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Tracer diffusion in polyatomic liquids. III

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Tracer diffusivities are reported for argon, krypton, xenon, methane, carbon tetrachloride, and tetraalkyltins (methyl, ethyl, *n*-propyl, and *n*-butyl) in normal octane, decane, and tetradecane for temperatures ranging from 25 to 160 °C. The diffusivities were measured by the Taylor dispersion method. With temperature-dependent solvent diameters fitted from the tracer diffusivity of one of the solutes, a rough-hard-sphere theory predicts well the observed tracer diffusivities of all the other solutes in *n*-octane and, at high temperatures, *n*-decane (60–160 °C) and *n*-tetradecane (100–160 °C). The data are well correlated by either the Arrhenius equation, a free-volume formula, or the $D\mu^*$ -correlation.

I. INTRODUCTION

In a recent paper¹ we demonstrated the success of a rough-hard-sphere (RHS) theory in predicting the tracer diffusion at 25 °C of argon, krypton, xenon, methane, carbon tetrachloride, and tetraalkyltins (methyl, ethyl, *n*-propyl, *n*-butyl) in solvents of fairly compact molecules such as benzene, carbon tetrachloride, cyclohexane, and *n*-hexane. We also showed that the model breaks down for hydrogen-bonded solvents and for large non-compact solvents. For example, the theory was found to underestimate the tracer diffusivities of all the solutes in methanol by 30%. It consistently overestimates tracer diffusivities in *n*-decane at 25 °C by 30%.

Subsequently, we reported that the RHS theory has proven successful in interpreting the tracer diffusion of the same solutes in cyclohexane from 25 to 143 °C.² The combination of the results so far has permitted the RHS theory to be tested over the widest-ranging solute-solvent mass and size ratios and the most extended temperature range achieved to date. A consistent scheme has been devised to understand both tracer and self-diffusion within the framework of the RHS theory. The RHS theory provides insights into the origins of the activation energy of diffusion and of the Batschinski-Hildebrand free-volume correlation.

In the present study, tracer diffusion of the same solutes in *n*-octane, *n*-decane, and *n*-tetradecane was measured over the temperature range 25 to 160 °C using the Taylor dispersion technique.² Since the solvents which were used in this work are neither spherical in shape nor polar, the test of the RHS theory over a large temperature range may provide a basis for establishing conditions of applicability of the RHS theory where the restrictions on molecular shape are relaxed. One of the major reasons for carrying out the experiments was our expectation that the RHS theory would be more appropriate for non-compact molecules at higher temperatures where rapid rotational motion would average our nonspherical effects.

Other goals of this study are to relate the tracer diffusion behavior to the free-volume empiricism determined by Dymond³ from hard-sphere computer simulations, similar in content to Batschinski's free-volume model, and to extend the $D\mu^*$ -correlation⁴ over a wide temperature range for solvents in a homologous series.

II. EXPERIMENTAL

The experimental apparatus, the procedures, the methods for reducing the temperature and pressure where necessary, and the source and purity of solutes were described previously.²

The solvents *n*-octane (99%+, Aldrich), *n*-decane (99%+, Aldrich), and *n*-tetradecane (99%, Alfa) were filtered (0.5 μm Millipore) before usage.

III. RESULTS AND DISCUSSION

The tracer diffusivities of the dissolved gas (Ar, CH₄, Kr, Xe) and liquid solutes (CCl₄, R₄Sn: R = CH₃, C₂H₅, *n*-C₃H₇, *n*-C₄H₉) in *n*-octane, *n*-decane, and *n*-tetradecane from 25° to 160 °C are reported in Table I. Each diffusion coefficient is the result of at least four measurements; the standard deviation is mostly ±1%, and no worse than ±3%.

It is traditional to fit temperature-dependent diffusion data to the Arrhenius equation:

$$D_{12}/T = D^0 \exp(-E_D/RT), \quad (1)$$

where the constants D^0 and E_D are the pre-exponential and activation energy of diffusion and T is the absolute temperature. The values of D^0 and E_D for all of the solute-solvent pairs are given in Table II. Equation (1) was found to reproduce the experimental results within ±1% and, therefore, provides a useful interpolation and extrapolation formula.

Although it was shown previously that the rough-hard-sphere (RHS) theory fails to describe tracer diffusion in *n*-decane at 25 °C,¹ the idea that thermal motion at higher temperatures may average out molecular orientation prompted us to test the theory on the measured diffusivities starting from the highest temperature.

