# Estimation of Viscosities of Mixed Polymer Solutions

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## Synopsis

A semiempirical model for estimation of viscosities of concentrated polymer solutions[1] can be applied to mixtures of polymers in a common solvent. The data required for estimation of mixture viscosity are: solvent viscosity, polymer molecular weight, density, concentration, and intrinsic viscosity in the particular solvent. Calculated and experimental viscosities agree to within a few per cent for the relatively nonpolar systems for which comparative data are available. The model does not appear to be adequate for mixtures in which there are extensive hydrogen-bonding interactions.

Results of the new model are equivalent to those of an empirical equation[2] reported to be effective for fairly concentrated binary polymer mixtures.

Specific interactions between polymeric solutes can be conveniently assessed by comparing measured mixture viscosity to that calculated from the model presented. It is not clear, however, that such assessments have any fundamental significance, since the interactions which are calculated depend on the assumptions inherent in the estimation of the "ideal" mixture viscosity. The same reservations apply to other models which have been proposed for this purpose.

## INTRODUCTION

A model has been presented recently for prediction of viscosities of concentrated polymer solutions.[1] The model has also been applied to account for concentration effects[3] and universal calibration[4] in gel-chromatographic analysis of polymer molecular weight distributions. This report extends the calculations to mixtures of polymers in a common solvent.

The literature data suitable for comparison of predicted and experimental mixture viscosities have been developed in the course of studies aimed primarily at investigation of specific interactions between polymeric solutes. Such interactions are assumed to be related to the difference between the measured mixture viscosity and that of an "ideal" system in which only hydrodynamic forces are significant (see refs. 2 and 5 for leading references). The current approaches in this connection are reviewed below, since it is useful to compare predictions of our model with those of other ideal estimates as well as with experimental viscosities.

Our concern in this article is, however, primarily with prediction of absolute viscosities of polymer mixtures, rather than estimation of specific interactions, despite the nature of the data available for comparison. The

model presented permits calculation of such viscosities of relatively non-polar polymer–solvent systems to an accuracy sufficient at least for technologic applications (as in surface-coating solutions). The model differs from others proposed for specific interaction studies in that experimental values of viscosities of concentrated single polymer solutions are not required. The present theory resembles the others, however, in that it assumes purely hydrodynamic interactions and is derived with some semiempirical steps.

## IDEAL MIXTURE VISCOSITIES

Krigbaum and Wall[5] derived an expression for ideal mixture viscosity by analogy from the virial expression for specific viscosity $\eta_{sp}$ in terms of weight concentration $C$ of a single solute mixture:

$$\eta_{sp} = [\eta]C + bC^2 \qquad (1)$$

where $\eta_{sp} = (\eta - \eta_0)/\eta_0$, with $\eta$ and $\eta_0$ representing the solution and solvent viscosities, respectively; and $[\eta]$ is the intrinsic viscosity (limiting viscosity number). The specific viscosity $\eta_{sp,m}$ of a mixed-polymer solution, was then written as

$$\eta_{sp,m} = [\eta]_1 C_1 + [\eta]_2 C_2 + b_{11}C_1{}^2 + 2b_{12}C_1C_2 + b_{22}C_2{}^2 \qquad (2)$$

where $[\eta]_i$ is the intrinsic viscosity of a solution of component $i$ alone in the common solvent, and the $b_{ij}$ coefficients reflect the interactions between the subscripted polymeric species. An ideal mixture is defined as one in which $b_{12} = (b_{11}b_{22})^{1/2}$. Deviations from ideality are assessed by comparing the experimental $\eta_{sp,m}$ to that calculated from eq. (2) and the ideal $b_{12}$, with $b_{11}$ and $b_{22}$ obtained from plots of $\eta_{sp}$ against $C$ for each polymer alone in solution.

This is essentially a semiempirical definition of ideality. It is consistent with a power law expression for mixture viscosities proposed some time earlier[6] and reduces correctly at infinite dilution to a mixture intrinsic viscosity equal to the weight average of the intrinsic viscosities of the components.[7,8] Equation (2) permits calculation of mixture viscosities given the intrinsic viscosities and $b_{ii}$ coefficients of the components. It is evidently useful only for very dilute mixtures (for which it was intended), to which eq. (1) can be expected to apply.

