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

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ABSTRACT: The translational diffusion coefficients, D_t, 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_t, 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, σ, and the well-known, dimensionless quantity h^*. In the h^* representation, σ varies with chain length. Our analysis is not conclusive in the sense that both h^* and σ 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 σ could be the best choice owing to its simplicity.

Introduction

In the preceding paper,[1] we evaluated the translational diffusion coefficients, D_t, 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_t using the approximate Kirkwood double-sum formula.[7] These works differ in the assignation of the frictional radius, σ, of the CH_2 repeating unit as well as in the way of evaluating the averages of the reciprocal interunit distances, $\langle R_{ij}^{-1}\rangle$, needed in Kirkwood's formula.

The intrinsic viscosity has also been computed for *n*-alkanes in the studies of Perico and Rossi,[8] Bloomfield and co-workers,[9,10] 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_t are observed. The analysis of experimental $[\eta]$ data[12,14,15] poses an additional problem that is not found for D_t: 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[12] for *n*-alkanes, C_nH_{2n+2}, with $n < 12$ in C_6H_6 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[16,17] thermodynamic theory of binary liquid mixtures, Freire et al.[12] 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 σ (independently of n) for the CH_2 groups. One limiting case, in which beads representing neighboring CH_2 groups are tangent, corresponds to $\sigma \simeq 0.76$ Å, which is half the C–C bond distance in *n*-alkanes, $b = 1.53$ Å. The other possibility is to use as the adjustable constant the parameter defined by[5,6,18]

$$h^* = \zeta/(12\pi^3)^{1/2}\eta_0 b' \qquad (1)$$

where

$$b' = \langle r^2\rangle^{1/2}/N^{1/2} \qquad (2)$$

In eq 1 and 2, ζ 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 ζ, eq 1 reduces to

$$h^* = 0.9772\sigma(\langle r^2\rangle/N)^{-1/2} \qquad (3)$$

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

At first glance, it seems possible to ascertain which of the two parameters, σ or h^*, is best. We can do so by comparison of the calculated variation of the transport properties, for fixed h^* or for fixed σ, with the experimental ones. We can also look at the concordance of the values of h^* and σ 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_t and $[\eta]$, as recently shown by Zimm[19] and ourselves.[1,20]

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

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Table I
Intrinsic Viscosities of Binary Mixtures of Alkanes and Benzene

		intrinsic viscosity, $cm^3\ g^{-1}$			
solvent	solute	$[\eta]_\eta + [\eta]_G$[a]	$[\eta]_\eta + [\eta]_V$[a]	$[\eta]_\eta + {}^1/_2[\eta]_G + [\eta]_V$[b]	exptl[a]
benzene	cyclohexane	−0.639	−0.032	−0.335	−0.430
cyclohexane	benzene	−1.800	−1.041	−1.420	−1.562
benzene	*n*-hexane	−2.080	−1.296	−1.688	−1.67
benzene	*n*-heptane	−1.729	−0.951	−1.340	−1.34

[a] From Bloomfield and Dewan.[9] [b] Equation 7.

rigorous form of the Kirkwood–Riseman theory and include improvements such as the modified Oseen tensor and translation–rotation coupling. In addition, we analyze two transport properties, $[\eta]$ and D_t, and we also examine the two alternative hydrodynamic interaction parameters, σ and h^*. Another relevant aspect of this paper is that in the course of the calculation of the solvent effects on $[\eta]$, we have found a modification of the method of Bloomfield and Dewan[9] that yields a better agreement between the corrected values of $[\eta]$ for two solvents, Cl_4C and C_6H_6, and between these values and the theoretical results.

Intrinsic Viscosity

Experimental Values and Solvent Effects. The intrinsic viscosities of *n*-alkanes in C_6H_6 and Cl_4C have been reported by several workers.[12,14,15] We shall use here the set of experimental values of Freire et al.[12] As already pointed out, the experimental viscosities are not directly comparable with those predicted by the usual continuum hydrodynamic theories owing to the preponderance of solvent effects and solvent–solute interactions at low *n*. Accordingly, the contribution from those effects has to be subtracted prior to comparison with the hydrodynamic results. If $[\eta]_{\text{exptl}}$ represents the experimental data, the corrected intrinsic viscosities will be given as

$$[\eta]_{\text{corr}} = [\eta]_{\text{exptl}} - [\eta]_s \tag{4}$$

where $[\eta]_s$ takes care of all the possible solute and solute–solvent effects.

