

Intrinsic Viscosity Dependence on Polymer Molecular Weight and Fluid Temperature

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Received 8 July 2002; accepted 15 November 2002

ABSTRACT: Experimental solution intrinsic viscosity responses to temperature and polymer molecular weight variations were used to test the modeling capability of a simplified intrinsic viscosity equation. The multiple linear equation contains three parameters that are related to the thermodynamic properties of a polymer solution. Simple linear regression was used to produce an intrinsic viscosity equation containing unique fitted parameters for each of

three solutions. These parameters describe the polymer coil size at unperturbed conditions and the polymer coil expansion capabilities of the solvent as a function of fluid temperature and molecular weight. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2831–2835, 2003

Key words: solution properties; thermodynamics; modeling; calculations

INTRODUCTION

When high molecular weight polymer molecules dissolve in a fluid, they typically expand to form spherical coils. In dilute solutions, the volume associated with each polymer coil contains one polymer molecule surrounded by a much larger mass of solvent. A polymer coil's hydrodynamic volume depends upon the polymer molecular weight and its thermodynamic interaction with the solvent. As the polymer molecular weight increases, the coil volume becomes greater. Favorable polymer–solvent thermodynamic interactions also increase the polymer coil hydrodynamic volume. When the polymer–solvent interactions are unfavorable, the polymer coil volume is decreased. With unfavorable polymer–solvent interactions, polymer coils can completely collapse and become insoluble in the fluid. Polymer–solvent thermodynamic interactions depend upon the polymer molecular structure and concentration, the solvent molecular structure, and the solution temperature.

The hydrodynamic volume occupied by a given polymer mass is the intrinsic viscosity, $[\eta]$, a parameter that can be determined by dilute solution viscosity experiments. Intrinsic viscosity is a primary determinant for polymer solution behavior in many applications. For example, dilute polymer solution properties such as drag reduction and extensional viscosity are largely dependent on the solution's intrinsic viscosity. Thus, knowledge of the intrinsic viscosity dependence

on the solution temperature and polymer molecular weight is necessary for an understanding of a solution's rheological properties at applied conditions.

Several theories have been proposed to explain the relationship between a polymer coil's hydrodynamic volume and solution temperature. Most theories are based on the work of Flory¹ in which a theta temperature, θ , is defined as the critical miscibility temperature for a given polymer–solvent system in the limit of infinite polymer molecular weight. At theta conditions, the excess chemical potential of mixing is zero and the coil volume is a minimum. If the heat of polymer–solvent mixing is endothermic (requires heat), an increase in the solution temperature will increase the polymer coil hydrodynamic volume. If the heat of polymer–solvent mixing is exothermic (releases heat), an increase in solution temperature will decrease the polymer coil hydrodynamic volume.

Based on Flory's work, Stockmayer and Fixman² developed an intrinsic viscosity relationship for high molecular weight flexible-chain polymers, neglecting solvent draining effects:

$$[\eta] = K_{\theta} \sqrt{M} + \frac{0.51 \Phi_o M}{N_A V_s \rho_p^2} (1 - 2\chi) \quad (1)$$

In eq. (1), K_{θ} is the Mark–Houwink–Sakurada K value at the theta temperature; M , the weight-average polymer molecular weight; χ , the polymer–solvent interaction parameter; V_s , the solvent molar volume; ρ_p , the polymer density; Φ_o , the Flory constant (2.8×10^{23}); and N_A , Avogadro's number.

Polymer–solvent interaction parameter

Originally, the polymer–solvent interaction parameter, χ , introduced by Flory was only intended to ac-

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Contract grant sponsor: U.S. Dept. of Energy.

