

The Influence of Solvent Type on the Viscosity of Concentrated Polymer Solutions

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Synopsis

The viscosity of concentrated (17.5 g/dl) solutions of cellulose acetate in 11 single solvents and in four binary solvent mixtures was related to a thermodynamic measure of solvent power. In single solvents, the specific viscosity varied from 4600 in dimethyl sulfoxide to 78,000 in diacetone alcohol, with the specific viscosity increasing with decreasing absolute value of the partial molar free energy of dilution. This behavior can be accounted for by the hypothesis that the number of chain entanglements increases with decreasing solvent power. In solvent mixtures, the specific viscosity often attains a minimum value at a composition where the average solubility parameter locus is near the center of the solubility region of the polymer.

INTRODUCTION

Many applications of polymers utilize a concentrated solution in some stage of processing, and the viscosity of the solution may have an important influence upon the properties of the finished product. The application of particular interest to our group was the fabrication of reverse osmosis membranes for water desalination.

These membranes are commonly made by forming a thin layer of concentrated polymer solution, exposing it to air for a few seconds to a few minutes, followed by immersion in a nonsolvent to effect gelation and desolvation.^{1,2,3} The morphology and osmotic properties of the resultant membrane are controlled by the composition of the solvent mixture in the casting solution, and it is believed that this control is exerted through the effect of the solvents upon the configuration of the dissolved polymer molecules³ and upon the rate of desolvation and gelation.⁴ Because the viscosity influences the rate of desolvation and gelation, and because the specific viscosity gives information about the chain configuration in solution, we desired to know how the viscosity of membrane casting solutions is affected by solvent composition.

Although there is considerable knowledge of the relationship between viscosity and solvent type in dilute solutions (concentrations no larger than 1 g/dl),⁵ there is little published information about the relationship in concentrated solutions (10 g/dl or larger).

The specific viscosity, η_{sp} , is defined by $(\eta - \eta_0)/\eta_0$, where η and η_0 are the solution and solvent viscosities, respectively, and the limiting value of η_{sp}/C , where C is polymer concentration, as C approaches zero is called the intrinsic viscosity, $[\eta]$. The intrinsic viscosity is related to the volume of individual molecules in solution and increases with increasing solvent power; i.e., in good solvents the chains are extended, and in poor solvents the chains are coiled tightly to reduce thermodynamically unfavorable contacts with the solvent. The nature of the solvent also affects the rate at which η_{sp} increases with concentration. But even this basic knowledge of dilute polymer solution is not useful for understanding the properties of cellulose acetate solutions because $[\eta]$ and $d\eta_{sp}/dC$ exhibit no systematic variation with solvent power.⁶

Only two articles dealing with the effect of solvent on the viscosity of concentrated solutions were found. Gandhi and Williams⁷ studied the behavior of poly(methyl methacrylate) solutions and discovered that at a concentration of 20 g/dl, η_{sp} in *m*-xylene (a poor solvent) was about ten times as large as η_{sp} in chlorobenzene (a good solvent). At the same concentration of poly(vinyl acetate), Ferry et al.⁸ found that η_{sp} of a trichloropropane solution was about 50 times that of a methyl ethyl ketone solution.

The purpose of the present investigation was to determine how the specific viscosity of cellulose acetate solutions is related to the type of solvent or solvent mixture.

EXPERIMENTAL

Viscosities of greater than 50 poises were measured with a Brookfield electric viscometer; the viscosities of thinner solutions were measured in Cannon-Fenske viscometers. All measurements were made at 25.0°C. The cellulose acetate was Type E-383-40 from Eastman Chemical Products. According to the manufacturer, its number-average molecular weight is approximately 52,000 and the weight-average value is slightly less than twice as large. The degree of acetyl substitution is 2.3 (average number of acetyl substituents per anhydroglucose unit), giving a mer molecular weight of 259. All solvents were reagent grade or the best lower grade available.

Dissolution of the polymer was accomplished by rolling bottles of the mixtures at a rate to give maximum shear, i.e., the rolling speed was lowered with solutions of higher viscosity. It was discovered that to obtain constant successive viscosity readings with solutions made from low-viscosity solvents such as acetone, methyl acetate, and tetrahydrofuran (THF), it is necessary to continuously roll the solutions. Upon standing the apparent viscosity decreases with time. For example, the steady-state viscosity of a THF solution was 310 poises, but the apparent viscosity of the same sample, when statically thermostated, decreased over two-day intervals to 230, 190, and 130 poises, respectively. Repetitive

measurements on rolled samples gave values with an average deviation of 5% to 10%. Unless stated otherwise, all solution concentrations were 17.5 g/dl of solvent.