A suitable way of estimating $[\eta]_s$ that is soundly based on thermodynamic grounds has been proposed by Bloomfield and co-workers.[9,10] 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 Dewan[9] suggested that $[\eta]_s$ corresponds to the superposition of three terms, $[\eta]_\eta$, $[\eta]_G$, and $[\eta]_V$. $[\eta]_\eta$ comes from the differences in viscosities between the pure solvent and solute. Actually, it takes the value

$$[\eta]_\eta = \frac{v_0}{M_2} \ln \frac{\eta_0}{\eta_2} \tag{5}$$

where v_0 is the molar volume of the solvent, M_2 is the molecular weight of the solute, and η_0 and η_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 Dewan[9] found that either $[\eta]_\eta + [\eta]_G$ or $[\eta]_\eta + [\eta]_V$ 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, $[\eta]_\eta + [\eta]_G + [\eta]_V$ leads to a great underestimation of the mixture's intrinsic viscosity. This indicates, as Bloomfield and Dewan[9,10] conclude, that although the underlying phenomena in both theories should be simultaneously present in the solution, their contributions cannot be just added.

Looking at the results in Table II of ref 9, we have found that any combination like $[\eta]_\eta + a_G[\eta]_G + a_V[\eta]_V$, where a_G and a_V are positive and smaller than 1, would give a better reproduction of the experimental results than those considered by Bloomfield and Dewan, If we take, for instance, $a_G = a_V = {}^1/_2$, we get $[\eta]_\eta + {}^1/_2[\eta]_G + {}^1/_2[\eta]_V$, which works fairly well. In fact, the least-squares regression analysis of this linear combination vs. $[\eta]_{\text{exptl}}$ yields a slope (0.996) closer to 1, an intercept (−0.031) closer to 0, and a correlation coefficient (0.990) nearer to 1 than any of the combinations used in ref 9. Table I in the present paper shows that our linear combination yields a substantial improvement in the concordance with experimental results. The agreement is excellent for the *n*-alkane (solute)–benzene (solvent) systems with $n = 6$ and 7, which are precisely of the kind considered in our study of hydrodynamic properties.

Therefore, we propose

$$[\eta]_s = [\eta]_\eta + \tfrac{1}{2}[\eta]_G + \tfrac{1}{2}[\eta]_V \tag{6}$$

as the correction term in eq 4. The individual values of $[\eta]_\eta$, $[\eta]_G$, and $[\eta]_V$ for the homologous series of *n*-alkanes in benzene at 20 °C were calculated by Dewan et al.[10] In Table II we have listed $[\eta]_{\text{exptl}}$ taken from ref 12 along with $[\eta]_{\text{corr}}$ as obtained from eq 4 and 6. For the sake of comparison, the two other possibilities for $[\eta]_{\text{corr}}$, namely, $[\eta]_{\text{exptl}} - \{[\eta]_\eta + [\eta]_V\}$ and $[\eta]_{\text{exptl}} - \{[\eta]_\eta + [\eta]_G\}$ are also listed in Table II.

In order to include in our analysis the available experimental $[\eta]$ data in carbon tetrachloride, we have carried out a calculation of $[\eta]_\eta$, $[\eta]_G$, and $[\eta]_V$ at 20 °C for Cl_4C (solvent)–*n*-alkane (solute) systems from the expressions given in ref 9 The parameters related to the properties of the pure solvent are taken from data tabulated by Abe and Flory.[16] The viscosity of pure Cl_4C at 20 °C is interpolated from the values at 0 and 25 °C given in ref 9, assuming that η is an exponential function of temperature. The parameters related to the properties of *n*-alkanes are directly obtained as functions of *n*, employing some approximate equations given in ref 10.