count for the enthalpic contributions during mixing. Through experimentation, however, Flory discovered that χ had both enthalpic and entropic components. Thus, the χ parameter characterizes the overall interaction of a polymer segment with solvent molecules. Presently, it is common practice to express χ as the sum of an enthalpic and an entropic contribution:

$$\chi = \chi_s + (\chi_h/T) \quad (2)$$

χ_h and χ_s are considered constants that depend on the polymer and solvent but are independent of the fluid temperature, T , and polymer molecular weight, M . Recent findings have shown that χ_s is correlated with χ_h and the polymer-solvent theta temperature θ^3 :

$$\chi_s = (1/2) - (\chi_h/\theta) \quad (3)$$

Thus, the dependence of χ on the temperature can be expressed as the sum of enthalpic, χ_h/T , and entropic, $\chi_s = 1/2 - (\chi_h/\theta)$, contributions:

$$\chi = 1/2 - \chi_h [(1/\theta) - (1/T)] \quad (4)$$

Use of this expression for χ in eq. (1) gives

$$[\eta] = K_\theta \sqrt{M} + \frac{1.02\Phi_o M}{N_A V_s \rho_p^2} \left(\frac{\chi_h}{\theta} \right) - \frac{1.02\Phi_o M}{N_A V_s \rho_p^2} \left(\frac{\chi_h}{T} \right) \quad (5)$$

K_θ and χ_h are constants for a given polymer and solvent. Usually, the solvent molar volume, V_s , and the polymer density, ρ_p , vary only slightly with the temperature. Equation (5) can be used to predict the dependence of the solution intrinsic viscosity on both the temperature and the polymer molecular weight.

Explanation of intrinsic viscosity relationship

The first term on the right side of eq. (5) is the intrinsic viscosity at the theta condition. At the theta condition, the polymer coil volume or intrinsic viscosity is at a minimum because, at this condition, the polymer coil is not swollen by the presence of a solvent. At the theta condition, the polymer coil volume is only due to molecular conformational constraints and $[\eta] = [\eta]_\theta = K_\theta M^{1/2}$.

The second term on the right side of eq. (5) is the partial change in the intrinsic viscosity associated with a change in system entropy. This term accounts for changes in the system order due to polymer-solvent interaction and is proportional to the ratio of χ_h to θ .

The third term on the right side of eq. (5) is the partial change in the intrinsic viscosity associated with a change in the system enthalpy. This term accounts for changes in the system heat due to polymer-solvent interaction and is proportional to the ratio of χ_h to T .

Examination of eq. (5) reveals that four possible solution conditions may exist with respect to fluid temperature changes. Intrinsic viscosity variations due to fluid temperature changes depend upon the sign of χ_h and the fluid temperature, T , relative to the theta temperature, θ .

A negative value of χ_h indicates that mixing the polymer with the solvent is exothermic and mixing is improved at lower temperatures, that is, χ becomes less at lower temperatures. As shown by eq. (4), the value of χ depends upon the solution temperature, T , in relation to the theta temperature, θ . Two possibilities exist: $T > \theta$ or $T < \theta$, accounting for two of the four dilute solution conditions. At these two conditions, the intrinsic viscosity decreases as the fluid temperature increases.

In contrast, a positive value of χ_h indicates that mixing the polymer with the solvent is endothermic and mixing is improved at higher temperatures, that is, χ becomes less at higher temperatures. Again, the value of χ depends upon the solution temperature, T , in relation to the theta temperature, θ . Two possibilities exist: $T > \theta$ or $T < \theta$, giving the remaining two dilute solution conditions. At these two conditions, the intrinsic viscosity increases as the fluid temperature increases.

Working equation relating intrinsic viscosity to polymer molecular weight and temperature

Equation (5) can be arranged to form eq. (6):

$$\frac{[\eta]}{M} = \frac{1.02\Phi_o \chi_h}{N_A V_s \theta \rho_p^2} + \frac{K_\theta}{\sqrt{M}} - \frac{1.02\Phi_o \chi_h}{N_A V_s \rho_p^2} \cdot \frac{1}{T} \quad (6)$$

Provided that V_s and ρ_p are not significantly dependent upon the temperature (the usual case), eq. (6) is a multiple linear equation of the form

$$z = a + bx + cy \quad (7)$$

where

$$z = \frac{[\eta]}{M} \quad x = \frac{1}{\sqrt{M}} \quad y = \frac{1}{T}$$

$$a = \frac{1.02\Phi_o \chi_h}{N_A V_s \theta \rho_p^2} \quad b = K_\theta \quad c = -\frac{1.02\Phi_o \chi_h}{N_A V_s \rho_p^2}$$

