuoss¹ gives some information about ionic polymers that are soluble in polar organic solvents. In the literature are also data on the properties of concentrated solutions in organic solvents of cellulose derivatives containing some bound metal ions.^{2,3,4} The fact remains, however, that there has not been adequate recognition of the fact that many commercial polymers contain bound ions in amount sufficient to influence markedly even dilute solution properties.

About ten years ago the methods for measuring the amount of metal ions bound to carboxyl or sulfuric half-ester groups in cellulose derivatives were well advanced. It became apparent that there was frequently as much as one equivalent of bound metal per cellulose chain. The question immediately arose whether these bound ions would influence the usual methods for estimation of molecular weight. It might be anticipated

that the metal ions would be osmotically active, leading to high values of osmotic pressure. There was even more reason to fear that the bound metal ions, particularly if divalent, would lead to cross-linking and therefore to higher viscosities than would correspond to the length of the basic polymer chain.

As will be shown, the effects on viscosity and osmotic pressure are very pronounced. Fortunately, they tend to disappear in dilute solution. There is no evidence that the bound metal ions contribute to osmotic pressure when extrapolated to infinite dilution. All observed effects can be attributed to association.

When it became apparent that the degree of association could be controlled by varying the amount and nature of bound metal, the significance of these data with regard to methods for determining solvent power was realized. It will be shown that as the tendency for association rises the polymer gets less soluble, the slope of the reduced viscosity-concentration curve rises, and the slope of the reduced osmotic pressure-concentration curve falls.

Selection of Materials.—It was desired to vary independently the amount and nature of bound metal as well as the chain length of the polymer. These requirements could be fulfilled, however, only if the polymer would survive chemical manipulation without change of degree of polymerization or substitution. Also, the methods of manipulation had to be such that

(1) R. M. Fuoss, *et al.*, *J. Polymer Sci.*, **3**, 246, 602, 603 (1948); *ibid.*, **4**, 97, 191, 457 (1949); *Ann. N. Y. Acad. Sci.*, **51**, 836 (1949).

(2) H. M. Spurlin, in E. Ott, "Cellulose and Cellulose Derivatives," Interscience Publishers, Inc., New York, N. Y., 1943, p. 872.

(3) C. J. Maim, U. S. Patents, 2,126,488–9 (1936).

(4) C. J. Maim, *et al.*, *Ind. Eng. Chem.*, **42**, 730 (1950).

there could be no question of fractionation. De-ashed ethyl cellulose met these requirements very well. It was thus possible to neutralize in solution the carboxyl groups to any desired extent, to recover the product by evaporation of the solvent and then to redissolve the dried product in other solvents. There is a negligible amount of degradation under the conditions employed.

The ethyl celluloses were de-ashed by repeated washing in an acidic medium of controlled swelling power. Since the de-ashing procedure removes an appreciable amount of low molecular weight material, it was necessary to base all comparisons on neutralized de-ashed material.

Commercial samples of ethyl celluloses used in this investigation had quite a range of bound carboxyl, from 15 to 84 microequivalents per gram (abbreviated $\mu\text{eq./g.}$) after de-ashing. In general, the amount of carboxyl decreased as the chain length rose. This and other evidence indicates that the carboxyls are largely present as end groups.

In order to secure a series of samples with varying carboxyl content but the same chain length, additional carboxyl groups were introduced in the commercial sample of lowest content by reaction with chloroacetic acid in alkaline medium. De-ashing the original and the carboxymethylated products fractionated the two materials to the same extent and, hence, yielded products of the same chain length as was shown by the equal intrinsic viscosities of the free-acid forms in suitable solvents.

Most of the samples studied had received no fractionation other than that involved in the de-ashing treatment. One fraction, however, was studied, but unfortunately it had such a low substitution (45% ethoxyl) that samples neutralized with barium were insoluble in representative non-polar solvents. The other samples studied were in the range 47–48% ethoxyl and were soluble in a wide variety of solvents. In the figures and the accompanying discussions, the individual samples are designated as follows: The initial letter shows the parent ethyl cellulose as described in Table I, and the following number and symbols give the microequivalents per gram of carboxyls which carry the indicated ion or radical.

Viscosity.—Since this study was intended to apply primarily to the methods used to estimate molecular weights, all viscosities reported are in the dilute solution range. Several concentrations ranging down from 1 g. per 100 ml. were used in order to allow extrapolation to zero concentration. The results were plotted on semi-logarithmic paper: specific viscosity divided by concentration (η_{sp}/C) against concentration (C) in grams per 100 ml.⁵

The magnitude of the effects found is shown in

(5) A. F. Martin, Am. Chem. Soc. meeting, Memphis, Tenn., April, 1942; *cf.*, E. Ott, ref. 2, p. 966.