RESULTS AND DISCUSSION

From the viscosity data of cellulose acetate in 11 solvents, it became apparent that at a concentration of 15–20 g/dl the specific viscosity varied considerably with the solvent. For example, the specific viscosity of a diacetone alcohol solution was 18 times greater than that of a dimethylsulfoxide (DMSO) solution. The results for solutions of cellulose acetate in 11 solvents are given in Table I. From these data, it is also seen that the combined effects of differences in specific viscosity and solvent viscosity permit a 40-fold range of solution viscosities. It was also observed that differences between specific viscosities are larger at higher polymer concentrations. For example, the ratio η_{sp} (acetone)/ η_{sp} (pyridine) changes from only 1.08 at 1 g/dl to 7.35 at 25 g/dl. This concentration dependence of specific viscosity is shown in Figure 1.

Before the concentration dependence is analyzed, we will examine how η_{sp} is related to a thermodynamic measure of solvent power. The universally used measure of solvent power is the Flory-Huggins parameter χ , defined by

$$\overline{\Delta F}_1 = \mu_1 - \mu_1^0 = RT \left[\ln(1 - \phi_2) + \left(1 - \frac{1}{N}\right) \phi_2 + \chi \phi_2^2 \right] \quad (1)$$

where $\overline{\Delta F}_1$ is the partial molar free energy of dilution; μ_1 and μ_1^0 are the chemical potentials of the solvent in a polymer solution and in a pure state, respectively; R is the gas constant; T is the temperature; ϕ_2 is the

TABLE I
Viscosity of Cellulose Acetate Solutions^a

Solvent	Solvent viscosity η_0 , cps	Solution viscosity η , cps $\times 10^{-3}$	Specific viscosity η_{sp} , $\times 10^{-3}$
Acetone	0.316	9.2	29
Acetonitrile	0.345	9.5	27
γ -Butyrolactone	1.60	23	14
Diacetone alcohol ^b	2.84	220	78
Dioxane	1.25	30	24
Dimethylformamide	0.773	6.3	8.2
Dimethyl sulfoxide	1.96	9.0	4.6
Methyl acetate	0.364	18	49
Methyl acetate ^b	0.473	5.5	12
Morpholine	2.08	17	8.3
Pyridine	0.90	5.4	6.0
Tetrahydrofuran	0.46	31	68

^a All solution concentrations were 17.5 g/dl.

^b Technical-grade materials.

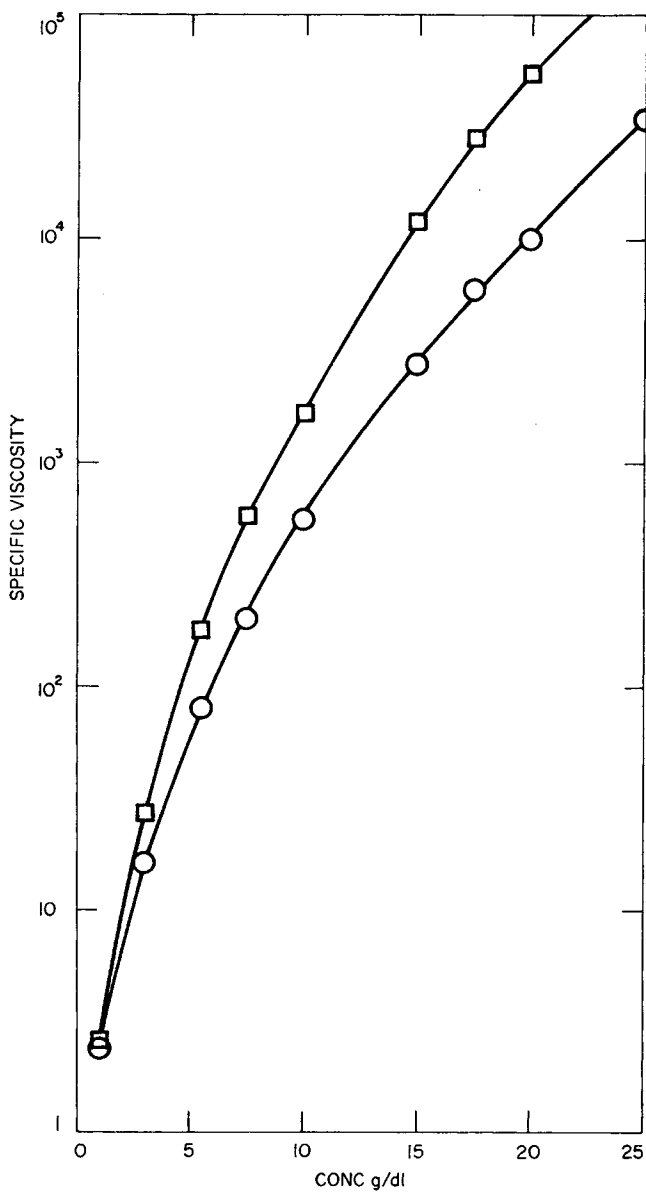


Fig. 1. Concentration dependence of viscosity of cellulose acetate solutions: (□) acetone solutions; (○) pyridine solutions.