Equation (7) can be fitted by linear regression⁴ to data points defined by experimental measurements of the intrinsic viscosity, $[\eta]$, at specific polymer molecular weights, M , and solution temperatures, T , to determine the coefficients a , b , and c . Knowledge of these coefficients enables determination of the unknown parameters K_θ , θ , and χ_h :

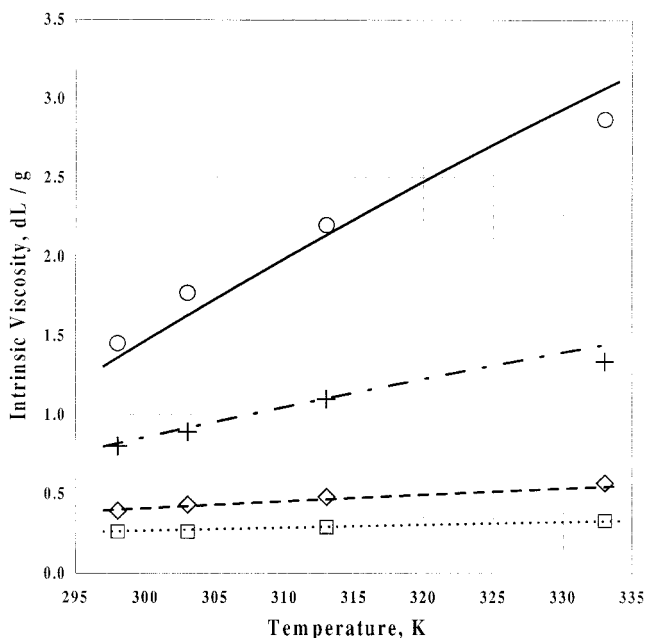


Figure 1 Solution intrinsic viscosities of polyisobutylene in benzene. (Solid curve and circles) 1,260,00 g/mol molecular weight polymer; (dashed-dot curve and pluses) 463,000 g/mol; (dashed curve and diamonds) 110,000 g/mol; (dotted curve and squares) 48,000 g/mol.

$$K_{\theta} = b \quad \theta = \frac{c}{a} \quad \chi_h = \frac{-cN_A V_s \rho_p^2}{1.02\Phi_0}$$

The values of K_{θ} , θ , and χ_h define how the solution's intrinsic viscosity will vary with the polymer molecular weight and the fluid temperature.

Application of the working viscosity equation to literature data

A review of the scientific literature produced many journal articles which contain tabulated data reporting intrinsic viscosity values over ranges of polymer molecular weights and fluid temperatures. However, the intrinsic viscosity working equation is only fitted to three data sets here to demonstrate the utility of the relationship.

Data set I: polyisobutylene in benzene

This data set was taken from a 1949 article by Fox and Flory.⁵ Polyisobutylene molecular weights ranged from 1,260,000 to 48,000 g/mol. Fluid temperatures varied from 25 to 60°C. Intrinsic viscosities were determined using an Ubbelohde viscometer. The polymer density, ρ_p , and the solvent molar volume, V_s , are 0.915 g/mL and 88.7 mL/mol, respectively.

Figure 1 shows the experimental data and the fit curves resulting from a multiple linear regression of eq. (7) to the data. The values determined by the

regression for θ , K_{θ} , and χ_h were 297.6 K, 0.119 mL g^{-3/2} mol^{1/2}, and 60.2 K, respectively. For this polymer-solvent system, Fox and Flory determined that θ and K_{θ} had values of 295 K and 0.110 mL g^{-3/2} mol^{1/2}, respectively. Thus, the intrinsic viscosity equation parameters, θ and K_{θ} , appear to be consistent with the values determined by Fox and Flory.

As shown by Figure 1, the curves produced from the intrinsic viscosity equation fit the experimental data well. The adjusted correlation coefficient between the experimental data and the corresponding fit values is 0.994. This high value suggests that the intrinsic viscosity equation is adequate for fitting the experimental data. For this polymer-solvent system, the intrinsic viscosity increases with an increasing fluid temperature and an increasing polymer molecular weight.