According to the rough-hard-sphere theory, the diffusion coefficient in the liquid state can be predicted from the expression^{5-7,1}

$$D_{12} = h_{12}(D_{12}^{HS}/D_{12}^E)D_{12}^E, \quad (2)$$

where h_{12} is the rotational factor accounting for angular momentum transfer upon collision, D_{12}^{HS}/D_{12}^E , the ratio of smooth-hard-sphere to Enskog diffusivity, the factor accounting for dynamically correlated motions such as backscattering and "vortex formation," and D_{12}^E the

TABLE I. Tracer diffusivities in long chain hydrocarbons.^{a,b}

T °K	Solute									
	Solvent	Ar	CH ₄	Kr	Xe	CCl ₄	Me ₄ Sn	Et ₄ Sn	Pr ₄ Sn	Bu ₄ Sn
298	C ₈	6.68 ₃ ^c	6.08 ₃	5.00 ₄	4.06 ₂	2.56 ₂	2.33 ₁	1.85 ₂	1.46 ₁	1.26 ₁
	C ₁₀	4.87 ₇	4.38 ₆	3.51 ₆	2.86 ₃	1.70 ₂	1.57 ₂	1.22 ₁	0.955 ₄	0.802 ₆
	C ₁₄	3.40 ₇	2.78 ₄	2.37 ₂	1.72 ₁	0.897 ₆	0.812 ₇	0.608 ₃	0.475 ₆	0.388 ₅
313	C ₈	3.12 ₂	...	2.26 ₁
	C ₁₄	1.20 ₂	1.09 ₂	0.81 ₁	0.65 ₁	0.512 ₆
333	C ₈	9.9 ₁	9.45 ₄	7.63 ₁	6.12 ₄	4.05 ₄	3.65 ₃	2.96 ₂	2.35 ₂	2.00 ₁
	C ₁₀	7.72 ₇	7.16 ₄	5.75 ₃	4.60 ₃	2.89 ₂	2.58 ₃	2.05 ₁	1.63 ₁	1.39 ₁
343	C ₁₄	6.16 ₇	5.47 ₄	4.46 ₄	3.45 ₃	1.81 ₂
373	C ₈	14.46 ₄	14.20 ₃	10.96 ₆	9.10 ₄	6.06 ₆	5.58 ₂	3.71 ₃ ^d	3.70 ₂	3.22 ₂
	C ₁₀	7.13 ₅	4.58 ₅	4.14 ₁	...	2.67 ₃	2.29 ₂
374	C ₁₄	8.35 ₉	7.80 ₉	6.50 ₄	5.03 ₅	2.59 ₅	2.54 ₃	2.02 ₂	1.56 ₁	1.32 ₁
403	C ₈	18.0 ₂	18.1 ₁	14.0 ₁	11.80 ₆
430	C ₁₄	13.6 ₂	13.0 ₁	10.0 ₁	8.24 ₃	...	4.38 ₃	3.35 ₂	2.76 ₆	2.32 ₃
433	C ₈	9.14 ₆	7.60 ₃	6.24 ₅	5.56 ₅
	C ₁₀	19.3 ₂	18.8 ₂	14.6 ₁	12.2 ₁	...	7.27 ₄	5.86 ₂	4.77 ₄	4.18 ₃

^aC₈=*n*-octane; C₁₀=*n*-decane; C₁₄=*n*-tetradecane.^bNumber given in 10⁵ cm²/s.^c6.68₃ denotes 6.68 ± 0.03.^dAt 353 °K.

Enskog diffusivity in the dense gas region.

As in the model we pursued previously,¹ h_{12} was set equal to 0.78 for monatomic solutes and 0.7 for polyatomic solutes at all temperatures, and the ratio D_{12}^{HS}/D_{12}^E was obtained by interpolating or extrapolating between the solutes solvent size and mass ratios available from the computer simulations on hard-sphere fluids. All available literature values were gleaned and figures were prepared for interpolation and extrapolation.¹⁵ The parameter D_{12}^E is given by

$$D_{12}^E = \frac{3}{8n\sigma_{12}^2 g_{12}(\sigma)} \left(\frac{kT}{2\pi m_{12}} \right)^{1/2}, \quad (3)$$