Fig. 1. This is representative of the behavior of a normal medium viscosity ethyl cellulose in a very non-polar solvent. It will be noted that the de-ashed sample, D 28-H, showed a perfectly normal behavior in benzene; by extrapolation, its intrinsic viscosity is about 3.0. A startling rise in viscosity, that is, from 12 to 400 c.p.s., for a 1% solution, results from neutralization of the carboxyls by barium (D 28-Ba). Even sodium (D 28-Na) produces a large effect. The effect diminishes with concentration. Without too much stretching of the imagination, all three curves could be extrapolated to the same value of intrinsic viscosity.

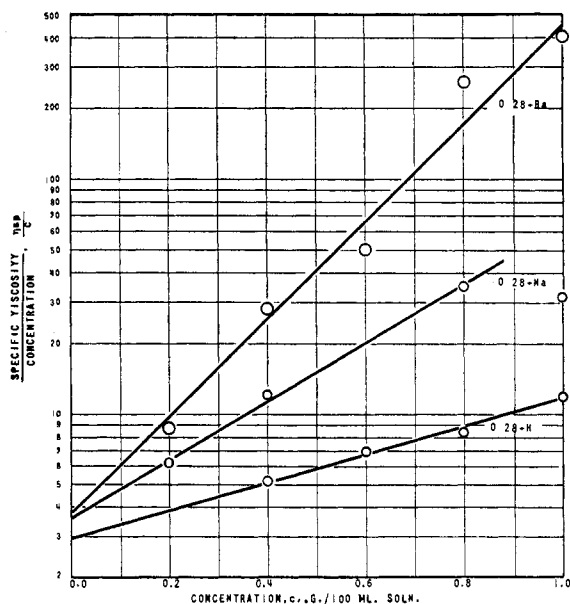


Fig. 1.—Viscosity-concentration data for N-300 ethyl cellulose (D) in benzene.

The scatter of the points shown in Fig. 1 for the neutralized samples is due to two main factors: the very great sensitivity of the solutions to water, and precipitation on dilution. The sensitivity to water is illustrated by the data shown in Fig. 2. Successive measurements of the flow times of a 1% solution of D 28-Ba in benzene decreased steadily. In desperation, drying tubes were attached, the instrument allowed to stand overnight, and dry air bubbled through. There was an immediate rise in viscosity. In order to make sure that this was not due to evaporation, the drying tubes were removed. The viscosity dropped rapidly as soon as air from the room came in contact with the solution.

The other troublesome effect was precipitation on dilution. The 1% stock solutions appeared to be perfectly stable, even after standing for several weeks. During the course of the work, however, some of the more dilute solutions deposited almost invisible droplets of gel. In the later stages of the work dilution viscometers

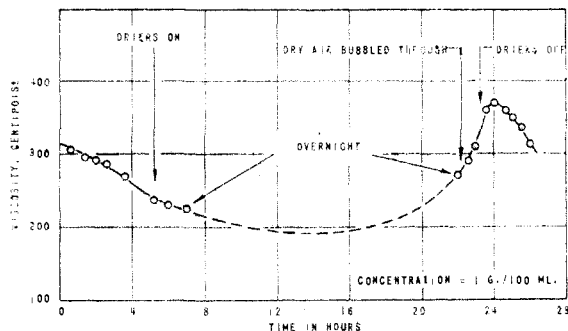


Fig. 2.—Effect of water absorption on viscosity of ethyl cellulose D 28-Ba in benzene.

(see experimental section) were adopted to minimize this phenomenon.

Rather than attempting to cope with these experimental difficulties, attention was concentrated on finding conditions under which the effects of bound metal were more amenable to measurement. The use of more polar solvents, such as mixtures of alcohol and aromatic solvents, was found to eliminate most of these difficulties.

Mixtures of alcohol and aromatic solvents are very widely used with ethyl cellulose. Thus, in a solvent of 70% benzene and 30% alcohol, Sample D 28-Ba exhibits somewhat higher viscosity than its free acid analog, D 28-H, as shown in Fig. 3. Within experimental error, the same intrinsic viscosity is obtained for both samples upon extrapolation. Sample C 84, with shorter chain length and correspondingly greater carboxyl content, shows an increased effect for barium but none for sodium. It may be noted that both these samples have about the same number of carboxyls per chain.