Data set II: polystyrene in cyclohexane

This data set was taken from a 1986 article by Gundert and Wolf.⁶ Polystyrene molecular weights ranged from 1,800,000 to 17,500 g/mol. Fluid temperatures varied from 32 to 50°C. Intrinsic viscosities were determined at each solution condition using an Ubbelohde viscometer. The polymer density, ρ_p , and the solvent molar volume, V_s , are 1.04 g/mL and 108.1 mL/mol, respectively.

Figure 2 shows the experimental data and the fit curves resulting from a multiple linear regression of

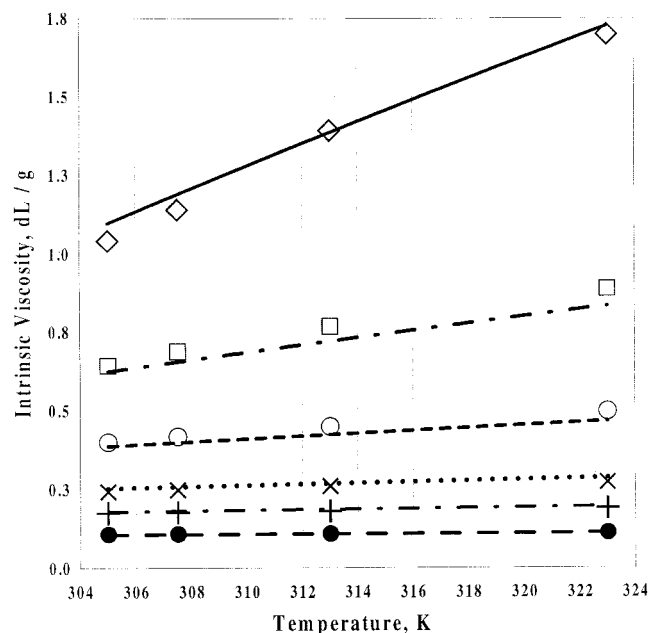


Figure 2 Solution intrinsic viscosities of polystyrene in cyclohexane. (Solid curve and diamonds) 1.8 $\cdot 10^6$ g/mol molecular weight polymer; (dashed-dot curve and squares) 600,000 g/mol; (dashed curve and open circles) 233,000 g/mol; (dotted curve and x's) 100,000 g/mol; (solid curve and pluses) 50,000 g/mol; (dashed curve and solid circles) 17,500 g/mol.

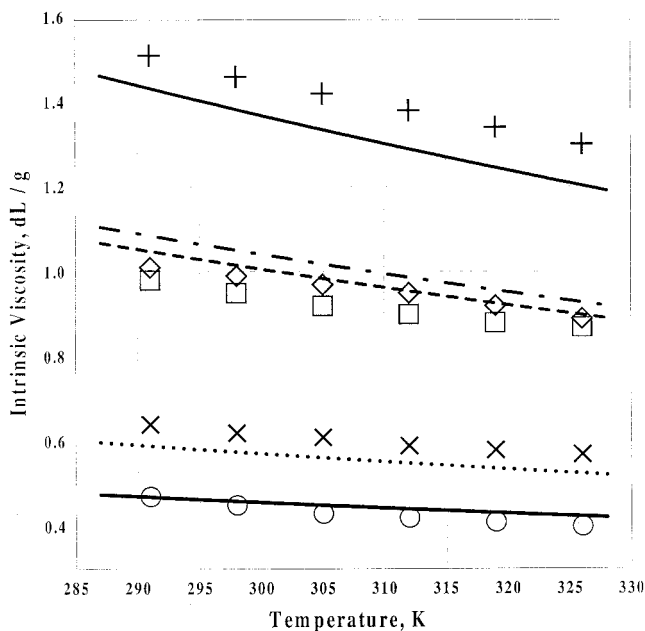


Figure 3 Solution intrinsic viscosities of poly(vinyl acetate) in chloroform. (Solid curve and pluses) 217,000 g/mol molecular weight polymer; (dashed-dot curve and diamonds) 148,000 g/mol; (dashed curve and squares) 141,000 g/mol; (dotted curve and x's) 61,000 g/mol; (solid curve and circles) 43,000 g/mol.

eq. (7) to the data. The values determined by the regression for θ , K_θ , and χ_h were 304.1 K, 0.079 mL g^{-3/2} mol^{1/2}, and 47.1 K, respectively. Kok and Rudin reported that K_θ had a value of 0.072 mL g^{-3/2} mol^{1/2} for the same polymer-solvent system.⁷ Flory reported θ and K_θ values of 307 K and 0.082 mL g^{-3/2} mol^{1/2}, respectively. Thus, the intrinsic viscosity equation parameters appear to be consistent with the reported values.