where n is the fluid density, $g_{12}(\sigma)$ the contact value of the pair correlation function of hard spheres, k Boltzmann's constant, T absolute temperature, σ_{12} the mean of σ_1 and σ_2 , and m_{12} the reduced mass of solute (1) and solvent (2). Contact values of the pair correlation function for tracer diffusion ($n_1 \approx 0$) or self-diffusion were computed from the formula

$$g_{12}(\sigma) = \frac{1}{1-\eta} + \frac{3\eta\sigma_1}{(1-\eta)^2(\sigma_1+\sigma_2)} + \frac{\eta^2\sigma_1}{2(1-\eta)^3\sigma_2}, \quad (4)$$

where σ_1 and σ_2 are solute effective hard-sphere diameters and $\eta = \pi n \sigma_2^3/6$. In the case of self-diffusion, we set σ_1 equal to σ_2 . Equation (4) has been demonstrated¹⁶ to be accurate for hard-sphere fluids.

In the study of tracer diffusion in cyclohexane as a function of temperature,² the temperature-dependent σ_2 was determined by fitting the RHS theory to self-diffusion data at different temperatures. Since the predicted diffusivity is insensitive to small variations in σ_1 , the value of σ_1 at 25 °C found by Evans, Davis, and Tominaga¹ was used for all temperatures. In the present work, the same set of σ_1 's was used. For lack of self-diffusion data for *n*-octane, *n*-decane, and *n*-tetradecane at temperatures above 100 °C, σ_2 for each solvent was determined by fitting the measured tracer diffusivity of one of the solutes at each temperature to the RHS theory. This value of σ_2 was then used to predict tracer diffusion for the rest of the solutes in the same solvent at the same temperature. In Table III are given the so-determined solvent diameters, the solute diameters, the number densities of the solvents, and the comparison of prediction to experiment for tracer diffusion in all three solvents. The theory works very well for *n*-octane

TABLE II. E_D and D^0 for Arrhenius equation.^{a,b}

		Ar	CH ₄	Kr	Xe	CCl ₄	Me ₄ Sn	Et ₄ Sn	Pr ₄ Sn	Bu ₄ Sn
<i>n</i> -octane	E_D	1578	1789	1641	1736	1886	1889	1980	2053	2121
	$10^6 D^0$	3.226	4.211	2.704	2.574	2.078	1.904	1.756	1.575	1.508
<i>n</i> -decane	E_D	1901	2052	1987	2042	2206	2203	2269	2345	2422
	$10^6 D^0$	4.075	4.731	3.416	3.020	2.418	2.171	1.895	1.689	1.614
<i>n</i> -tetra decane	E_D	1970	2281	2105	2340	2395	2543	2623	2678	2779
	$10^6 D^0$	3.181	4.441	2.826	3.047	1.750	2.035	1.743	1.499	1.428

^a E_D in cal/g mole.^b D^0 in cm²/s K.

TABLE III. Comparison of prediction to experiment.^a

T °K	n(cm ⁻³) ^b	$\sigma_1(\text{\AA})$ $\sigma_2(\text{\AA})$	Ar	CH ₄	Kr	n-octane		Me ₄ Sn	Et ₄ Sn	Pr ₄ Sn	Bu ₄ Sn
						Xe	CCl ₄				
433	3.002 × 10 ²¹	6.14	0.98	1.00	0.99	0.94
403	3.165 × 10 ²¹	6.16	1.02	0.98	1.02	0.99
373	3.349 × 10 ²¹	6.18	1.00	0.97	1.02	1.01	0.91	0.98	...	1.01	0.98
333	3.533 × 10 ²¹	6.21	1.05	1.01	1.06	1.06	0.90	0.99	1.01	1.03	1.02
313	3.620 × 10 ²¹	6.23	0.96	...	1.06
298	3.684 × 10 ²¹	6.28	1.00	1.02	1.06	1.05	0.89	0.97	0.99	0.99	0.96
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T °K	n(cm ⁻³) ^b	$\sigma_1(\text{\AA})$ $\sigma_2(\text{\AA})$	Ar	CH ₄	Kr	n-decane		Me ₄ Sn	Et ₄ Sn	Pr ₄ Sn	Bu ₄ Sn
						Xe	CCl ₄				
433	2.611 × 10 ²¹	6.65	0.98	0.96	1.02	1.00	...	0.96	1.01	1.03	1.01
373	2.828 × 10 ²¹	6.71	1.06	0.91	1.00	...	1.02	1.01
333	2.961 × 10 ²¹	6.78	0.98	0.98	1.04	1.04	0.89	0.99	1.00	1.02	0.94
<hr/>											
T °K	n(cm ⁻³) ^b	$\sigma_1(\text{\AA})$ $\sigma_2(\text{\AA})$	Ar	CH ₄	Kr	n-tetradecane		Me ₄ Sn	Et ₄ Sn	Pr ₄ Sn	Bu ₄ Sn
						Xe	CCl ₄				
430	2.006 × 10 ²¹	7.61	0.93	0.97	1.03	1.04	...	1.07	1.09	1.04	0.99
373	2.143 × 10 ²¹	7.64	0.94	0.95	0.95	1.03	1.10	1.11	1.09	1.05	1.00