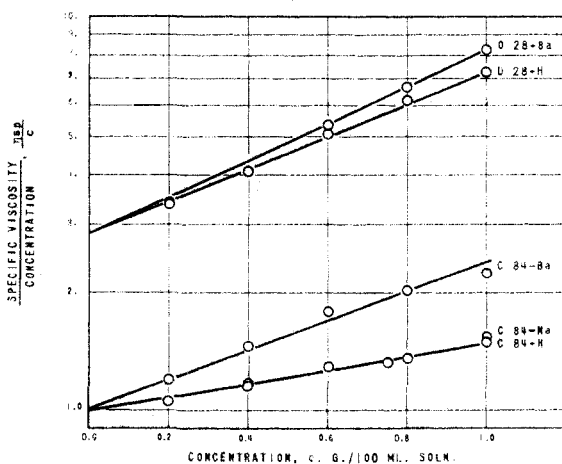


Fig. 3.—Viscosity-concentration data for N-14 (C) and N-300 (D) ethyl celluloses in 70% benzene-30% alcohol.

Sample A 15 was chosen to illustrate a greater number of variations in the same solvent (Fig. 4). There is no perceptible difference, in benzene-

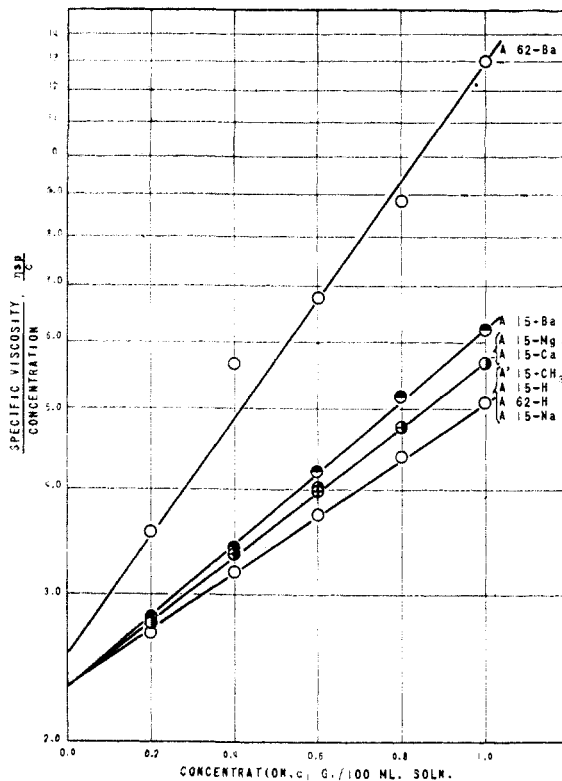


Fig. 4.—Viscosity-concentration data for K-120 ethyl cellulose (A) in 70% benzene-30% alcohol.

alcohol solvent, between the acid form, the methyl ester, the sodium salt, and the acid form of the carboxymethylated product (A 62-H). Magnesium and calcium give about half as much in-

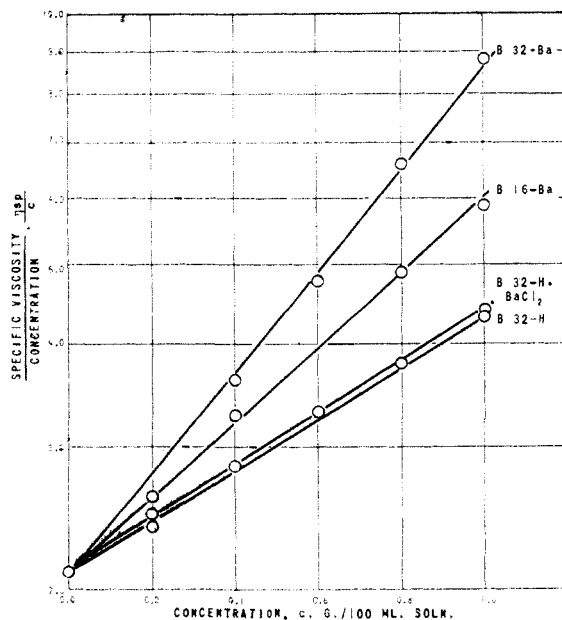


Fig. 5.—Viscosity-concentration data for N-100 ethyl cellulose (B) in 70% benzene-30% alcohol.

crease as barium. The effect with barium is roughly proportional to the amount of barium. (Solutions of Samples A 62-Ba separate into two fluid phases after several weeks.) A further comparison of barium content is shown in Figs. 5, 6 and 7. In these samples the extents of neutralization but not the carboxyl content were varied. The effect of bound barium is again roughly proportional to the amount present.