Catsiff and Hewett[2] have pointed out that the nonadditivity of mixed-polymer solution viscosities is evident particularly at total concentrations greater than about 1 wt-%. The apparent success of some of the earlier correlations which coincided with the formulation of Krigbaum and Wall was thought to be related to the high dilution or close similarity of the chemical natures of the solutes. Catsiff and Hewett presented an empirical additivity rule which was valid up to a total concentration of nearly 4% (w/v) for the systems studied. The definition of ideality from this work

could eliminate some specific interactions indicated by application of eq. (2). The additivity equation of Catsiff and Hewett can be represented as

$$\eta_{sp,m} = C_1\eta_{r1}(C_t) + C_2\eta_{r2}(C_t) \tag{3}$$

where $\eta_{r_i}(C_t)$ is the reduced viscosity $(\eta_r = \eta_{sp}/C_t = (\eta - \eta_0)/(C_t\eta_0)$ that component $i$ would have in a single-polymer solution of concentration $C_t = C_1 + C_2$. Equation (3) is equivalent to eq. (2) if $b_{12} = (1/2)(b_{11} + b_{22})$. That is to say, in this case an ideal mixture is defined as one in which the arithmetic rather than the geometric mean of the individual slope constants, $b_{ii}$, applies. The $b_{ij}$ values are taken from experimental data for single polymer solutions, as in the method of Krigbaum and Wall. A mineral oil mixture of a methacrylate copolymer and polyisobutene was found to exhibit ideal behavior, as defined by eq. (3), at total concentrations up to 4 wt-% and at two temperatures.

More recently, Williamson and Wright[9] studied the behavior of a number of mixtures of commercial polymers in a variety of solvents at high dilutions and concluded that the equation of Catsiff and Hewett provides a useful reference base for studying viscosities of such solutions.

An alternative representation follows from the relation between the slope constant $K'$ in the expression for intrinsic viscosity[10]

$$\frac{\eta_{sp}}{C} = [\eta] + K'[\eta]^2C. \tag{4}$$

From eqs. (1) and (4),

$$K' = b_{11}/[\eta]_1^2 \tag{5}$$

Cragg and Bigelow[11] have focused on the Huggins' constant of mixed polymer systems rather than the mixture viscosity. By assuming that the interaction coefficient is the geometric mean of the individual polymer–solvent interaction coefficients

$$K_{ij} = (K_iK_j)^{1/2}, \tag{6}$$

the following expression for the slope constant $K_m'$ of a mixed polymer system is obtained:

$$K_m' = \frac{K_1'[\eta_1]^2W_1^2 + K_2'[\eta_2]^2W_2 + 2K_1'K_2'[\eta_1][\eta_2]W_1W_2}{([\eta_1]W_1 + [\eta_2]W_2)^2} \tag{7}$$

where the subscripted quantities refer to the contributions of each component at its given concentration, and $W_i$ is the weight fraction of component $i$ in the solute. Deviations from ideality were assessed by comparing measured to "ideal" $K'$ values.

## VISCOSITY MODEL

The equations required for calculation of viscosity of a single polymer in a given solvent have been derived elsewhere.[1] They are outlined briefly below for convenience in following the present article.

The volume $v$ of an unswollen polymer molecule (assumed spherical) is estimated from

$$v = \frac{M}{\rho N_0} \frac{cm^3}{\text{molecule}} \qquad (8)$$

where $\rho$ is the amorphous density of the polymer at the mixture temperature, $N_0$ is Avogadro's number, and $M$ is the polymer molecular weight. In practical situations, $M$ is evidently an average molecular weight. $\bar{M}_v$ is the preferred average for these calculations, for reasons apparent from eq. (10). At infinite dilution the polymer molecule is swollen by solvent to an effective hydrodynamic volume $v\epsilon_0$, where $\epsilon_0$ is a unitless volume factor given by

$$\epsilon_0 = \frac{K M \rho^\alpha}{2.5} = \frac{[\eta]\rho}{2.5}. \qquad (9)$$

In eq. (9), $K$ and $\alpha$ are the constants in the Mark–Houwink–Sakurada expression linking the limiting viscosity number $[\eta]$ and viscosity-average molecular weight in the given solvent:

$$[\eta] = K \bar{M}_v{}^\alpha. \qquad (10)$$

At finite concentration $C$ (g/cm$^3$), the effective volume factor is decreased from $\epsilon_0$ to $\epsilon$, where

$$\frac{1}{\epsilon} = \frac{1}{\epsilon_0} + \frac{C}{0.507\rho} \left[ \frac{\epsilon_0 - \epsilon_x}{\epsilon_0 \epsilon_x} \right] \qquad (11)$$

and the critical volume factor $\epsilon_x$ is a function of polymer molecular weight $M$ and of the formula weight of the repeating unit, $M_0$, as follows:

$$\epsilon_x = 2.60 + \left( 0.34 \times 10^{-3} \frac{M}{M_0} \right). \qquad (12)$$