The ratio of molecular contact areas per segment, $\sigma' = S_2/S_1$, is taken as a constant value for this homologous series. We use the value $\sigma' = 1.08$ for the Cl_4C–C_6H_{14} system, calculated from the values reported in ref 16 for the Cl_4C–C_6H_{14} and C_6H_6–Cl_4C systems. We also obtain in a similar way the ratio of the number of segments in solute and solvent, $\rho = r_2/r_0$, for the Cl_4C–C_6H_{14} 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[10]

$$\frac{r_2}{r_0} = 1.327\left(\frac{n+1}{7}\right) \tag{7}$$

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

Table II
Experimental and Corrected $[\eta]$'s of *n*-Alkanes (20 °C)

	$[\eta]_{\text{exptl}}$		$[\eta]_{\text{exptl}} - \{[\eta]_\eta + [\eta]_V\}$		$[\eta]_{\text{exptl}} - \{[\eta]_\eta + [\eta]_G\}$		$[\eta]_{\text{exptl}} - \{[\eta]_\eta + {}^1/_2[\eta]_V + {}^1/_2[\eta]_G\}$	
n	C_6H_6	Cl_4C	C_6H_6	Cl_4C	C_6H_6	Cl_4C	C_6H_6	Cl_4C
5	−2.08		−0.08		0.67		0.22	
6	−1.66		−0.11		0.49		0.14	
7	−1.36		−0.26		0.44		0.09	
11	−0.15		−0.10		0.90		0.42	
12	0.09	0.33	−0.03	−0.01	1.04	0.66	0.56	0.32
13	0.29	0.49	−0.01	0.01	1.19	0.74	0.59	0.36
14	0.56	0.79	0.16	0.13	1.38	0.96	0.76	0.54
15	0.66	0.95	0.11	0.15	1.43	1.05	0.73	0.60
16	0.84	1.26	0.19	0.34	1.59	1.31	0.82	0.82
17	0.98	1.32	0.23	0.28	1.68	1.32	0.88	0.80
18	1.13	1.52	0.28	0.38	1.78	1.48	0.98	0.93
19	1.28	1.63	0.38	0.40	1.88	1.56	1.08	0.98
20	1.40	1.85	0.43	0.50	1.95	1.74	1.15	1.13
21	1.57	1.97	0.55	0.57	2.12	1.83	1.27	1.20
22	1.70	2.09	0.60	0.61	2.25	1.90	1.40	1.27
23	1.83	2.27	0.68	0.72	2.38	2.08	1.49	1.40
24	1.99	2.35	0.79	0.74	2.49	2.13	1.64	1.43
25	2.09	2.55	0.84	0.88	2.57	2.32	1.72	1.60
26	2.24	2.66	0.94	0.93	2.69	2.41	1.84	1.67
27	2.35	2.80	1.00	1.01	2.80	2.53	1.95	1.77
28	2.48	2.90	1.08	1.07	2.93	2.62	2.03	1.84

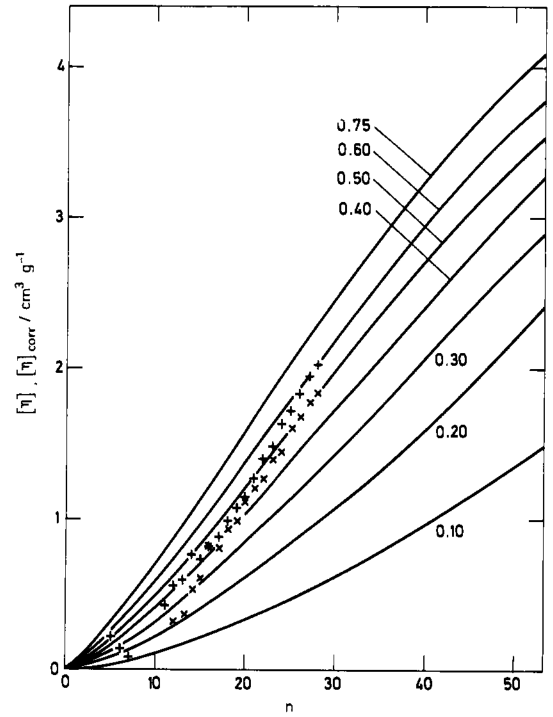

Figure 1. Theoretical and corrected experimental values of the intrinsic viscosity of *n*-alkanes, C_nH_{2n+2}. The crosses and pluses are experimental results[12] at 20 °C, in carbon tetrachloride and benzene, respectively, after discounting solvent contributions given by eq 7. The continuous lines represent theoretical values obtained in our previous paper[1] for the indicated values of σ.