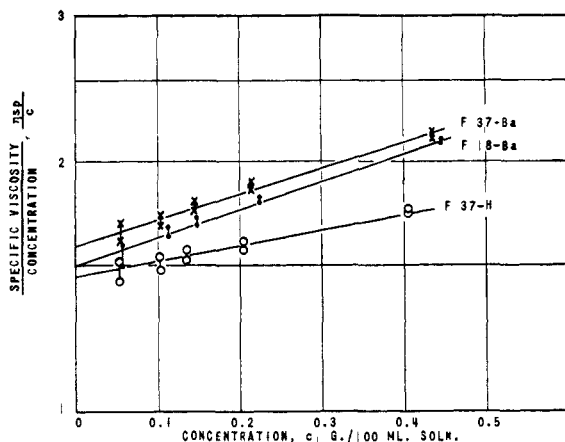


Fig. 6.—Viscosity-concentration data for ethyl cellulose (F) in 70% benzene-28.5% alcohol-1.5% water.

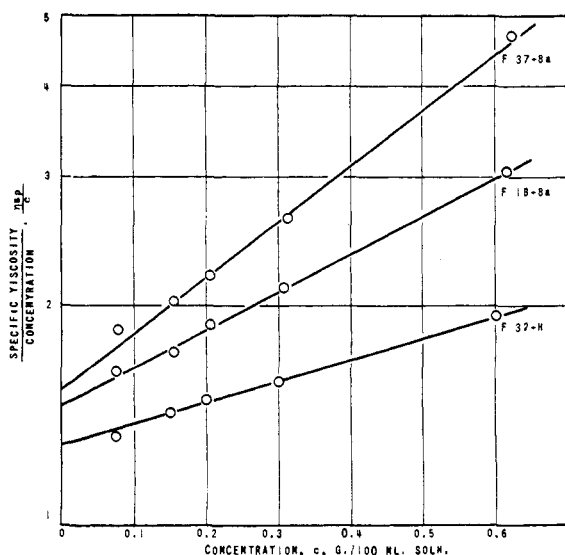


Fig. 7.—Viscosity-concentration data for ethyl cellulose (F) in anhydrous ethylene dichloride.

It has been repeatedly recognized that the abnormal viscosity behavior is associated with the ash content of cellulosic derivatives. A number of experiments were carried out to prove that the metal content must be present as the salt of the bound carboxyls if there is to be any effect in these dilute solutions. One of these experiments is shown in Fig. 5. Barium chloride added to the de-ashed ethyl cellulose had a negligible

effect in comparison with the effect of bound barium. In other experiments the amount of base was increased above that required to neutralize the carboxyls. The excess was found to have no effect.

The measurements were extended to higher dilutions in the experiments shown in Figs. 6 and 7. The probable error is indicated in Fig. 6. As is evident, it is impossible to decide whether there is any difference in intrinsic viscosity among the three samples. It is certain that there is a difference in viscosity at higher concentrations, however. There appears to be a definite trend of the intrinsic viscosity of Sample F 37 in ethylene dichloride. This parallels the behavior of Sample D 28 in benzene (*cf.* Fig. 1).

Methyl acetate containing methanol shows a behavior roughly similar to benzene-alcohol, as is shown by a comparison of Fig. 8 with Figs. 3 and 4.

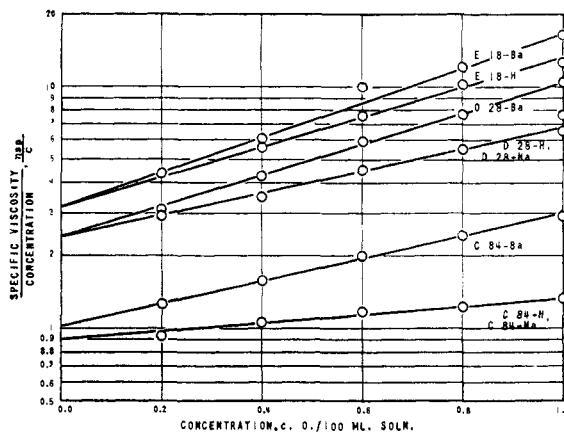


Fig. 8.—Viscosity-concentration data for N-14 (C), N-300 (D) and N-1000 (E) ethyl celluloses in methyl acetate.