At any concentration $C$, the volume fraction $\phi$ of solvated polymer is

$$\phi = \frac{C}{M} N_0 v \epsilon. \qquad (13)$$

The viscosity of the mixture, $\eta$, is given in terms of the solvent viscosity $\eta_0$ by

$$\frac{\eta_0}{\eta} = 1 - 2.5\phi + 11\phi^5 - 11.5\phi^7. \qquad (14)$$

The quantitative estimates of the decrease in effective hydrodynamic volume with increased polymer concentration are based, with some modifications, on the work of Maron and co-workers.[12,13] The equation linking solution viscosity and volume fraction of solvated polymer was suggested by Ford[14] for suspensions of rigid spheres. The viscosity of very dilute

systems (solute assumed spherical) is given by the familiar Einstein expression

$$\eta = \eta_0 (1 + 2.5\phi).$$ (15)

Equations (14 and (15) are mutually consistent only in the limit of infinite dilution when $\phi$ is essentially equal to zero. Equation (14) has been shown[1] to give good estimates of viscosities of concentrated solutions up to a critical concentration $C_x$, which is higher than any used in the binary polymer mixtures discussed below. The nature of $C_x$ and extensions of the model to higher concentrations need not concern us here.

To extend the viscosity calculations to a mixture of two polymers in a common solvent, we simply consider that one polymer is being dissolved in the solution of the other. Equation (14) provides a value of $\eta_1$, the viscosity of a solution containing only polymer 1 in pure solvent at a concentration equal to the concentration of this polymer in the final mixture,

$$\frac{1}{\eta_1} = \frac{1}{\eta_0}(1 - 2.5\phi_1 + 11\phi_1^5 - 11.5\phi_1^7)$$ (14a)

where $\phi_1$ is the volume fraction of polymer 1, from eq. (13) and its predecessors.

The calculations for polymer 2 are exactly the same, except that the mixture viscosity $\eta_{1.2}$ is given by

$$\frac{\eta_1}{\eta_{1.2}} = 1 - 2.5\phi_2 + 11\phi_2^5 - 11.5\phi_2^7).$$ (14b)

Thus, in general,

$$\eta_{i,j}\ldots = \eta_0 / \prod_{ij} (1 - 2.5\phi_i + 11\phi_i^5 - 11.5\phi_i^7)$$ (16)

where the $\phi_i$ values are calculated as above for species $i$ at its particular concentration in the mixture. The mixture specific viscosity is

$$\eta_{sp,m} = \frac{\eta_{ij} - \eta_0}{\eta_0}.$$ (17)

The parameters for use in eq. (3), of Catsiff and Hewett, can also be calculated directly from the model, using eq. (14) and the preceding equations, with $C_i$ set equal to the weight concentration of each polymer. Such estimates are reported in the next section, where it is shown that eq. (16) gives results equivalent to those of eq. (3).

## RESULTS

Calculated viscosities are compared with literature values for binary polymer systems in this section. Most of the data available are in terms of relative, $\eta/\eta_0$, or specific viscosities, $(\eta/\eta_0) - 1$. Since the systems quoted are generally dilute, $\eta$ and $\eta_0$ are fairly close in magnitude, and prediction

TABLE I
Viscosities of Single-Polymer Mixtures in Benzene[a]