As shown by Figure 2, the curves produced from the intrinsic viscosity equation fit the experimental data well. The adjusted correlation coefficient between the experimental data and the corresponding fit values is 0.998. This high value indicates that the intrinsic viscosity equation is also adequate in fitting these experimental data.

Data set III: poly(vinyl acetate) in chloroform

This data set was taken from a 1962 article by Moor and Murphy.⁸ Poly(vinyl acetate) molecular weights ranged from 217,000 to 43,000 g/mol. Fluid temperatures varied from 18 to 53°C. Intrinsic viscosities were determined at each solution condition using a capillary viscometer. The polymer density, ρ_p , and the solvent molar volume, V_s , are 1.19 g/mL and 80.5 mL/mol, respectively.

Figure 3 shows the experimental data and the fit curves resulting from a multiple linear regression of eq. (7) to the data. The values determined by the

regression for θ , K_θ , and χ_h were 427.1 K, 0.161 mL g^{-3/2} mol^{1/2}, and -69.0 K, respectively. Kok and Rudin reported that K_θ had a value of 0.093 mL g^{-3/2} mol^{1/2} for this polymer-solvent system.⁷ Thus, the intrinsic viscosity equation gives a K_θ parameter that is about 50% larger than the Rudin reported value.

As shown in Figure 3, solution intrinsic viscosity decreases as temperature increases. However, the curves produced from the intrinsic viscosity equation fit the experimental data poorly. Although the correlation coefficient between the experimental data and the corresponding fit values is 0.984, many of the fit curves are significantly different from the corresponding data points.

It appears that the intrinsic viscosity working equation correctly accommodates temperature changes but does not adequately adjust for polymer molecular weight variations. This inadequacy of the function to fit the data could be an experimental problem such as a molecular weight determination error or it could be associated with the simplifications used to develop the working intrinsic viscosity equation, that is, the assumption that the χ value is not dependent upon the polymer molecular weight and the parameters K_θ , V_s , and ρ_p are not dependent on the temperature.

DISCUSSION

Table I gives a summary of the results in fitting the working intrinsic viscosity equation to the three sets of experimental data. Included in Table I are the polymer-solvent enthalpic contribution to the overall interaction parameter, χ_{hr} , the calculated polymer-solvent entropic contribution to the overall interaction parameter, χ_{sr} , and the calculated overall polymer-solvent interaction parameter, χ , for both 25 and 60°C. The intrinsic viscosity values calculated using the working equation for polymers having a molecular weight of 250,000 g/mol at 25 and 60°C are also listed in Table I.

The entropic contribution to the polymer-solvent interaction parameter, χ_{sr} , was calculated from the enthalpic contribution to the polymer-solvent interaction parameter, χ_{hr} , and the theta temperature, θ , using eq. (3). The overall polymer-solvent interaction parameter, χ , was calculated for fluid temperatures of 25 and 60°C using eq. (2). When χ is 0.5, the polymer-solvent system is at its theta condition. As χ values begin to exceed 0.5, extremely high molecular weight polymer molecules will phase-separate from the solution. As χ values become less than 0.5, the polymer coils expand and the intrinsic viscosity increases.

