Intrinsic Viscosities and Translational Diffusion Coefficients of n-Alkanes in Solution

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ABSTRACT: The translational diffusion coefficients, $D_0$, and intrinsic viscosities, [$\eta$], of n-alkanes up to C$_{28}$ in carbon tetrachloride and benzene are analyzed by comparison of experimental results with hydrodynamic calculations reported in the preceding paper. While $D_0$, when put in the form of a hydrodynamic radius, seems to be independent of the solvent, for [$\eta$] one has to correct for solvent effects prior to comparison with theoretical values. This is done by a slightly modified thermodynamic treatment of the viscosity of liquid mixtures developed by Bloomfield and co-workers. Our aim is to find a suitable hydrodynamic interaction parameter for real chains of this type. We consider two plausible parameters: the Stokes radius of the CH$_2$ repeating units, $h^*$, and the well-known, dimensionless quantity $h^*$. In the $h^*$ representation, $\sigma$ varies with chain length. Our analysis is not conclusive in the sense that both $h^*$ and $\sigma$ show similar performances. This is due, in part, to remaining uncertainties in the corrected experimental [$\eta$]'s. Nonetheless, we conclude that there is no reason for preferring $h^*$, and $\sigma$ could be the best choice owing to its simplicity.

Introduction

In the preceding paper,$^1$ we evaluated the translational diffusion coefficients, $D_0$, and intrinsic viscosities, [$\eta$], for three types of macromolecular models, namely, freely jointed chains, freely rotating chains, and polymethylene chains. Of these three models, the last corresponds to real n-alkane molecules, for it actually includes both short- and long-range intramolecular interactions. The purpose of the present article is to analyze experimental data of the two transport properties, taken from the literature, along with the theoretical values.

A similar aim was pursued in earlier works. Thus Dewan and Van Holde,$^2$ Paul and Mazo,$^3$ Jain and Tewari,$^4$ Freire et al.$^5$ and Mokrys et al.$^6$ calculated $D_i$ using the approximate Kirkwood double-sum formula. These works differ in the assignation of the frictional radius, $\sigma$, of the CH$_2$ repeating unit as well as in the way of evaluating the averages of the reciprocal interunit distances, $<R_{ij}^{-1}>$, needed in Kirkwood's formula.

The intrinsic viscosity has also been computed for n-alkanes in the studies of Perico and Rossi,$^7$ Bloomfield and co-workers,$^8,9$ and Freire and co-workers.$^{11,12}$ The first two groups used the Kirkwood–Riseman approximation, including preaveraging$^{13}$ in which the contribution of each of the $N + 1$ repeating units to [$\eta$] is obtained as the solution of a system of $N + 1$ linear equations. However, the third group used a bead-and-spring formalism yielding remarkably higher intrinsic viscosities. Among these studies, differences similar to those commented above for $D_i$ are observed. The analysis of experimental [$\eta$] data$^{12,14,15}$ poses an additional problem that is not found for $D_i$: for a given n-alkane, [$\eta$] in carbon tetrachloride is quite different from that in benzene. These solvent effects are so pronounced that negative values of [$\eta$] are experimentally found$^{15}$ for n-alkanes, C$_n$H$_{2n+2}$, with $n < 12$ in C$_2$H$_4$ at 20 °C.

This means that the experimental [$\eta$]'s must be corrected for solvent effects prior to their comparison with hydrodynamic calculations. While Bloomfield et al.$^{9,10}$ estimated the solvent corrections from Flory's$^{10,17}$ thermodynamic theory of binary liquid mixtures, Freire et al.$^5$ used rather simple arguments based solely on the solvent's molar volume. The resulting corrections are different, but the differences happened to fortuitously cancel with those in the hydrodynamic calculations so that in both works the experimental variation of [$\eta$] with $n$ was well predicted.

The comparison of the theoretical dependence of the transport properties on the number of repeating units, $n$, with experimental data relies on the choice of a suitable parameter that gauges the strength of hydrodynamic interactions. One possibility is to assume a constant value of $\sigma$ (independently of $n$) for the CH$_2$ groups. One limiting case, in which beads representing neighboring CH$_2$ groups are tangent, corresponds to $\sigma = 0.76$ A, which is half the C–C bond distance in n-alkanes, $b = 1.53$ A. The other possibility is to use as the adjustable constant the parameter defined by$^{6,8,18}$

$$h^* = \frac{\xi}{(12\pi n/2)^{1/2}}n_b$$

(1)

where

$$b = \langle r^2 \rangle^{1/2}/N^{1/2}$$

(2)

In eq 1 and 2, $\xi$ is the friction coefficient of the CH$_2$ units, $\langle r^2 \rangle$ is the mean-square end-to-end distance, and $N$ is the number of C–C bonds (note that $N + 1 = n$). If we take the Stokes law value for $\xi$, eq 1 reduces to

$$h^* = 0.9772a \langle r^2 \rangle / N^{1/2}$$

(3)

As $\langle r^2 \rangle / N$ depends on $N$ except for infinitely long chains, it turns out that assuming constancy of $h^*$ implies that $\sigma$ varies with $N$.