volume fraction of polymer in the solution; and N is the number-average molecular weight of the polymer.⁹ If the entropy of solution were ideal, χ would simply be a measure of the polymer-solvent interaction energy, relative to that of pure polymer and pure solvent. However, as it is defined, it includes the excess entropy of mixing. Thermodynamically, the

best solvent for a specific polymer may be taken as that which gives the largest negative free energy of mixing,

$$\Delta F_m = RT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi n_1 \phi_2) \quad (2)$$

where n_1 and n_2 are the number of moles of solvent and polymer, respectively. Because the first two terms are negative, the strongest solvent will be the one with the smallest value of χ . For most polymer-solvent systems, χ values range between 0 and 0.5, although negative values have been reported.

Moore studied the viscosity and thermodynamic properties of dilute solutions of cellulose acetate and found no relationship between the intrinsic viscosity or the slope of η_{sp} versus concentration, and either χ or $\overline{\Delta F}_1$.^{6,10,11} These results are shown in Table II (k of Table II is defined by

TABLE II
Viscosity and Thermodynamic Properties of Dilute Cellulose Acetate Solutions^a

Solvent	χ	$[\eta]$	k	Vol. hexane, ^b ml/25 ml	$-\overline{\Delta F}_1$ (30°C), ^c (cal/mole) $\times 10^3$
Acetone	0.45	1.49	0.61	2.5	5.9
Methyl acetate	0.46	1.48	0.28	1.5	5.1
Pyridine	0.28	1.46	0.22	10.5	10.7
Nitromethane	0.44	1.73	0.48	—	5.2
Aniline	0.375	1.96	0.45	—	9.7
<i>m</i> -Cresol	—	1.82	0.27	42	—
Dioxane	0.38	1.70	0.39	3.8	8.8

^a Data from references 10 and 11.

^b At a concentration of 0.25 g/dl.

^c At a concentration of 1 g/dl.

$\eta_{sp}/C = [\eta] + k[\eta]^2C$). However, a useful key for our study of concentrated solutions was provided by the observation that there is a direct correlation between χ or $\overline{\Delta F}_1$ and the volume of hexane required to precipitate the polymer from solution. With this lead, all solutions previously used for viscosity studies were titrated with hexane, with the results given in Table III and displayed in Figure 2. (No titration data are reported for acetonitrile, γ -butyrolactone, DMF, or DMSO solutions because immiscibility is encountered before polymer precipitation. Carbon tetrachloride or benzene are generally not suitable as a substitute for hexane because their larger index of refraction often obscures the point of precipitation. Even where endpoints could be seen during titration, the volumes did not correlate with the volumes of hexane. For all solvents, good endpoints were obtained by titration with diethyl ether, but the data were only poorly correlated with η_{sp} data.) It is seen that η_{sp} monotoni-

cally increases as the solvent power decreases, i.e., as the partial molar free energy of dilution becomes less negative or the hexane titer decreases.

Similarly, the increasing difference in specific viscosity of acetone and pyridine solutions with increasing polymer concentration is correlated with

TABLE III
Properties of Celulose Acetate Solutions

Solvent	Specific viscosity, ^a $\times 10^{-3}$	Hexane titration, ml/25 ml	$-\overline{F}\Delta_1$, ^b cal/mole
Pyridine	6.0	12.4	17
Morpholine	8.3	8.6	—
Methyl acetate ^c	12	5.4	—
Dioxane	24	3.8	7
Acetone	29	3.4	8
Methyl acetate	49	1.5	4
Tetrahydrofuran	68	2.0	—

^a At a concentration of $\phi_2 = 0.115$.

^b At a concentration of $\phi_2 = 0.230$. Data from reference 12.

^c Technical-grade material.