^aThe comparison made in terms of $D_{\text{pred}}/D_{\text{exp}}$.^bThe number density n calculated from observed density, F. D. Rossini, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds* (Carnegie, Pittsburgh, 1953).

across the entire temperature range. The average error of prediction is 3% and the maximum error is 11%. Additionally, the σ_2 from tracer diffusion predicts self-diffusion of n -octane at 25 and 70 °C⁸ to within 2% and 6%, respectively. For the solvents n -decane and n -tetradecane, the model performs equally well at temperatures where the ratio $D_{12}^{\text{HS}}/D_{12}^{\text{E}}$ can be estimated reliably from the existing computer simulations on systems where $V/V_0 \geq 1.5$, the ratio of the molar volume to that of the close-packed hard-sphere fluid. However, the solvent diameter σ_2 determined from tracer diffusion in n -decane does not predict self-diffusion as well as it did for n -octane; the prediction is off by 20% at 80 °C.⁸ This insufficiency of the theory recalls the previous finding¹ that the RHS theory with solvent diameters fit from self-diffusion data does not accurately predict tracer diffusivities in n -decane at 25 °C. For n -tetradecane, there is no experimental self-diffusivity at 100 °C or higher to be compared with the prediction.

Dymond³ has found that the computer results for the viscosity μ and self-diffusivity D of hard spheres can be fitted accurately to the formulas

$$\frac{1}{\mu} = \frac{14520}{(MT)^{1/2} V_0^{1/3}} (V - 1.384 V_0) \quad (5)$$

and

$$D = \frac{2.306 \times 10^{-5} (T/M)^{1/2}}{V_0^{2/3}} (V - 1.384 V_0), \quad (6)$$

where M is the molecular weight, V the molar volume, and V_0 the hard-sphere close-packed molar volume

$$V_0 = N_0 \sigma^3 / \sqrt{2}, \quad (7)$$

in which N_0 is Avogadro's number. With T the absolute

temperature in °K and V and V_0 in cgs units μ and D are computed from Eqs. (5) and (6) in the cgs units P and cm²/s.

Aside from a factor of $T^{1/2}$, Eq. (5) is similar to the free-volume equation

$$1/\mu = \tilde{\alpha} (V - \tilde{V}_\mu) \quad (8)$$

proposed long ago by Batschinski⁹ for real liquids and reestablished in recent years by Hildebrand.¹⁰ In the free-volume theory, $\tilde{\alpha}$ and \tilde{V}_μ are constants characteristic of the fluid. As emphasized by Hildebrand, the viscosity of a nonassociated fluid can be correlated surprisingly well by Eq. (8). The success of the RHS theory, in which the tracer diffusivity of a real solute in a real fluid is directly proportional to the tracer diffusivity of a related hard-sphere system, leads one to expect, in analogy with Eq. (6), that tracer diffusivity will obey an equation of the form