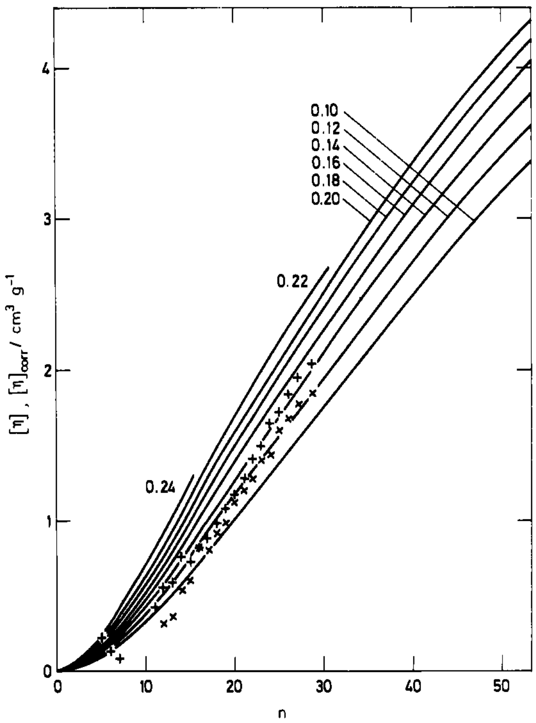

Figure 2. Same as in Figure 1 but the theoretical curves are plotted for fixed h^*.

the experimental data of excess enthalpies for different molar fractions of the Cl_4C–C_6H_{14} system reported by Harsted et al.[21] Applying Flory's theory of liquid mixtures (i.e., using eq 34′ of ref 17 and eq 1 and 2 of ref 16), we have obtained X_{12} = 3.3 cal/cm³.

The values so calculated are listed along with those in C_6H_6 in Table II. Readers interested in the individual values of $[\eta]_\eta$, $[\eta]_V$, and $[\eta]_G$ 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. Table III in ref 1 gives the reduced intrinsic viscosity, $[\eta]^*$, as a function of n for fixed values of σ. These results can be converted into actual intrinsic viscosities by means of the relation

$$[\eta] = (N_A/M)[\eta]^* \qquad (8)$$

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 σ.

To obtain the chain-length dependence of $[\eta]$ for fixed h^*, we drew plots of $[\eta]$ vs. σ at constant N. For a given h^* and N, σ is calculated according to eq 3 using the $\langle r^2 \rangle$ values for polymethylene chains obtained in our previous paper[1] (which, in turn, agree closely with those from other

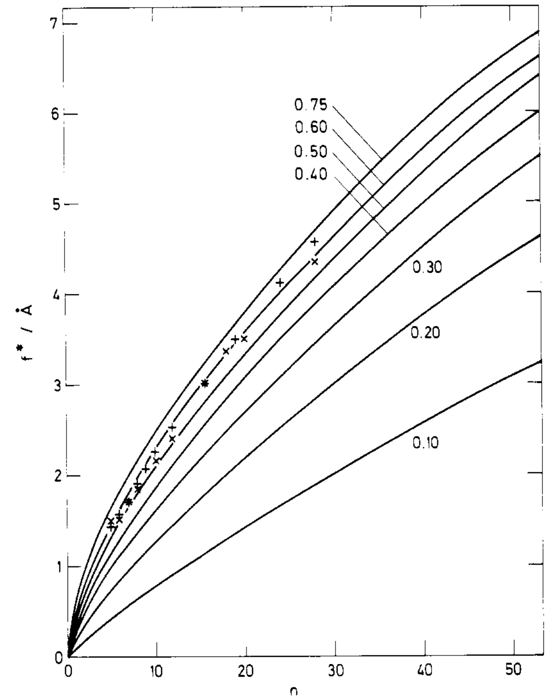

Figure 3. Theoretical and experimental values of the Stokes radius f^* (eq 9) for n-alkane chains of varying length. Experimental results at 25 °C in carbon tetrachloride (×) and in benzene (+) are taken from Dewan and Van Holde[2] and Stepto and coworkers,[6,23] respectively. The theoretical results plotted as continuous lines for several values of σ come from ref 1.

works[5,22]). Finally, $[\eta]$ for this σ is evaluated in the above-mentioned interpolation plots. The results are presented in Figure 2. When $h^* > 0.20$, $[\eta]$ 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 $[\eta]$'s in C_6H_6 and Cl_4C 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 $[\eta]$ must be similar.