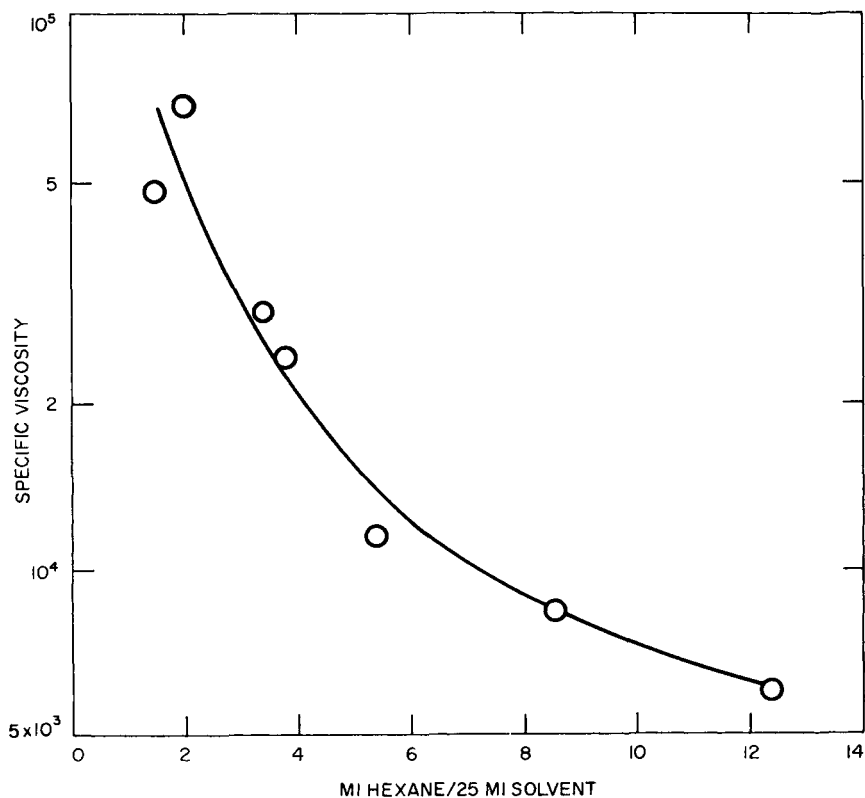


Fig. 2. Relationship between viscosity and hexane tolerance of solution.

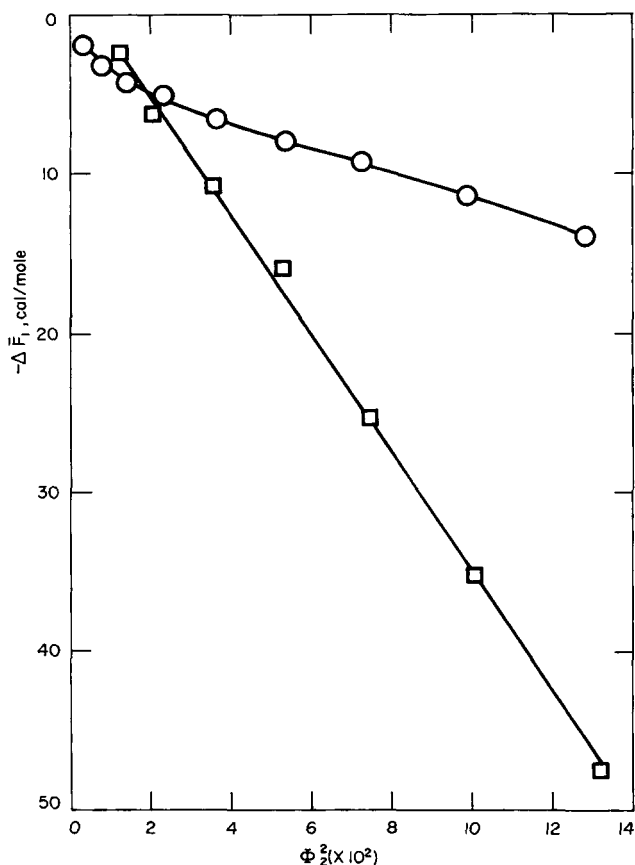


Fig. 3. Partial molar free energy of dilution and polymer concentration: (O) acetone; (□) pyridine.

the divergence in $\overline{\Delta F}_1$ values with increasing concentration. The latter fact is shown by graphing Moore's data¹² in Figure 3. This differential behavior is expected from eq. (1), which for constant χ gives

$$\frac{\partial \Delta F}{\partial \phi_2} = \phi_2 \left[2\chi - \frac{1}{1 - \phi_2} \right] \quad (3)$$

Because $\chi < 1/2$, $\overline{\Delta F}$ becomes more negative as ϕ_2 increases and the rate of change is larger for smaller values of χ , i.e., for better solvents. It is, therefore, to be expected that, in general, η_{sp} will increase with polymer concentration more rapidly with a poor solvent than with a good solvent.

It now remains to discover a plausible mechanism to account for the relationship between the specific viscosity and the free energy of mixing of polymer and solvent. An important feature of polymer solutions is the fact that at concentrations of approximately 1 g/dl, chain entanglement occurs and changes the dependence of viscosity on concentration from

first-power to a third- or higher-power relationship. Because of this sensitivity of viscosity to polymer concentration it seems reasonable to ascertain if solvent type could influence the degree of entanglement in a way which would alter the viscosity in the observed direction.