$$D_{12} = \tilde{\beta} T (V - \tilde{V}_D), \quad (9)$$

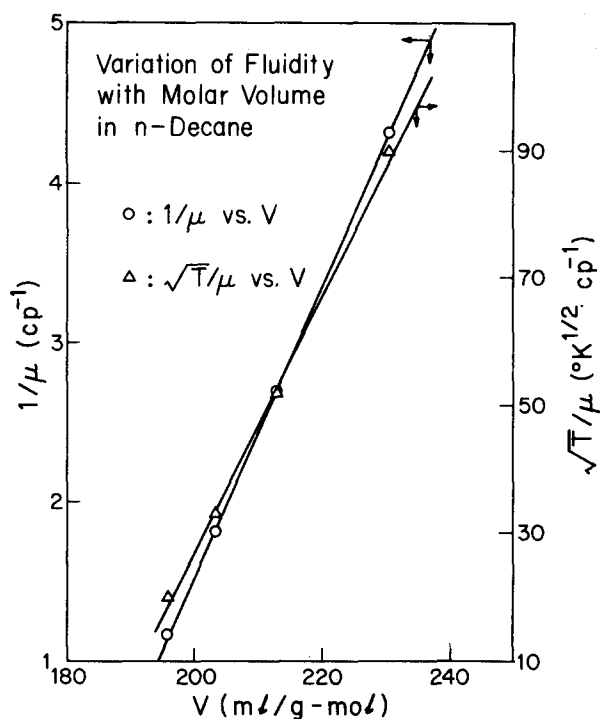
where $\tilde{\beta}$ and \tilde{V}_D are constants, $\tilde{\beta}$ characteristic of the solute-solvent pair and \tilde{V}_D related primarily to the solvent and not very different from \tilde{V}_μ . If \tilde{V}_D were equal to \tilde{V}_μ , Eqs. (8) and (9) would imply the Stokes' law correlation $D_{12}\mu/T = \text{constant}$. This is not true in general^{11,12} and, therefore, \tilde{V}_D and \tilde{V}_μ will not be identical.

Dymond's results for hard spheres suggest that instead of Eqs. (8) and (9) the preferred equations should be

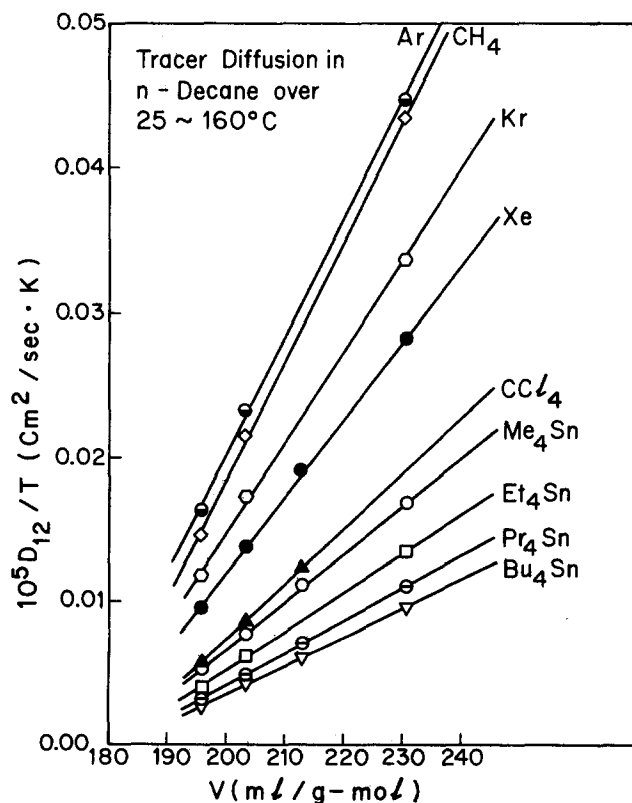
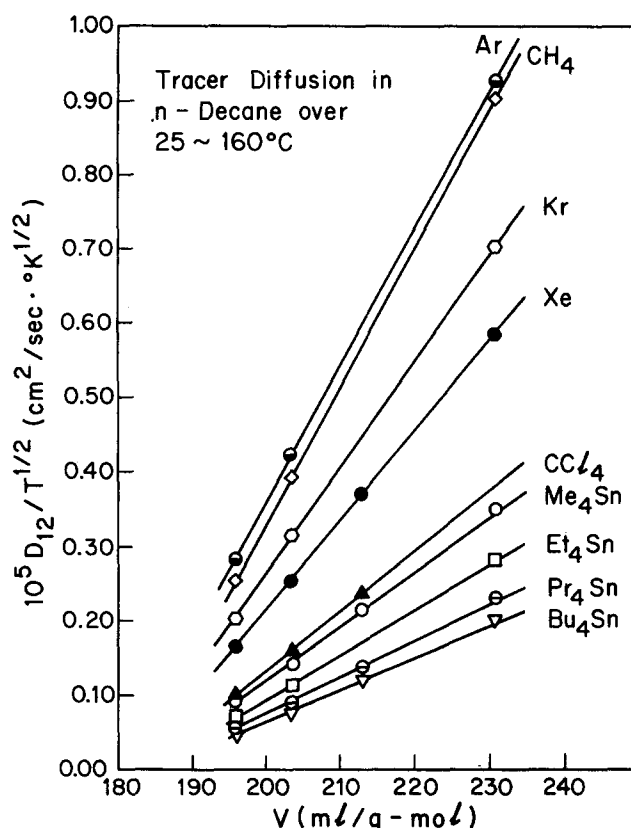
$$\sqrt{T}/\mu = \alpha (V - V_\mu), \quad (10)$$

$$D_{12}/\sqrt{T} = \beta (V - V_D). \quad (11)$$

We have made a least squares fit of Eqs. (8)–(11) to the experimental data for the solutes and solvents stud-