The results presented here can be considered under a unified viewpoint. As is shown in Fig. 9, the slope of the reduced viscosity plot ($\Delta \log \eta_{sp}/C / \Delta C$) seems to have a minimum value for a chain with no bound metal ions. Furthermore, the Martin equation,⁵ $\log \eta_{sp}/C = \log [\eta] + K[\eta]C$, which implies a slope constant proportional to the intrinsic viscosity, holds only for the ash-free samples; the effect of metal ion increases in the order $\text{Na}^+ < \text{Mg}^{++} \approx \text{Ca}^{++} < \text{Ba}^{++}$; free carboxyl groups have no effect; and, finally, the effect of bound metal ions decreases as the water or alcohol content of the solvent increases.

The intrinsic viscosity determined by extrapolation of experimentally determined points is not influenced appreciably by bound metal if solvents containing large amounts of water or alcohol are used. However, extrapolation from one experimental point by means of the Martin or a similar equation should not be attempted unless the sample is ash-free.

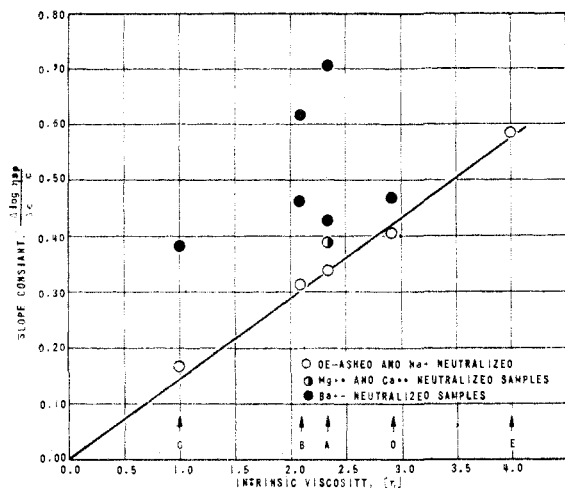


Fig. 9.—Slope constants of viscosity-concentration curves vs. intrinsic viscosities for 70% benzene-30% alcohol solutions.

Osmotic Pressure.—Much effort has been expended in trying to find an effect of bound metal ions on osmotic pressure. In general, there appears to be no effect on the value of π/C extrapolated to zero concentration, provided moderately good solvents containing hydroxyl groups are employed. The value of osmotic pressure at finite concentrations appears to be lowered by bound metal. In fact, a condition that leads to a high slope of the η_{sp}/C curve leads to a low slope of the π/C curve.

The measurements with barium-neutralized samples have not been too satisfactory. To some extent this was due to diffusion through the membrane of the unfractionated samples. Base exchange with the membrane may be another source of error.

Some of the better runs are presented in Fig. 10. No curves are available for D 28-H in methyl acetate. The two upper curves (G and E 18-H) give the slope of de-ashed samples in methyl acetate. On long standing, D 28-Ba separated into two phases at concentrations below 0.4% in benzene.

Discussion

There is no doubt that the effect of bound metal ions is to produce large electrostatic forces of attraction between the chains to which they are attached. Accordingly, the effect of water or alcohol added to the solvent is understandable from two points of view. The metal ions will be solvated, increasing their radius and therefore decreasing their force of attraction for the negative carboxyl groups. Also, the solvent of high dielectric constant will cluster around the ions, still further decreasing the force. The large effect of sodium in benzene may appear surprising, but it must be remembered that sodium salts in general are quite insoluble in anhydrous benzene.

The results on ethyl cellulose reported by

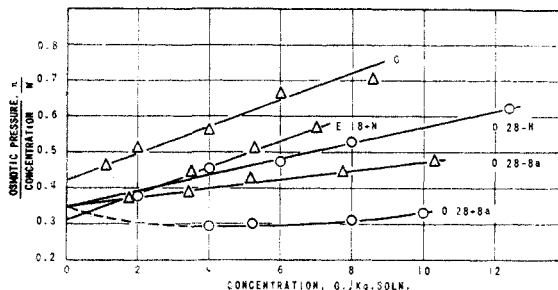


Fig. 10.—Osmotic pressure-concentration data for N-300 (D), N-300 (G) and N-1000 (E) ethyl celluloses in methyl acetate (Δ) and benzene (\circ).