Translational Diffusion Coefficients

The translational diffusion coefficients of n-alkanes have been measured in carbon tetrachloride[2] and in benzene[6,24] at 25 °C. The primary source for the solvent dependency of D_t, namely, the viscosity of the solvent, η_0, can be eliminated if one expresses the results as Stokes radii of the n-alkane chains, f^*:

$$f^* = k_BT/6\pi\eta_0D_t \qquad (9)$$

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 η_0 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.[1] Then in Figure 3 we have also plotted the theoretical curves corresponding to different values of σ.

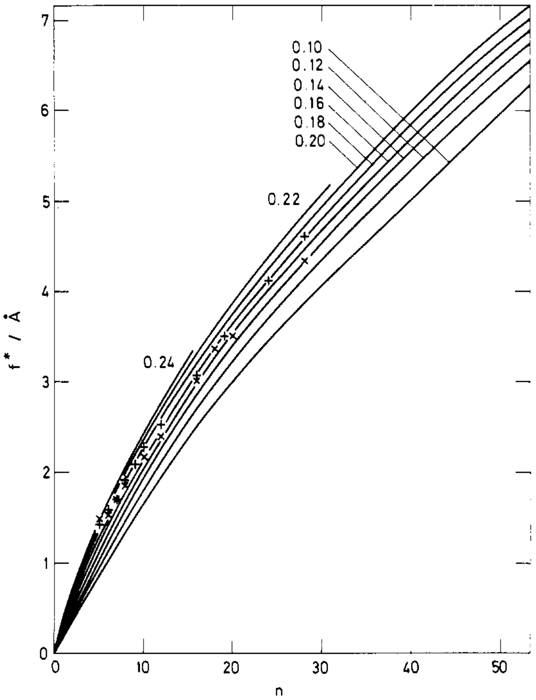

Figure 4. Same as in Figure 3, but considering h^* as the adjustable parameter.

As in the study of $[\eta]$, it is desirable to analyze the experimental results in terms of h^* as the adjustable hydrodynamic interaction parameter. To do so, we obtained curves of f^* vs. n for fixed h^* using the same interpolation procedure described above for $[\eta]$. These curves, along with the experimental f^*'s, are plotted in Figure 4.

Discussion

By simple inspection of Table II and Figures 1 and 2 it is evident that for the longest chains considered, both $[\eta]_{\rm exptl}$ and $[\eta]_{\rm exptl} - \{[\eta]_\eta + [\eta]_G\}$ are much higher than the values calculated for the highest physically meaningful value of the hydrodynamic interaction parameter. On the other hand, $[\eta]_{\rm exptl} - \{[\eta]_\eta + [\eta]_V\}$ 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.[2-12] Thus, we are led to the belief that this unexpected behavior of $[\eta]_{\rm exptl} - \{[\eta]_\eta + [\eta]_V\}$ 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 $[\eta]_s$ (eq 7), in addition to working well for the simple mixtures in Table I, gives $[\eta]_{\rm corr}$ values that are comparable with those calculated for reasonable values of σ. Moreover, the differences between $[\eta]_{\rm corr}$ 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 $[\eta]_{\rm corr}$ 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 $[\eta]_{\rm corr}$, and we obtain σ = 0.20–0.40 Å for low

n ($n < 20$) and $\sigma = 0.50$–0.60 for high n ($n > 20$). Some improvement is found when the parameter is h^*, as seen in Figure 2. The trend of $[\eta]_{\mathrm{corr}}$ is again steeper than that of the theoretical curves but the difference is not so noticeable. We have found $h^* \simeq 0.10$ for low n and $h^* \simeq 0.13$ 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 $n^* = 0.15$–0.17 at high n.

These disparities make it difficult to apply the two criteria suggested in the Introduction for deciding which of the σ 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^*), σ 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 σ nor h^* is able to describe with a single value the variation of the hydrodynamic properties over the whole range of n (except σ for D_t), we can consider separately the regions of low and high n. For low n, σ 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 σ 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[6,23,24] found that σ 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 σ, we have a slight preference for σ 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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