In addition to a concentration dependence, the extent of chain entanglement will depend upon the size of a polymer coil, which is a function of molecular weight and solvent type.⁹ The statistical diameter d of a dissolved polymer chain is given by

$$d = 2\alpha\sqrt{\bar{S}_0^2}$$

where $\sqrt{\bar{S}_0^2}$ is the so-called "random flight" or root-mean-square radius of gyration and α is an expansion coefficient which incorporates the solvent dependence. The radius of gyration S_0 is proportionate to the square root of molecular weight, and α is given by

$$\alpha_5 - \alpha^3 = \frac{K}{V_1} \frac{\Delta\bar{F}_1}{RT\phi_2^2} \quad (4)$$

where V_1 is the molar volume of the solvent and K is a constant depending on S_0 , polymer density, and molecular weight.⁹ For E-383-40 cellulose acetate, $\sqrt{\bar{S}_0^2}$ is approximately 82 Å and K is 530. The expansion coefficient itself will vary much more slowly than the value of $\alpha^5 - \alpha^3$, so that η_{sp} must be very sensitive to coil size. A model which can qualitatively explain the observed behavior is readily developed.

As the friction between neighboring polymer coils must increase rapidly as the number of entanglements (N_e) increases, we will examine how N_e might be expected to change with concentration and size of individual polymer chains. It is postulated that the number of entanglements is proportional to the product of the overlap volume (V_0) between neighboring coils and the square of the number density (ρ) of chain segments in each coil; $N_e \simeq \rho^2 V_0$. For simplicity of analysis, it will be assumed that the polymer chains are present as roughly spherical coils of diameter d . Let ξ represent the average distance between the centers of the polymer coils:

$$\xi \simeq (C N_a / 100 M)^{-1/3}$$

where C is the polymer concentration in g/dl, N_a is Avogadro's number, and M is the molecular weight. The density of polymer segments (of an arbitrary size) will be $\rho \simeq d^{-3}$, and the overlap volume between adjacent coils will be $V_0 \simeq d^2 (d - \xi)$. One then obtains $N_e \simeq (d - \xi)/d^4$, or

$$N_e \simeq \frac{2\alpha\sqrt{\bar{S}_0^2} - (CN_a/100M)^{-1/3}}{8\alpha^4(\bar{S}_0^2)^2} \quad (5)$$

Using eq. (5) and quoted values of S_0 and M for cellulose acetate, the behavior of relative values of N_e with changes in α and polymer concentration is shown in Figure 4. It is seen that according to this model the number of entanglements increases as α decreases (i.e., with poorer sol-

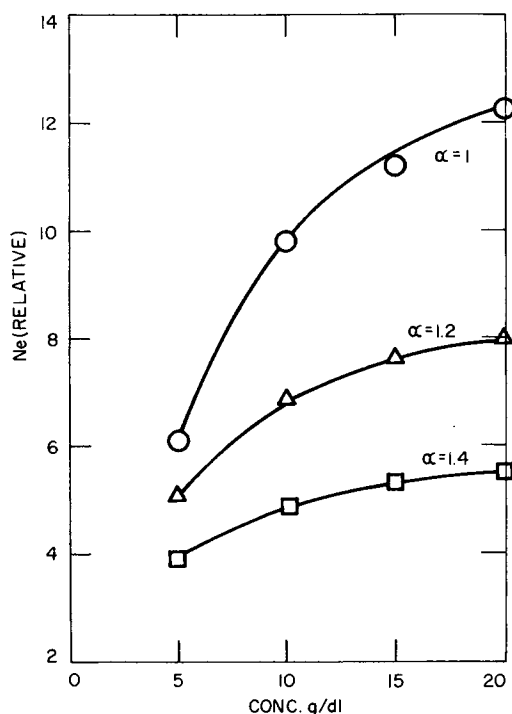


Fig. 4. Dependence of number of entanglements on polymer concentration and coil expansion factor.

vents), and the rate of increase of N_e with polymer concentration is larger for solvents giving smaller values of α . The calculated behavior of α for acetone and pyridine solutions of cellulose acetate is shown below.

Polymer concentration		Acetone		Pyridine	
Volume fraction	g/dl	$\alpha^5 - \alpha^3$	α	$\alpha^5 - \alpha^3$	α
0.15	25	2.8	1.42	3.2	1.44
0.30	50	0.83	1.21	4.2	1.50

These data and the relationship between N_e , α , and C as expressed in eq. (5) account for the divergence of the specific viscosity of acetone and pyridine solutions as the polymer concentration increases. However, the calculated equality of α values at a concentration of 25 g/dl should imply that the number of entanglements (and therefore the specific viscosity) in each solution should be the same, whereas the viscosities differ considerably. The resolution of this difficulty will have to await further data or a more refined theory.