Steurer⁶ are similar to those reported here. Steurer, however, did not recognize that the effect was due to bound metal ions. His experience leads to the question whether other cases of abnormal behavior in solution that have been reported in the literature are due to bound metals. This question has been examined by Morey and Tamblin,⁷ who could find no evidence that the abnormal order of precipitation of low molecular cellulose acetate with non-polar diluents was due to bound metal. These investigations did find a correlation with the content of end groups. In the present work the carboxyl content of commercial samples has been found to be roughly equal to the number of end groups. Sully⁸ has described qualitative effects with polystyrene containing acid end groups neutralized with a metal ion that are similar to those found in our work.

It is our opinion that any portion of a long-chain molecule, which is inherently insoluble in the medium, will lead to association effects similar to those due to bound metals. The results with Sample A 62 are significant in this connection since there were too many carboxyls to allow a significant fraction of them to be end groups. In spite of this, the effects of neutralization with barium were quite similar to those with the commercial samples. We may expect that random fluctuations in the structure of cellulose derivatives or of copolymers will allow the local accumulation of groups that have a high attractive force for similar groups in other chains. The effect of these groups on viscosity and osmotic pressure in poor solvents should be scarcely distinguishable from that of metal ions.

When the content of bound barium was increased above about 70 $\mu\text{eq./g.}$, the samples became insoluble in benzene. This was true, for example, with Sample C 84-Ba. The increase in viscosity observed with lower contents is thus a stage in the progression toward insolubility. This conclusion is also supported by the osmotic pressure work, a lower slope of the reduced

(6) E. Steurer, *Z. Physik. Chem.*, **190**, 1 (1942).

(7) D. R. Morey and J. W. Tamblin, *J. Phys. Chem.*, **50**, 12 (1946).

(8) B. D. Sully, *Nature*, **159**, 882 (1947).

osmotic pressure curve being generally conceded to be evidence of lower solubility.

In our work, a conclusive comparison between changes of slope of the reduced viscosity curve and solubility is possible, since the intrinsic viscosity was substantially unchanged by the effect which resulted in lower solubility. In other systems this is not true. For example, if the behavior of different solvents on a given polymer is examined, both the intrinsic viscosity and the slope of the viscosity curve are usually changed. Spurlin⁹ has proposed that the proper base of comparison in such cases is the constant *K* in Martin's equation. Certainly the correlation in Fig. 9 and others not reported here support the conclusion that the solvent power is inversely related to *K*.

It is true that these conclusions found experimental support only in the case where the tendency toward insolubility was due to only a small portion of the polymer molecule. It is equally true that one of the most urgent problems at present is a system of evaluation of the solvent power of plasticizers. Plasticizers are most useful with polymers which show a tendency to the same type of gelation behavior with poor solvents that is shown by the celluloses. Gelation rather than precipitation is characteristic of polymers with comparatively few poorly soluble groups along the chain.

It is apparent that the type of polymer under discussion requires mixed solvents for best solubility. If the results presented here are any criterion, many workers in the past have spent too much effort in purifying their solvents for osmotic and viscosity work with polymers. In fact, they would usually have been better advised to add some water and possibly alcohol or acetic acid. We have uniformly found better reliability in our results if we used solvents which gave a low slope of the reduced viscosity plot and a high slope for the reduced osmotic plot.

Experimental

Materials.—Ethyl celluloses A, B, C, D and E were commercial products with the properties described in Table I. Ethyl cellulose F was a large fraction obtained from a fractionation of a G-100 ethyl cellulose. The de-ashed (see below) G-100 ethyl cellulose was dissolved in methyl acetate at 40° and brought almost to the precipitation point by the addition of hexane. Fifty-nine per cent. of the ethyl cellulose was removed in thirteen fractions by successive lowerings of the temperature. Ethyl cellulose F was the fourteenth fraction and represented 18.7% of the sample.

The 70:30 (by weight) benzene:alcohol solvent employed was prepared from commercial benzene and denatured 2B alcohol (95%). Benzene and ethylene dichloride, when used as single solvents, were dried by removal of the solvent-water azeotrope and then distilled. The methyl acetate was commercial material and, hence, contained methanol.