The expected intrinsic viscosity response to temperature is shown in the last four columns of Table 1. For both polyisobutylene in benzene and polystyrene in cyclohexane solutions, the χ values decrease as the temperature increases from 25 to 60°C and the intrinsic

TABLE I
Solubility Parameters

Data set	θ (K)	K_{θ} (mL g ^{-3/2} mol ^{1/2})	χ_h (K)	χ_s	χ (at 298 K)	η_{intr} (at 298 K, dL/g, $M = 250,000$)	χ (at 333 K)	η_{intr} (at 333 K, dL/g, $M = 250,000$)
I. Polyisobutylene in benzene	297.6	0.119	60.2	0.298	0.500	0.60	0.479	0.94
II. Polystyrene in cyclohexane	304.1	0.079	47.1	0.345	0.503	0.36	0.487	0.53
III. Poly(vinyl acetate) in chloroform	427.1	0.161	-69.0	0.662	0.430	1.54	0.454	1.28

insic viscosity values increase by about 50%. Note that both solutions are almost at the theta condition ($\chi = 0.5$ and polymer coils have a minimum size) when the temperature is 25°C. Above 25°C, both solvents swell the polymer coils to larger dimensions as reflected by smaller χ values and larger intrinsic viscosities at 60°C compared to 25°C.

In contrast, for the poly(vinyl acetate) in the chloroform solution where the χ value increases from 0.430 to 0.454 as the temperature increases from 25 to 60°C, the intrinsic viscosity value decreases by about 17%. Above 25°C, chloroform is less capable of expanding the polymer coils and the coils contract in volume as reflected by both a larger χ value and a smaller intrinsic viscosity at 60°C versus 25°C.

CONCLUSIONS

The intrinsic viscosity responses to temperature and molecular weight variations of three polymer solutions were used to test the modeling capability of a simplified intrinsic viscosity equation. The equation contains three parameters (θ , K_{θ} , and χ_h) that are related to the thermodynamic properties of polymer solutions. These parameters describe the polymer coil size at unperturbed conditions and the polymer coil expansion capabilities of the solvent as a function of the fluid temperature. Linear regression to experimental data produced an intrinsic viscosity equation containing unique fitted parameters for each solution. Each equation closely modeled experimental polymer intrinsic viscosity data over a range of molecular weights and fluid temperatures. These results imply that the simplified intrinsic viscosity equation is acceptable in modeling the polymer coil size response to the solvent composition, temperature, and polymer molecular weight.

The authors wish to acknowledge the National Energy Technology Laboratory, National Petroleum Technology Office, Tulsa, OK, United States Department of Energy, for its support of this work.

NOMENCLATURE

a, b, c	coefficients in the linear form of the intrinsic viscosity function used in eq. (7)
K	Mark-Houwink-Sakurada K value
K_{θ}	Mark-Houwink-Sakurada K value at theta condition
M	weight-average polymer molecular weight
N_A	Avogadro's number ($6.02 \times 10^{23} \text{ mol}^{-1}$)
T	absolute temperature
V_s	solvent molar volume
x	polymer molecular weight independent variable in the linear form of the intrinsic viscosity function
y	temperature independent variable in the linear form of the intrinsic viscosity function
z	dependent variable in the linear form of the intrinsic viscosity function
χ	overall polymer-solvent interaction parameter related to the enthalpic contribution to the overall polymer-solvent interaction parameter
χ_h	entropic contribution to the overall polymer-solvent interaction parameter
χ_s	entropic contribution to the overall polymer-solvent interaction parameter
$[\eta]$	intrinsic viscosity
$[\eta]_{\theta}$	intrinsic viscosity at theta conditions (polymer coil unperturbed by solvent)
θ	theta temperature (temperature corresponding no polymer-solvent interaction)
Φ_o	Flory constant (2.8×10^{23} in the cgs system)
ρ_p	polymer density

References

- Flory, P. J. Principles of Polymer Chemistry: Cornell University: Ithaca, NY, 1953.
- Stockmayer, W. H.; Fixman, M. J Polym Sci 1963, 1, 137-141.
- Van Dijk, M. A.; Wakker, A. Polymer 1993, 34, 132-137.
- Draper, N. R.; Smith, H. Applied Regression Analysis, 2nd ed.; Wiley: New York, 1981.
- Fox, T. G.; Flory, P. J. J Phys Colloid Chem 1949, 53, 197-212.
- Gundert, F.; Wolf, B. A. Makromol Chem 1986, 187, 2969-2990.
- Kok, C. M.; Rudin, A. J App Polym Sci 1982, 27, 353-362.
- Moore, W. R.; Murphy, M. J Polym Sci 1962, 56, 519-532.