VISCOSITY CHARACTERISTICS OF TERNARY SOLUTIONS

Next, we will consider the more complex case of polymer solutions made from a mixture of two liquids. The behavior of the viscosity of such mix-

TABLE IV
Multiple Solubility Parameters of Liquids Used

Name	Abbreviation	Solubility parameter, cal/mole ^{1/2}	Hydrogen-bonding index	Polarity index
Acetone	AC	9.8	3.4	5.1
Acetonitrile	AN	11.9	3.0	8.8
1-Butanol	BU	11.3	7.7	2.8
γ -Butyrolactone	BL	12.8	3.6	8.1
Diacetone alcohol	DAA	10.2	5.3	4.0
Diethyl ether	EE	7.6	2.5	1.4
Dimethylformamide	DF	12.1	5.5	6.7
Dimethyl sulfoxide	DS	12.9	5.0	8.0
Dioxane	DO	10.0	3.6	0.9
Formamide	FM	17.8	9.3	12.8
Hexane	HX	7.2	0	0
Methanol	ME	14.3	10.9	6.0
Methyl acetate	MA	9.6	4.5 ^a	2.6 ^a
Morpholine	MO	10.5	4.5	2.4
Nitroethane	NE	11.1	2.2	7.6
1-Pentanol	PE	10.6	6.8	2.2
1-Propanol	PR	12.0	8.5	3.3
Propylene carbonate	PC	13.3	2.0	8.8
Propylene glycol	PG	14.8	11.4	4.6
Pyridine	PY	10.6	2.9	4.3
Tetrahydrofuran	THF	9.5	3.9	2.8

^a Assumed to be the same as that of ethyl acetate.

tures as the composition of the solution changes (e.g., by evaporation or leaching) is of importance in the paint and coatings industry. Because of lack of adequate thermodynamic data for binary mixtures of polar liquids and the complexity and imprecision of estimated thermodynamic properties, the solvent power of mixtures will be estimated from a solubility parameter diagram.

Hildebrand defined the solubility parameter δ by

$$\delta^2 = E_v/V$$

where E_v is the energy of vaporization and V is the molar volume. Although the solubility of nonpolar polymers can be understood in terms of δ values of nonpolar solvents, an extension of the concept is necessary for an understanding of the solution properties of polymers containing polar or hydrogen-bonding groups. That is, it is necessary to take into account the separate contribution of dipolar and hydrogen-bonding interactions to the total cohesive energy of the solvent.^{13,14} A polymer may fail to dissolve in a liquid which has the same solubility parameter as the polymer if the polarity index (δ_p) or hydrogen-bonding index (δ_h) is either too small or too large. For example, cellulose acetate is soluble in many solvents (such as DMF) with a δ of about 12 (cal/mole)^{1/2}, but insoluble in other liquids with same value of δ if the δ_h is too small (nitromethane) or too

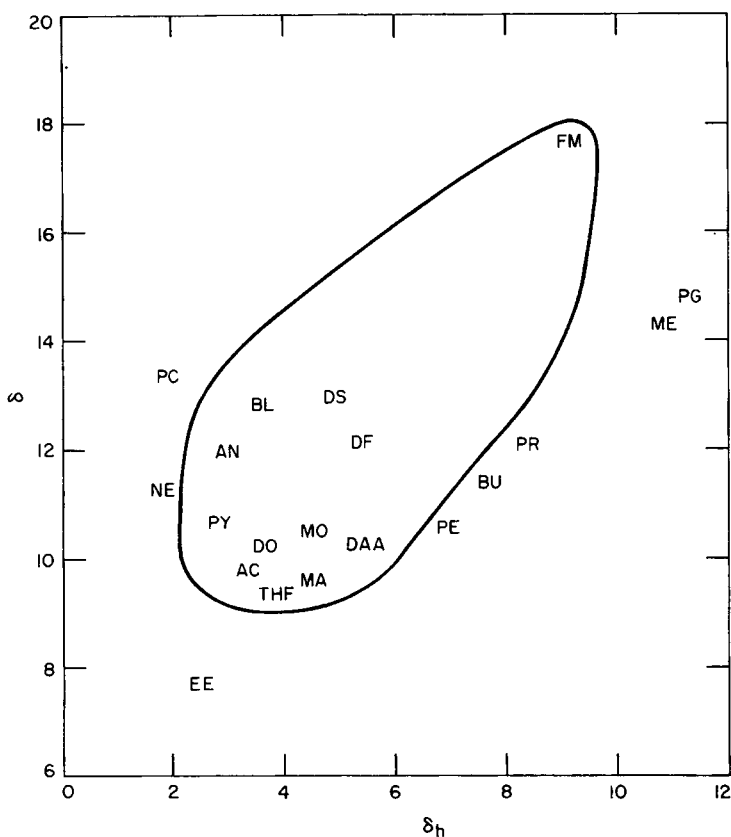


Fig. 5. Solubility diagram for cellulose acetate.

large (propanol). A list of polarity and hydrogen-bonding indices (taken from reference 15) is given in Table IV.