| Polymer | Concn, g/dl | $\eta_{exp}$, poises $\times 10^{-2}$ | $\eta_{calc}$,[b] poises $\times 10^{-2}$ | $\eta_{sp exp}$ | $\eta_{sp calc}$ | $\left[\dfrac{\eta_{sp}}{C}\right]_{exp}$ dl/g | $\left[\dfrac{\eta_{sp}}{C}\right]_{calc}$ dl/g |
|---|---|---|---|---|---|---|---|
| Rubber | 0.1039 | 1.1598 | 1.0025 | 0.9177 | 0.6576 | 8.8325 | 6.3293 |
| $[\eta] = 5.48$ dl/g | 0.0905 | 1.0642 | 0.9448 | 0.7595 | 0.5621 | 8.3927 | 6.2111 |
| | 0.0825 | 1.0145 | 0.9110 | 0.6774 | 0.5063 | 8.2160 | 6.1411 |
| | 0.0633 | 0.8997 | 0.8336 | 0.4876 | 0.3784 | 7.7024 | 5.9777 |
| | 0.0242 | 0.6984 | 0.6877 | 0.1548 | 0.1370 | 6.3960 | 5.6609 |
| Polystyrene | 0.0696 | 0.6646 | 0.6614 | 0.09888 | 0.09355 | 1.4217 | 1.3450 |
| $[\eta] = 1.31$ dl/g | 0.0556 | 0.6507 | 0.6498 | 0.07596 | 0.07447 | 1.3652 | 1.3338 |
| | 0.0485 | 0.6439 | 0.6439 | 0.06463 | 0.06469 | 1.3337 | 1.3349 |
| | 0.0348 | 0.6306 | 0.6327 | 0.04259 | 0.04619 | 1.2248 | 1.3285 |
| | 0.0278 | 0.6241 | 0.6271 | 0.03183 | 0.03687 | 1.1442 | 1.3252 |
| Ethyl cellulose $A$ | 0.1039 | 0.7177 | 0.6997 | 0.18669 | 0.15688 | 1.7971 | 1.5102 |
| $[\eta] = 1.46$ dl/g | 0.0908 | 0.7007 | 0.6873 | 0.15863 | 0.13648 | 1.7471 | 1.5031 |
| | 0.0805 | 0.6879 | 0.6777 | 0.1374 | 0.12055 | 1.7069 | 1.4975 |
| | 0.0601 | 0.6637 | 0.6588 | 0.0973 | 0.08934 | 1.6204 | 1.4865 |
| Ethyl cellulose $B$ | 0.2473 | 0.9384 | 0.8265 | 0.5516 | 0.3665 | 2.2305 | 1.4824 |
| $[\eta] = 1.36$ dl/g | 0.1731 | 0.8120 | 0.7560 | 0.3426 | 0.2500 | 1.9791 | 1.4442 |
| | 0.1484 | 0.7768 | 0.7333 | 0.2844 | 0.2125 | 1.9168 | 1.4317 |
| | 0.1237 | 0.7417 | 0.7110 | 0.2263 | 0.1755 | 1.8300 | 1.4195 |
| | 0.0989 | 0.7090 | 0.6890 | 0.1723 | 0.1392 | 1.7422 | 1.4074 |
| | 0.0742 | 0.6771 | 0.6674 | 0.1195 | 0.1035 | 1.6113 | 1.3955 |
| Polyethylene glycol | 2.2296 | 0.7473 | 0.7246 | 0.2357 | 0.1981 | 0.1057 | 0.0889 |
| $[\eta] = 0.077$ dl/g | 1.9509 | 0.7241 | 0.7076 | 0.1972 | 0.1700 | 0.1011 | 0.0871 |
| | 1.6722 | 0.7048 | 0.6912 | 0.1652 | 0.1429 | 0.0989 | 0.0854 |
| | 1.3935 | 0.6834 | 0.6754 | 0.1299 | 0.1168 | 0.0933 | 0.0838 |
| | 1.1148 | 0.6655 | 0.6603 | 0.1004 | 0.0917 | 0.0900 | 0.0823 |
| | 0.5100 | 0.6269 | 0.6292 | 0.0365 | 0.0403 | 0.0716 | 0.0791 |
| | 0.4371 | 0.6225 | 0.6256 | 0.0292 | 0.0344 | 0.0669 | 0.0787 |

| Polymer | Mark-Houwink constants benzene solutions | | | | Amorphous density $\rho$,[c] g/cm³ |
|---|---|---|---|---|---|
| | $K$, cm³/g | $\alpha$ | Temp., °C | Ref. | |
| Rubber | 0.0185 | 0.74 | 30 | (15) | 0.913 |
| Polystyrene | 0.00918 | 0.743 | 25 | (17) | 1.047 |
| Ethyl cellulose | 0.0292 | 0.81 | 25 | (18) | 1.15 |
| Polyethylene glycol | 0.129 | 0.50 | 25 | (19) | 1.13 |

[a] Data from Krigbaum and Wall.[5]
[b] Equation (14).
[c] From Lewis.[6]

errors are equal to larger fractions of $\eta_r$ or $\eta_{sp}$ than of $\eta$ itself. This is illustrated in Table I for single-polymer mixtures. The predicted solution viscosity $\eta$ is shown to agree with the experimental value to within a few per cent, whereas the errors in $\eta_{sp}$ are somewhat larger. The agreement between $\eta_{exp}$ and $\eta_{calc}$ is reasonably good, considering the semiempirical and *a priori* nature of the model. Most of the subsequent results are quoted for

solution viscosities, since the model is primarily intended for this application.

Krigbaum and Wall[5] report experimental viscosities for five different polymers in benzene solution. The kinematic viscosities reported were converted to dynamic viscosities by multiplying by 0.8685 g/cm$^3$, the density of benzene at 25°C. Solvent viscosity $\eta_0$ was taken as 0.6028 centipoises at 25°C. Table I compares experimental viscosities of single polymer solutions at various concentrations with those calculated from eq. (14), using the Mark-Houwink constants listed in this table. Solution viscosity ($\eta$) values are seen to agree fairly well. The relative agreement deteriorates, however, as one proceeds to $\eta_{sp}$ and $\eta_{sp}/C$ calculations, as mentioned above.