At first glance, it seems possible to ascertain which of the two parameters, $\sigma$ or $h^*$, is best. We can do so by comparison of the calculated variation of the transport properties, for fixed $h^*$ or for fixed $\sigma$, with the experimental ones. We can also look at the concordance of the values of $h^*$ and $\sigma$ fitted for two different properties. In both cases it is very important to have theoretical results of high accuracy because small deviations in them could significantly bias the values of the adjustable parameters. In regard to this, it should be pointed out that the earlier works used approximate hydrodynamic formalisms, which can be in error by even more than 10% in $D_i$ and [$\eta$], as recently shown by Zimm$^{20}$ and ourselves.$^{12}$

The comments in the above paragraphs illustrate the necessity of reconsidering theoretically the transport properties of n-alkanes as we have attempted in this paper. Thus, our theoretical values are obtained by using the most
Accordingly, the contribution from those effects has to be Bloomfield and Dewang suggested that \([\eta] = \eta_0 + [\eta]_G + [\eta]_V + [\eta]_I\), where \([\eta]_G\) takes care of all the possible solute and free energy per mole of solution. Finally, \([\eta]_V\) is the value of the viscosity of liquids and depends on the activation rate theory and free volume terms are both included, \([\eta]_I\) is taken as a constant value for this homologous series. We use the value \(\sigma' = S_2 / S_1\), is taken as a constant value for this homologous series. We use the value \(\sigma' = 1.08\) for the \(c\) system, calculated from the values reported in ref 16 for the \(c\) system, and \(c\) system, and \(c\) system, which is used as a reference. We get \(\rho = 1.327\) for that system and, therefore, the values for the rest of the series are calculated from

\[
\rho_n = \frac{1.327 (n + 1)}{7} \tag{7}
\]

The segmental interaction parameter \(X_{12}\) is taken as a constant value for the series. We have estimated it from

\[
\eta_{\text{corr}} = \eta_{\text{exptl}} - \eta_g^a
\]

where \([\eta]_g\) takes care of all the possible solute and solute–solute effects.

A suitable way of estimating \([\eta]_g\) that is soundly based on thermodynamic grounds has been proposed by Bloomfield and co-workers.\(^8\) In a study of liquid mixtures of small molecules, for which the continuum hydrodynamic contribution must be much smaller than the other ones, Bloomfield and Dewang\(^9\) suggested that \([\eta]_g\) corresponds to the superposition of three terms, \([\eta]_1, [\eta]_2, [\eta]_3\). \([\eta]_g\) comes from the differences in viscosities between the pure solvent and solute. Actually, it takes the value

\[
[\eta]_g = \frac{v_0}{M_2} \ln \frac{\eta_0}{\eta_2}
\]

where \(v_0\) is the molar volume of the solvent, \(M_2\) is the molecular weight of the solute, and \(\eta_0\) and \(\eta_2\) are the viscosities of the pure solvent and solute, respectively. \([\eta]_g\) is the contribution predicted by the absolute rate theory of the viscosity of liquids and depends on the activation free energy per mole of solution. Finally, \([\eta]_V\) is the value that gives the alternative formulation of the solution’s free volume. Bloomfield and Dewang\(^9\) found that either \([\eta]_g, [\eta]_I\) or \([\eta]_g, [\eta]_V\) provides a good reproduction of the experimental intrinsic viscosities of a number of binary solutions (Table II in ref 9). However, when the absolute rate theory and free volume terms are both included, \([\eta]_g + [\eta]_I + [\eta]_V\) leads to a great underestimation of the mixture’s intrinsic viscosity. This indicates, as Bloomfield and Dewang\(^9\), conclude, that although the underlying phenomena in both theories should be simultaneously