A solubility map for a polymer can be constructed by graphing δ , δ_h , and δ_p loci for liquids and noting the region of solubility. Fortunately, in many cases the solubility behavior of a polymer can be adequately represented by a two-dimensional graph of δ versus δ_h or δ versus δ_p . Such a solubility map for cellulose acetate is shown in Figure 5. It would be expected intuitively that the best solvents would be located near the center of the solubility diagram, and this idea is confirmed by two facts. One, solvents near the center require the largest amount of nonsolvent to cause precipitation (see reference 16). Two, solutions from solvents with loci near the center of the solubility envelope exhibit the lowest specific viscosities. The latter fact can be verified by comparing the data of Table I with the solvent loci in Figure 5.

It is a considerable simplification to assume that the solvent characteristics of a mixture can be represented by a few parameters representing some average properties of the mixture. Nevertheless, this assumption

TABLE V
Viscosity of Ternary Cellulose Acetate Solutions

Solvent mixture	Solvent proportion ^a	Solution viscosity, ^b cps $\times 10^{-3}$	Specific viscosity, ^b $\times 10^{-3}$
Propylene carbonate-methanol	3:1	21.3	15.5
	2:1	15.4	13.4
	1:1	17.4	18.5
Nitroethane-methanol	3:1	6.7	11.5
	2:1	5.8	10.2
	1:1	5.7	10.5
Nitroethane- <i>n</i> -butanol	1:2	9.6	17.5
	3:1	23.4	33
	2:1	21.3	28
Acetone-formamide	1:1	33.6	36
	8:2	6.0	9.4
	7:3	7.8	8.8
	6:4	9.7	8.2
	5:5	12.4	8.2
	4:6	16.2	8.4
	3:7	20.2	8.4
2:8	33.9	12.4	

^a By volume.

^b At a concentration of 17.5 g/dl.

will be shown to be a reasonable guide to understanding the viscosity of ternary solutions. The arithmetic average solubility parameter locus of the mixture provides a good key for correlating solution viscosity behavior. (A semiquantitative theory of the solubility parameter loci of mixtures has been described recently by Kaelble.¹⁷ It appears that the mixture's locus is a nonlinear function of the component loci when the two have markedly different polarities or hydrogen-bonding features.)

It is hypothesized that the specific viscosity of solutions of a polymer in a solvent mixture would exhibit a minimum value only if the mixture was a better solvent than either pure component. In such cases it would also be expected that the solubility-parameter locus of the optimum mixture would lie near the central region of the polymer's solubility envelope. It was reasoned that the least ambiguous test of the hypothesis would be provided by an examination of the viscosity of solutions made from a mixture of two nonsolvents. With such mixtures the solvency power must pass through a maximum if the mixture dissolves the polymer. Furthermore, for certain combinations of nonsolvents the solubility parameter loci should pass near the center of the solubility envelope if the separate parameters combine in a linear fashion.

The nonsolvent combinations selected were an alcohol and either propylene carbonate or nitroethane. In all three cases, the specific viscosity went through a minimum, thus confirming the hypothesis. These data are listed in Table V and the solvent combinations are displayed in Figure 6.