All the systems listed in Table I are rather dilute, except for the polyethylene glycol mixture. Viscosities are reported to four decimal places, as in the original article.[5] Not all the input data required for the calculations in Table I are as accurate as might be desired. For example, the Mark-Houwink constants for the rubber–benzene system are taken from experiments at 30°C, rather than the 25°C experimental temperature in this case. The density used for ethyl cellulose is not that for amorphous polymer, and the calculations assume that each solute molecule is an isolated spherical entity, although ethyl cellulose is known to associate in benzene solution.[5]

Table II lists viscosities of benzene mixtures of the rubber polymer with polystyrene and with ethyl cellulose. Data on ethyl cellulose–polyethylene

### TABLE II
#### Viscosities of Mixtures of Polymers in Benzene[a]

| Mixture | Weight fraction[b] | $\eta_{exp}$, poises $\times 10^{-2}$ | $\eta_{calc}$,[c] poises $\times 10^{-2}$ | $\eta_{calc}$,[d] poises $\times 10^{-2}$ | $\eta_{calc}$,[e] poises $\times 10^{-2}$ |
|---|---|---|---|---|---|
| Rubber–polystyrene* | 0.5001 | 0.7718 | 0.7599 | 0.7590 | 0.7753 |
| $g_t = 0.06954$ g/dl | 0.6001 | 0.7499 | 0.7402 | 0.7394 | 0.7510 |
| | 0.7001 | 0.7272 | 0.7205 | 0.7198 | 0.7277 |
| | 0.8001 | 0.7057 | 0.7008 | 0.7002 | 0.7053 |
| | 0.9000 | 0.6841 | 0.6811 | 0.6808 | 0.6839 |
| Rubber–ethyl cellulose $A$* | 0.4870 | 0.7552 | 0.7435 | 0.7434 | 0.7590 |
| $g_t = 0.0607$ g/dl | 0.5874 | 0.7363 | 0.7271 | 0.7270 | 0.7391 |
| | 0.6889 | 0.7154 | 0.7104 | 0.7102 | 0.7196 |
| | 0.7919 | 0.6970 | 0.6935 | 0.6934 | 0.7004 |
| | 0.8952 | 0.6790 | 0.6766 | 0.6766 | 0.6817 |
| Rubber–ethyl cellulose $A$* | 0.5880 | 0.7985 | 0.7709 | 0.7706 | 0.7920 |
| $g_t = 0.0807$ g/dl | 0.6894 | 0.7691 | 0.7481 | 0.7477 | 0.7641 |
| | 0.7919 | 0.7406 | 0.7249 | 0.7246 | 0.7369 |
| | 0.8954 | 0.7144 | 0.7015 | 0.7013 | 0.7106 |

[a] Data from Krigbaum and Wall.[5]
[b] Weight fraction given for component marked by asterisk.
[c] Equation (3).
[d] Equation (16).
[e] Equation (2).

glycol mixtures were not measured at fixed total polymer concentration[5] and could not be estimated in this work.

In general, the closest fit to experimental points is given by eq. (2), of Krigbaum and Wall. Applications of this equation require data on the viscosities of single-polymer solutions. The present calculations using the Catsiff and Hewett relation, eq (3), are made from single-polymer solution viscosities estimated from our eq. (14). These results are essentially equivalent to those obtained from our model directly through eq. (16). The only parameters required in either of the latter two methods are polymer intrinsic viscosity and molecular weight, for use in eqs. (9) and (12). The calculated values agree with experimental binary solution viscosities to within a few per cent. The experimental values are slightly underestimated by our model.

Data for other polymer systems were reported by Williamson and Wright,[9] again in very dilute mixtures. Experimental and calculated (from eq. (14)) values for single polymer solutions are given in Table III. The estimates for the two nonpolar polymers in butanone are fairly close to

TABLE III
Viscosities of Single-Polymer Mixtures[a]

| Concentra-tion, g/cm³ | Styrene–acrylonitrile copolymer in butanone (25°C) | | Poly(methyl methacrylate) in butanone (25°C) | | Poly(vinyl alcohol) in water (25°C) | |
|---|---|---|---|---|---|---|
| | $\eta_{exp}$, poises $\times 10^2$ | $\eta_{calc}$, poises $\times 10^2$ | $\eta_{exp}$, poises $\times 10^2$ | $\eta_{calc}$, poises $\times 10^2$ | $\eta_{exp}$, poises $\times 10^2$ | $\eta_{calc}$, poises $\times 10^2$ |
| 0.01 | 0.70 | 0.68 | 0.52 | 0.53 | 2.06 | 1.59 |
| 0.008 | 0.64 | 0.62 | 0.49 | 0.50 | 1.73 | 1.43 |
| 0.007 | 0.59 | 0.58 | 0.48 | 0.49 | 1.59 | 1.35 |
| 0.006 | 0.56 | 0.55 | 0.47 | 0.47 | 1.45 | 1.28 |
| 0.005 | 0.53 | 0.52 | 0.45 | 0.46 | 1.33 | 1.21 |
| 0.004 | 0.50 | 0.49 | 0.44 | 0.44 | 1.21 | 1.14 |
| 0.003 | 0.47 | 0.47 | 0.43 | 0.43 | 1.12 | 1.08 |
| 0.002 | 0.44 | 0.44 | 0.42 | 0.42 | 1.03 | 1.01 |
| 0.001 | 0.41 | 0.41 | 0.40 | 0.40 | 0.96 | 0.95 |