### Table I

<table>
<thead>
<tr>
<th>solvent</th>
<th>solute</th>
<th>([\eta]_I + [\eta]_G^a)</th>
<th>([\eta]_0 + [\eta]_V^a)</th>
<th>([\eta]_I + \frac{1}{4}[\eta]_G^b)</th>
<th>exp1(^a)</th>
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<tbody>
<tr>
<td>benzene</td>
<td>cyclohexane</td>
<td>-0.639</td>
<td>-0.032</td>
<td>-0.385</td>
<td>-0.430</td>
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<td>-1.296</td>
<td>-1.688</td>
<td>-1.67</td>
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<td>n-heptane</td>
<td>-1.729</td>
<td>-0.951</td>
<td>-1.340</td>
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</tr>
</tbody>
</table>

\(^a\) From Bloomfield and Dewang.\(^9\) \(^b\) Equation 7.
Table II
Experimental and Corrected \([\eta]\)'s of \(n\)-Alkanes (20 °C)

<table>
<thead>
<tr>
<th>(n)</th>
<th>(C_4H_8)</th>
<th>ClC</th>
<th>(C_4H_8)</th>
<th>ClC</th>
<th>(C_4H_8)</th>
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<td>0.45</td>
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<td>0.44</td>
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<td>7</td>
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<td>0.26</td>
<td>0.09</td>
<td>-0.10</td>
<td>0.90</td>
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<tr>
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<td>0.01</td>
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<td>0.45</td>
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<td>0.84</td>
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<tr>
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</table>

Figure 1. Theoretical and corrected experimental values of the intrinsic viscosity of \(n\)-alkanes, \(C_nH_{2n+2}\). The crosses and pluses are experimental results\(^\text{20}\) at 20 °C, in carbon tetrachloride and benzene, respectively, after discounting solvent contributions given by eq 7. The continuous line represents theoretical values obtained in our previous paper\(^\text{1}\) for the indicated values of \(\rho\).

The values so calculated are listed along with those in \(CsH_6\) in Table II. Readers interested in the individual values of \([\eta]_n\), \([\eta]_v\), and \([\eta]_c\) in the two solvents can obtain those values by simple manipulation of the data in Table II.

Hydrodynamic Results. The values of \([\eta]_{\text{corr}}\) are to be compared with those obtained in our previous paper.

Figure 2. Same as in Figure 1 but the theoretical curves are plotted for fixed \(h^*\).

Table III in ref 1 gives the reduced intrinsic viscosity, \([\eta]^*\), as a function of \(n\) for fixed values of \(\sigma\). These results can be converted into actual intrinsic viscosities by means of the relation

\[
[\eta] = (N_A/M)[\eta]^*
\]

where \(N_A\) is Avogadro's number and the molecular weight of the \(n\)-alkanes can be expressed as \(M = 14.026n + 2.016\). \([\eta]\) as a function of \(n\) is plotted in Figure 1 for several values of \(\sigma\).

To obtain the chain-length dependence of \([\eta]\) for fixed \(h^*\), we drew plots of \([\eta]\) vs. \(\sigma\) at constant \(N\). For a given \(h^*\) and \(N\), \(\sigma\) is calculated according to eq 3 using the \((r^2)\) values for polymethylene chains obtained in our previous paper\(^\text{1}\) (which, in turn, agree closely with those from other
works. Finally, [ŋ] for this σ is evaluated in the above-mentioned interpolation plots. The results are presented in Figure 2. When h* > 0.20, [ŋ] cannot be calculated for high n because the corresponding σ exceeds the highest value considered in ref 1 and falls in the region of overlapping neighboring beads.

The corrected experimental [ŋ]'s in C6H5 and C12C listed in the two last columns of Table II are included in Figures 1 and 2. In ref 1, a temperature of 25 °C was used for the calculation of the statistical weights of the t, g, and g' conformations, so the theoretical intrinsic viscosities presented in Figures 1 and 2 correspond to that temperature. However, the data in Table II come from measurements at 20 °C. In order to avoid a tedious recalculation of the intrinsic viscosities, in the comparison between calculated and experimental values that will be made in the Discussion we have overlooked this small difference in temperature. In fact, it gives a deviation of only 1% in the statistical weights, and the subsequent error in [ŋ] must be similar.