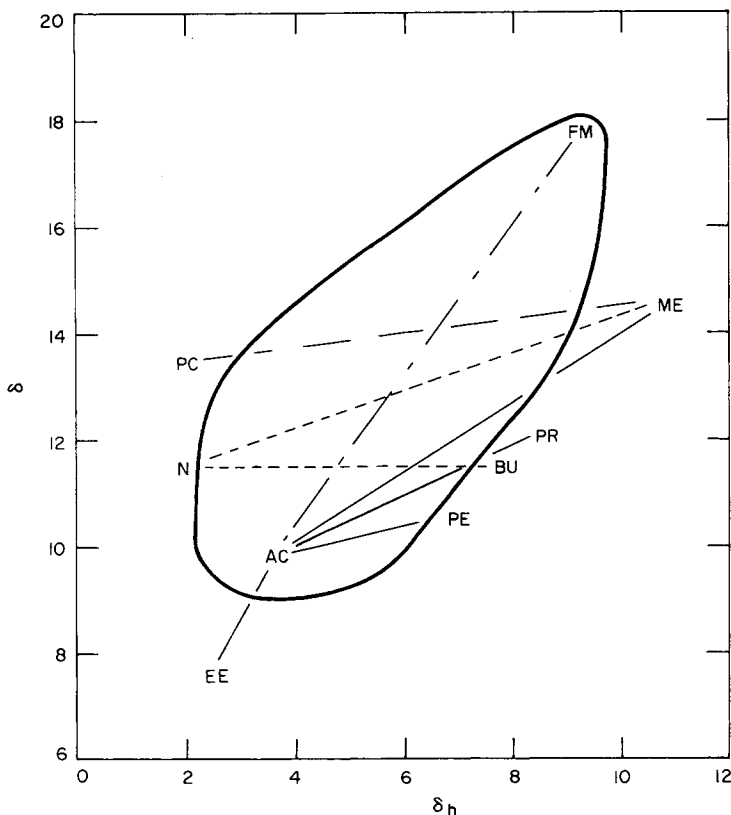


Fig. 6. Mixed solvent combinations used in viscosity studies.

Another interesting feature of these mixtures is the fact that both the ordinary solution viscosity and specific viscosity of nitroethane-methanol solutions are lower than those of acetone solutions.

For mixtures of a solvent and a nonsolvent, there is a clear behavior pattern for the specific viscosity. When either methanol or propylene glycol is added to acetone at constant polymer concentration, η_{sp} decreases and goes through a minimum. This behavior is to be expected as the solubility locus moves closer to the central region. It is perhaps noteworthy that the minimum η_{sp} attained by mixtures of acetone with either methanol or propylene glycol is nearly the same (approximately 13,000). When *n*-propanol is added to acetone, there is only a slight minimum in η_{sp} (24,000). As the solubility parameter and the hydrogen-bonding index of the nonsolvent decreases (e.g., with pentanol or diethyl ether), the specific viscosity monotonically increases until the insolubility limit of the polymer is reached.

Very interesting viscosity behavior is exhibited by cellulose acetate-acetone-formamide solutions. As shown by the data in Table V, the specific viscosity of these solutions varies by less than 10% over the com-

position range of 30% to 70% (by volume) acetone. This striking constancy could result from at least two factors. One, the solubility parameter loci could be curved parallel to the left or right side of the solubility envelope, thus giving a constant solvent power. Two, specific solute-solvent interactions could attenuate the influence of the average solubility-parameter properties of the mixture. For example, constancy of viscosity might result from a balance of preferential solvation of the polymer's hydroxyl group by formamide and solvation of the polymer's acetate groups by acetone. Information about this conjecture could be obtained by proton magnetic resonance studies of spin lattice relaxation times, as shown by Sato.¹⁸

SUMMARY AND CONCLUSIONS

For many polymer-solvent combinations, the intrinsic viscosity is largest with the thermodynamically best solvent, but others have shown that this relationship is not exhibited by cellulose acetate solutions. It was found that concentrated (17.5 g/dl) solutions of cellulose acetate in various solvents exhibit specific viscosities from 5000 to 80,000, with the difference between solvents increasing with polymer concentration. This effect was found to be related to the solvent power, as measured by $\overline{\Delta F}_1$, or the hexane titer required for precipitation, with the smallest specific viscosity obtained in the best solvent. This behavior can be accounted for by relating the extent of chain entanglement to polymer concentration and the size of the polymer chains, with the latter controlled by the type of solvent. The viscosity of solutions in a solvent mixture is qualitatively explicable in terms of the average solubility parameter, as measured by the solubility-parameter locus of the mixture in relation to the solubility envelope of the polymer. This method of analysis is particularly useful for understanding some solution properties of mixtures composed of a polymer and two nonsolvents.

In two recent publications, V. E. Dreval and others have carefully explored the effect of solvent upon the rheological properties of dilute and concentrated polymer solutions.^{19,20} They have shown that the different viscosities of a nonpolar polymer in various solvents can be accounted for by the effect of the solvent on the glass transition temperature of the solution. However, for a polar polymer such as poly(methyl methacrylate), Tg effects account for only a portion of the viscosity differences; it is necessary to consider the thermodynamic affect of the solvent. Dreval et al. showed that the Martin viscosity coefficient, K_m (inversely related to the second virial coefficient and the coil expansion factor), can be used to unify the viscosity data. For example, they demonstrated that, over a wide range of concentrations, a single viscosity-concentration curve is obtained when $\log \{ \eta_{sp} / (C[\eta]) \}$ is plotted against the function $K_m C[\eta]$. All the data for cellulose acetate in four pure solvents and in eight solvent mixtures fell on a single curve.

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