| Polymer–Solvent | Mark-Houwink constants | | | | Polymer density $\rho$, g/cm³ | Solvent viscosity, poises $\times 10^2$ | Polymer $\bar{M}_v$ | $M_0$[c] |
|---|---|---|---|---|---|---|---|---|
| | $K$, cm³/g | $\alpha$ | Temp., °C | Ref. | | | | |
| SANC–butanone[d] | 0.036 | 0.62 | 30 | (20) | 1.165 | 0.39 | 164,000 | 78.6[e] |
| PMMA–butanone | 0.0068 | 0.72 | 25 | (21) | 1.179 | 0.39 | 126,000 | 100.1 |
| PVA–water | 0.020 | 0.76 | 20 | (22) | 1.269 | 0.894 | 40,900 | 44.05 |

[a] Data from Williamson and Wright.[9]
[b] From Lewis.[16]
[c] Equation (12).
[d] Value quoted is for 38.3/61.7 mole ratio of acrylonitrile to styrene.
[e] Estimated for equimolar ratio of monomers.

the experimental values. The viscosities calculated for poly(vinyl alcohol) in water are underestimated at the higher concentrations in the experimental range. Uncertainties in the Mark-Houwink constants are unlikely to be a factor here, since the $\epsilon_0$ value is taken directly from the experimental $[\eta]$ for use in eq. (9), and errors in $\bar{M}_v$ have relatively little effect on $\epsilon_x$ calculated from eq. (12). It would appear that the model used here is inadequate for solutions, such as poly(vinyl alcohol) in water, in which there can be appreciable hydrogen bonding between solvent and solute. Another failure at matching viscosities in this system has been noted previously.[1]

Table IV lists experimental and predicted viscosities for equal concentration mixtures of the styrene–acrylonitrile copolymer and poly(methyl methacrylate) in butanone. For this dilute system of relatively nonpolar solutes, both eq. (16) and eq. (3), using single-polymer viscosities calculated from eq. (14), again produce equivalent calculations which coincide with experimental viscosities to within a few per cent.

### TABLE IV
#### Mixtures of SANC/PMMA in Butanone[a]

| Concen- tration, g/cc | Experimental | | | Calculated[b] | | | Calculated[c] | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\eta_{sp}/C$, $(\text{cm}^3/\text{g})$ $\times 10^{-2}$ | $\eta_r$ | $\eta$, poises $\times 10^2$ | $\eta_{sp}/C$, $(\text{cm}^3/\text{g})$ $\times 10^{-2}$ | $\eta_r$ | $\eta$, poises $\times 10^2$ | $\eta_{sp}/C$, $(\text{cm}^3/\text{g})$ $\times 10^{-2}$ | $\eta_r$ | $\eta$, poises $\times 10^2$ |
| 0.01 | 0.520 | 0.520 | 0.59 | 0.567 | 1.567 | 0.61 | 0.557 | 1.557 | 0.61 |
| 0.008 | 0.520 | 1.416 | 0.55 | 0.545 | 1.436 | 0.56 | 0.537 | 1.430 | 0.56 |
| 0.007 | 0.517 | 1.362 | 0.53 | 0.535 | 1.374 | 0.54 | 0.528 | 1.369 | 0.53 |
| 0.006 | 0.517 | 1.310 | 0.51 | 0.524 | 1.315 | 0.51 | 0.518 | 1.311 | 0.51 |
| 0.005 | 0.517 | 1.259 | 0.49 | 0.514 | 1.257 | 0.49 | 0.509 | 1.255 | 0.49 |
| 0.004 | 0.517 | 1.207 | 0.47 | 0.505 | 0.202 | 0.47 | 0.500 | 1.200 | 0.47 |
| 0.003 | 0.517 | 1.155 | 0.45 | 0.495 | 1.149 | 0.45 | 0.492 | 1.148 | 0.45 |
| 0.002 | 0.517 | 1.103 | 0.43 | 0.486 | 1.097 | 0.43 | 0.484 | 1.097 | 0.43 |
| 0.001 | 0.517 | 1.052 | 0.41 | 0.477 | 1.048 | 0.41 | 0.476 | 1.048 | 0.41 |

[a] Data from Williamson and Wright.[9]
[b] Equation (16).
[c] Equation (3).