Preparation of Samples

Deashing.—All of the ethyl celluloses were first de-ashed by the following procedure: The ethyl cellulose was

TABLE I

Ethyl cellulose	Type ^a	% Ethoxy	Carboxyls, ^b μ eq./g.
A	K-120	46.0	15
B	N-100	..	32
C	N-14	48.3	84
D	N-300	48.2	28
E	N-1000	47.4	18
F	G-100 fraction	..	37

^a Cf. trade booklet, "Ethyl Celluloses, Properties and Uses," Hercules Powder Company, Wilmington, Del.; the numbers refer to the viscosity in centipoises of 5% solution in toluene-alcohol solvent mixture; the letters designate the ethoxy range G (44.5-45.5%), K (45.5-46.8%) and N (46.8-48.5%). ^b The numbers designate the total free carboxyls, after de-ashing, in microequivalents per gram determined as described by McBurney, ref. (10).

steeped with agitation for two hours at room temperature in approximately six times its weight of alcoholic hydrochloric acid (300 ml. of 99% isopropyl alcohol + 700 ml. of water + 100 ml. of 0.1 *N* hydrochloric acid). After removing the free liquid by filtration, the process was repeated. The moist product was then steeped several times in dilute alcohol (300 ml. of isopropyl alcohol and 700 ml. of water) and finally was washed with distilled water until the filtrate was free of chloride ion. The de-ashed ethyl cellulose was then dried in a vacuum oven at 50-60°. The products were stored in a refrigerator or in an inert atmosphere to guard against oxidative degradation.

By this procedure it has been generally found that the sodium was reduced from several thousand parts per million to less than 100 p. p. m., the limit of the spectrographic method of analysis employed. Iron and magnesium were reduced to about 3-4 p. p. m. and calcium, nickel and other trace elements were reduced to below the limits of detection. Carboxyl determinations, performed as described by McBurney¹⁰ and given in Table I, showed that all of the carboxyls were in the free or acid form within the limits of the method ($\pm 1-2 \mu$ eq./g.). These de-ashed samples were designated A 15-H, B 32-H, C 84-H, D 18-H and F 37-H; the initial letters showing the parent ethyl celluloses, H shows that the carboxyls were not neutralized, and the number gives the microequivalents of carboxyl groups per gram.

Carboxymethylation.—Additional carboxyl groups were introduced into ethyl cellulose A by reaction with chloroacetic acid. A solution of ethyl cellulose A (200 g.) dissolved in 2.5 l. of benzene and 200 ml. of methanol was heated to refluxing on a water-bath in a 5-liter, 3-necked flask carrying a reflux condenser, a mercury-sealed stirrer and a dropping funnel. A solution of 48 g. of sodium dissolved in 500 ml. of methanol was added through the condenser over the period of 1.5 hours simultaneously with 90 g. of chloroacetic acid dissolved in 500 ml. of warm benzene. The rate of addition of the alkali was adjusted so as to maintain the reaction mixture on the alkaline side at all times. The product was recovered in small, uniform granules by pouring the reaction mixture slowly into boiling water. It was washed free of alkali with distilled water and then was de-ashed as described above. The final product was found to contain 62 μ eq. of free carboxyls per gram and was designated A 62-H.

Methylation and Neutralization.—In order to obtain a sample containing no free or neutralized carboxyl groups, the carboxyls of de-ashed ethyl cellulose A were methylated with diazomethane. Thus, to a solution of ethyl cellulose A 15-H dissolved in 90:10 benzene:methanol was added a solution of diazomethane in benzene until the reaction mixture attained a permanent yellow color. The product was precipitated by adding the solution dropwise to vigorously stirred, boiling water. The dried product

(9) H. M. Spurlin, *J. Polymer Sci.*, **3**, 714 (1948).

(10) L. F. McBurney, *Ind. Eng. Chem.*, **41**, 1252 (1949).

contained no detectable free or neutralized carboxyl groups by the titration method and was designated A 15-CH₃.

The samples containing bound cations were prepared by neutralizing the carboxyls of the de-ashed ethyl celluloses. A weighed quantity of de-ashed ethyl cellulose of known (free) carboxyl content was dissolved in 70:30 benzene:alcohol to make a solution of 5-10% concentration. The calculated amount of standard sodium methylate or of standardized aqueous barium hydroxide was added to neutralize the free carboxyls, either completely or partially as desired, with Na⁺ or Ba⁺⁺, respectively. For Ca⁺⁺ and Mg⁺⁺, the solutions of the de-ashed ethyl celluloses were stirred with an excess of finely powdered calcium hydroxide or magnesium hydroxide and the excess was removed by centrifugation. The neutralized solutions were then poured into glass trays and the solvents allowed to evaporate. The stripped films were dried in the vacuum oven at 50-60° for 24 to 48 hours. In some cases the films were cut into small pieces and put through a Wiley Mill (20-40 mesh screens) along with small pieces of Dry Ice before drying in the oven. The samples containing bound cations were prepared by these procedures and designated A 15-Na, A 15-Mg, A 62-Ba, B 16-Ba, etc., with the numbers giving the microequivalents per gram of bound cations.