Translational Diffusion Coefficients

The translational diffusion coefficients of n-alkanes have been measured in carbon tetrachloride and in benzene at 25 °C. The primary source for the solvent dependency of Dn, namely, the viscosity of the solvent, η0, can be eliminated if one expresses the results as Stokes radii of the n-alkane chains, f*:

\[ f^* = k_B T / 6 \pi \eta_0 D_n \]  \hspace{1cm} (9)

Figure 3 shows how the two sets of experimental f* data are nearly coincident, the differences for a given n being similar to the experimental errors. Hence, we can assume that no solvent effects other than that from η0 have to be considered, and, therefore, the experimental results in the f* form are directly comparable with the theoretical f*'s calculated in the preceding paper. Then in Figure 3 we

Discussion

By simple inspection of Table II and Figures 1 and 2 it is evident that for the longest chains considered, both [ŋ]corr and [ŋ]corr - [ŋ]corr are much higher than the values calculated for the highest physically meaningful value of the hydrodynamic interaction parameter. On the other hand, [ŋ]corr - [ŋ]corr is consistently low, but, surprisingly, it gives nearly identical results for the two solvents (see Table II), as should the correcting expression we were seeking. However, its performance in regard to the data in Table I is very bad, and if it were accepted as the corrective term, the comparison with theoretical results would give exceedingly low values for the hydrodynamic parameter (either σ or h*), well within the free-draining region and in strong disagreement with all the previous hydrodynamic studies on n-alkanes. Thus, we are led to the belief that this unexpected behavior of [ŋ]corr - [ŋ]corr is a fortuitous outcome of the remaining deficiencies in the treatment of the viscosity of liquid mixtures used in this work.

The combination we have proposed for [ŋ] (eq 7), in addition to working well for the simple mixtures in Table I, gives [ŋ]corr values that are comparable with those calculated for reasonable values of σ. Moreover, the differences between [ŋ]corr in the two solvents are not much larger than the experimental errors evidenced by the scatter in the data points.

Figure 1 shows that the chain-length dependence of [ŋ]corr is not well predicted by the theoretical curves with σ as an adjustable parameter. The slope of these curves for n between 10 and 30 is remarkably smaller than that followed by [ŋ]corr, and we obtain σ = 0.20–0.40 Å for low
n (n < 20) and σ = 0.50–0.60 for high n (n > 20). Some improvement is found when the parameter is \( h^* \), as seen in Figure 2. The trend of \( [\eta]_{corr} \) is again steeper than that of the theoretical curves but the difference is not so noticeable. We have found \( h^* \approx 0.10 \) for low n and \( h^* \approx 0.13 \) for high n.

When we turn to a similar analysis for translational diffusion, the findings are in conflict with the previous ones. The experimental \( f^* \)'s in the two solvents are very well predicted by the theoretical curves for \( \sigma = 0.55–0.70 \) Å over the whole range of n, as seen in Figure 3. However, Figure 4 reveals that when \( h^* \) is used, the slopes of the theoretical curves are greater than that of the experimental curve and we obtain discrepant results, \( h^* = 0.20–0.22 \) at low n and \( h^* = 0.15–0.17 \) at high n.

These disparities make it difficult to apply the two criteria suggested in the Introduction for deciding which of the \( \sigma \) and \( h^* \) representations is best. If one looks at individual properties, \( [\eta] \) seems to favor \( h^* \), but from the point of view of \( D_t \) (of \( f^* \)), \( \sigma \) works best.

As the experimental \( f^* \) values coincide in the two solvents while those of \( [\eta] \) need an elaborate correction for solvent effects that includes some approximations, one might wish to give more weight in the above comparison to the conclusion found from translational diffusion.

Since neither \( \sigma \) nor \( h^* \) is able to describe with a single value the variation of the hydrodynamic properties over the whole range of n (except \( \sigma \) for \( D_t \)), we can consider separately the regions of low and high n. For low n, \( \sigma \) as fitted for \( [\eta] \) deviates from that for \( D_t \), and the situation is quite similar in the case of \( h^* \). However, for high n, a single value of \( \sigma \) around 0.60 Å would provide an acceptable prediction of the experimental values of the two properties in the two solvents.

In their study of the same translational diffusion data considered here, Stepto and co-workers\(^6\) found that \( \sigma \) should vary with n, so that \( h^* \) would be a better parameter. However, we do not see any reason for preferring \( h^* \), since the two parameters have similar performances in the comparison with experimental data. Our disagreement with their conclusion could arise from their use of Kirkwood's formula, which as shown in our previous paper introduces an error of several percent that, in addition, depends on n. Although there is not much evidence in favor of either \( h^* \) or \( \sigma \), we have a slight preference for \( \sigma \) because its physical meaning is more intuitive, and its use is simpler since it does not require the previous evaluation of \( \langle r^2 \rangle \).

Regardless of the difficulties found in the analysis of the hydrodynamic interaction parameters, this paper shows that the use of the most rigorous version of the Kirkwood–Riseman theory enables a good simultaneous description of the chain-length dependence of two properties of n-alkanes in two different solvents. This is in contrast with previous studies, which considered a single property or two properties with different hydrodynamic treatments.

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