The SANC–PMMA–butanone system is listed by Williamson and Wright[9] as being nearly ideal, in that specific interactions between polymers are not experimentally significant. Other binary polymer mixtures reported in this reference were not estimated here, either because of lack of Mark-Houwink constants or because the experimental data appear to be uncertain.

The data of Cragg and Bigelow[11] refer to dilute mixtures of polystyrene and poly(methyl methacrylate) polymers in $m$-xylene at 25°C. For estimation purposes, $\epsilon_0$, eq. (9), was calculated from the experimental limiting viscosity numbers. Polymer molecular weights were taken as reported[11] and used in eq. (12) to derive $\epsilon_x$. Viscosities of mixed polymer solutions were estimated, at the cited mixture compositions, in the experimental con-

centration range (0.05–1.0 dl/g). A linear least-squares fit to the $(1/C)$ $(\eta/\eta_0 - 1)$ versus $C$ plot then provided calculated values of the limiting viscosity number and Huggins' constant $K'$ for the mixed system.

Figure 1 compares the estimated and experimental limiting viscosity numbers for the two mixtures reported by Cragg and Bigelow.[11] The calculated line coincides with experimental values. The present model reduces in this case (infinite dilution) to the ideal expression which equates
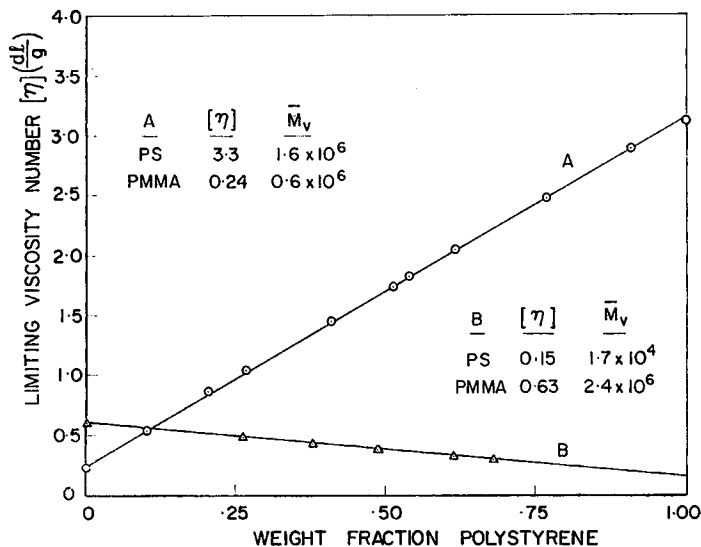


Fig. 1. Variation of $[\eta]$ with weight fraction polystyrene (PS) in $m$-xylene mixtures with poly(methyl methacrylate) (PMMA). Data from ref. (11).
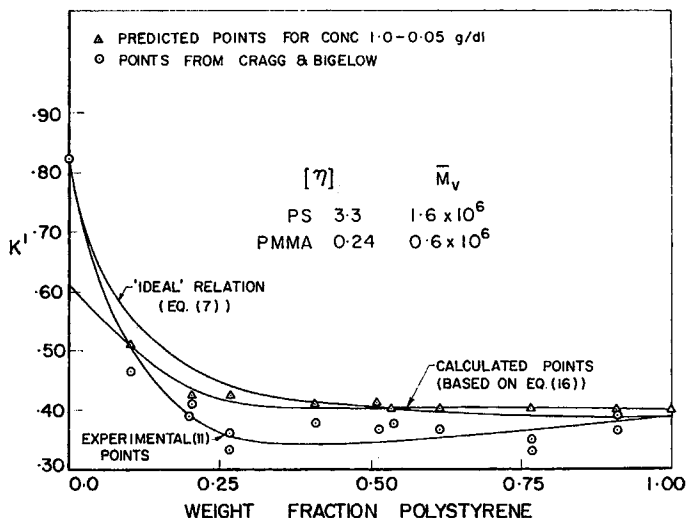


Fig. 2. Variation of $K'$ with weight fraction PS. Data from ref. (11).
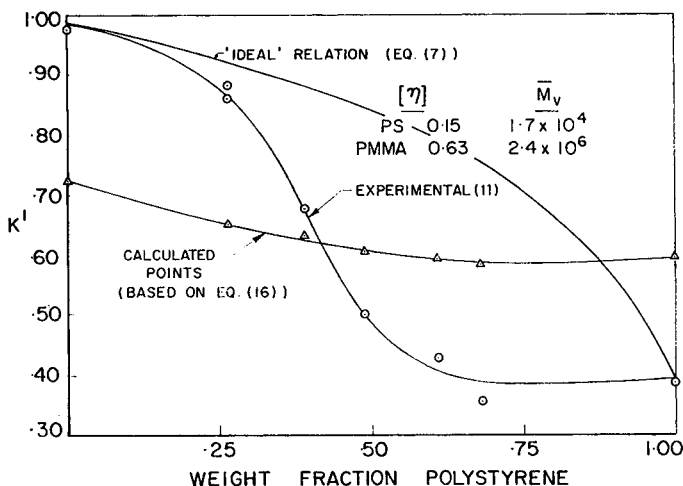
Fig. 3.   Variation of $K'$ with weight fraction PS.   Data from ref. (11).

intrinsic viscosity of the mixture to the weight average of the intrinsic
viscosities of the components.