Viscosity Determinations.—For most of the work, solutions at the given concentrations were prepared by weight dilutions of a stock solution. The stock solution was prepared at the highest concentration desired which was usually 1 g./100 ml. of solution. The stock solution was either filtered or allowed to stand in a closed bottle for 24 hours to allow any sediment to settle to the bottom and then the top portion was siphoned into a clean bottle. The viscosities of these solutions were then measured in Ubbelohde viscometers applying kinetic energy corrections to the observed flow times.

The data given in Figs. 6 and 7 for ethyl cellulose F samples were determined in a Ubbelohde viscometer modified so that dilution of the stock solution could be performed within the viscometer. This viscometer was designed by Dr. R. L. Spaulding and its use has been described by Davis and Elliott.¹¹

Osmotic Pressure Determinations.—The osmotic pressure measurements were made by the static elevation method in a Herzog and Spurlin¹² osmometer as modified

(11) W. E. Davis and J. H. Elliott, *J. Colloid Sci.*, **4**, 315 (1949).

(12) R. O. Herzog and H. M. Spurlin, *Z. physik. Chem., Bodenstedt-Festband*, p. 239 (1931).

by Fuoss.¹³ Membranes of undried cellophane were employed.

Acknowledgment.—It is impossible to list all of those who have contributed to this problem. We would like particularly to mention Dr. R. L. Spaulding, who carried out much of the program; Dr. F. C. Foster and Mr. R. A. Mock, who carried out the osmotic work; and Mr. W. H. Markwood and Dr. J. H. Elliott, who took great interest in the viscosity determinations.

Summary

Free carboxyls present in ethyl cellulose molecules have no effect upon the viscosity of dilute solutions. Neutralization of these carboxyls with metal ions, however, caused an increase in the viscosity of solutions at finite concentrations. This increase was greatest in non-polar solvents and least in solvents containing appreciable water or alcohol. In the latter solvents the intrinsic viscosity was not affected. The viscosity increase was least for sodium, greatest for barium, and intermediate for calcium and magnesium. Bound barium decreased the slope of the reduced osmotic pressure-concentration curve but did not alter the intercept at infinite dilution for those solvents containing alcohol or water.

For polymers containing bound metal ions it is recommended that solvents containing water, alcohol, or acetic acid be used for the determination of viscosity or osmotic pressure and that the values at infinite dilution be obtained by the extrapolation of experimentally determined values. The best results are obtained by using solvents with a low slope of the reduced viscosity-concentration curve and a high slope for the reduced osmotic pressure-concentration plot.

(13) R. M. Fuoss and D. J. Mead, *J. Phys. Chem.*, **47**, 59 (1943).

WILMINGTON, DEL.

RECEIVED APRIL 1, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Influence of a CF₃ Group on an Adjacent Double Bond. II

BY ALBERT L. HENNE, MALCOLM A. SMOOK¹ AND RALPH L. PELLEY¹

In a preceding paper,¹ we have shown that CF₃CH=CH₂ accepts hydrogen chloride or bromide to yield CF₃CH₂CH₂Cl or CF₃CH₂CH₂Br exclusively, and that it does so only at high temperature, in the presence of a Lewis acid as catalyst. These results were taken as indication that the electronegative induction of the CF₃ group had polarized the double bond to make its central carbon more negative than its outer carbon, and had rendered it less responsive to an electrophilic attack. It seemed, therefore, fair to expect a nucleophilic attack to be favored, yet

(1) Socony Vacuum Fellows, 1948-1949 and 1949-1950, respectively.

(2) Henne and Kaye, *THIS JOURNAL*, **72**, 3389 (1950).

it is reported that sodium methoxide, primary amines and sodium malonic esters do not add to trifluorinated olefins of the CF₃CH=CHR type,³ and we could not add acetic acid to either CF₃CH=CH₂ or CF₃CH=CHCF₃ in the presence of sodium acetate.⁴ These results looked illogical, in view of the fact that a triple bond flanked by CF₃ groups is very easily affected by a nucleophilic attack.⁵ We had suggested that the experimental failures were due to a parasite reaction, predominant solvolysis of the CF₃

(3) Campbell and Knobloch, Abstracts of Papers, 115th Meeting, Am. Chem. Soc., Atlantic City, September, 1949, p. 6M.

(4) Henne and Pelley, unpublished.

(5) Henne, Schmitz and Finnegan, *THIS JOURNAL*, **72**, 4195 (1950).