Figure 2 shows calculated and experimental $K'$ values for the mixture
containing high molecular weight polystyrene.   The experimental points
are rather scattered, and the point for pure poly(methyl methacrylate)
seems to be too high to be reliable.   The predicted values lie close to, but
slightly higher than, the experimental points.   The agreement here is about
as good as that produced by the ideality assumption, eq. (7), of Cragg and
Bigelow,[11] which uses experimental $[\eta]$ and $K'$ values from single-polymer
solutions.   Figure 3 shows a similar plot for the mixture containing high
molecular weight poly(methyl methacrylate).   The agreement here is not
good, but our predicted values do differ from those of the Cragg and Bigelow
model, which produced estimates that were always higher than the experi-
mental points.   Our "ideal" curve shows negative deviations in PMMA-
rich mixtures and positive deviations in PS-rich mixtures.

We note in this connection that the calculated values of Huggins' con-
stant depend to a small but significant extent on the concentration range
used for such estimations.   The use of the present model to predict Hug-
gins' constants will be reported separately.

## DISCUSSION

The data available are confined to dilute systems, and the comparison of
predicted and experimental values is therefore limited.   The predictions of
viscosities of single-polymer solutions in Tables I and III are quite close to
experimental values, considering that the main parameters required for the
calculations are polymer molecular weight and intrinsic viscosity in the
particular solvent.

The model is not adequate for poly(vinyl alcohol) mixtures and tends to be defective at higher concentrations of ethyl cellulose. This may indicate a general deficiency for systems in which hydrogen-bonding effects are significant. The model might need to be revised for such mixtures. It does appear to be useful, however, at least for relatively nonpolar synthetic polymers and their common solvents, as judged by the data presented here and in a previous report.[1]

For such systems, the viscosities of binary solute mixtures can be estimated with a reliability which should be adequate for most practical purposes (Tables II and IV). The model reduces to the correct values at infinite dilution (Fig. 1). Our eq. (16) gives essentially equivalent results to the empirical relation, eq. (3), of Catsiff and Hewett.[2] Thus, the latter equation is given some fundamental meaning if the present model is accepted for single polymer solutions. The equation of Catsiff and Hewett is stated to hold up to a total weight concentration of 4% for the systems studied. The new model should then be expected to apply at least up to this concentration.

The scheme presented here can, of course, be applied to estimate ideal mixture viscosities for assessment of specific interactions. It is particularly convenient for this purpose because the ideal viscosity is predictive and does not require measurements on single-polymer mixtures at various concentrations. It suffers in this respect, however, along with all the other approaches cited, in selecting ideal behavior in an essentially arbitrary manner. Any interactions assessed by comparing experimental with estimated solution viscosity are subject to the empirical assumptions involved in deciding ideal behavior. Since our calculations coincide with those of the Catsiff and Hewett method,[9] our model implicitly equates ideal behavior with an arithmetic mean of the $b_{ii}$ interaction coefficients mentioned above.

The only model for "ideal" solution behavior which is demonstrably based on fundamental grounds is that in which the intrinsic viscosities of binary and single-solute systems are compared. By this criterion the polystyrene–poly(methyl methacrylate) mixtures discussed above exhibit no specific interactions. This seems reasonable on physical grounds, since it is not clear why one of the two mixtures should deviate from ideality (as judged by $K'$ values) much more than the other. Data are not available for calculation of intrinsic viscosities of the other mixtures cited.

The basic model used to estimate viscosity of single-polymer mixtures rests on empirical relations, such as those between $\epsilon_x$ and $M$, eq. (12), and between $\eta$ and $\phi$, eq. (14). It could be useful to investigate the fundamental basis for such correlations and so perhaps improve the predictive character of the theory. We have delayed such investigations until the general value of the model is more clearly established. Since it is semiempirical, it must fail sooner or later. The present report and others cited[3,4] have explored extensions and applications of the model in this connection. The calculations of viscosities of mixed-polymer solutions seem to be reasonably suc-

cessful, at least within the limits noted. For many purposes, an error in solution viscosity of the magnitude of those found here may be compensated by the convenience of prediction without recourse to experiment for every new system.

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