FIG. 1. Variation of fluidity with major volume in *n*-decane.

ied in this and a previous paper.² The data are described very well by the linear relationships. As can be seen from the data displayed in Figs. 1, 2, and 3, the fit for viscosity is equally good whether Eq. (8) or (10) is

FIG. 2. Free-volume plot of tracer diffusion in *n*-decane from 25 to 160 °C.FIG. 3. Dymond's plot of tracer diffusion in *n*-decane from 25 to 160 °C.

used, and for diffusion the fit is equally good whether Eq. (9) or (11) is used. In fact, T^{λ}/μ and D_{12}/T^{ν} were found to be sensibly linear in molar volume V for any value of λ and ν lying between $-\frac{1}{2}$ and 1.

Since the RHS theory works well for cyclohexane and the normal alkanes C_8 , C_{10} , and C_{14} at high enough temperatures, we expect from Dymond's results that the characteristic diameter σ_{μ} computed from $V_{\mu} = 1.384 N_0 \sigma_{\mu}^3 / \sqrt{2}$ will be close to the characteristic solvent diameter computed from RHS theory. This expectation is borne out by comparisons presented in Table IV. Also listed are characteristic solvent diameters σ_D computed from $\bar{V}_D = 1.384 N_0 \sigma_D^3 / \sqrt{2}$, where \bar{V}_D is the average of the values of V_D determined for all solutes in a given solvent. The values of V_{μ} and V_D were determined by least squares fits of data to Eqs. (10) and (11). We interpret Table IV as an indication of consistency between the free-volume model and the RHS theory. It is significant that the values of σ_{μ} and σ_D are found as the low temperature intercept of the transport coefficient-volume plot and they agree best with the low temperature side of the RHS range of solvent diameters.

An approach entirely different from the free volume model is to use a correlation akin to Stokes' law. This is known as the $D\mu^p$ -correlation, according to which^{12,14,13}

$$D_{12}\mu^p = AT; \quad (12)$$

p and A are parameters characteristic of the solute (and solvent in more refined correlation schemes). The

TABLE IV. Diameters from RHS theory and from Dymond's empiricism.

Solvent	T °K	$\bar{V}_D \left(\frac{\text{ml}}{\text{g-mole}} \right)^a$	$V_\mu \left(\frac{\text{ml}}{\text{g-mole}} \right)^b$	σ_D (Å) ^c	σ_μ (Å) ^c	σ_{RHS} (Å) ^d
Cyclohexane	298–416	101 ± 2	104	5.55	5.61	5.54–5.31
<i>n</i> -octane	298–433	146 ± 2	152	6.28	6.36	6.28–6.14
<i>n</i> -decane	333–433	184 ± 2	187	6.78	6.82	6.80–6.65
<i>n</i> -tetradecane	373–433	249 ± 2	256	7.50	7.57	7.64–7.61

^a \bar{V}_D average of V_D over all solutes. V_D molar volume at which D_{12}/\sqrt{T} extrapolates to zero.

^b V_μ molar volume at which \sqrt{T}/μ extrapolates to zero.

^c σ_D calculated from $\bar{V}_D = 1.384 N_0 \sigma_D^3/\sqrt{2}$ and σ_μ from $V_\mu = 1.384 N_0 \sigma_\mu^3/\sqrt{2}$, where N_0 is Avogadro's number.

^d σ_{RHS} from fit of experimental diffusivities to rough-hard-sphere theory over given temperature range.

$D\mu^p$ -correlation has been shown to describe the experimental data quite well for all the solutes considered in this paper in a wide variety of solvents, including several alcohols.¹³ In the most useful version of Eq. (12), p and $\ln A$ are fitted to data as linear functions of inverse solute radius r_1^{-1} . The solute radii were determined following Bondi's procedures.¹⁴ We could, of course, use radii determined by the RHS theory. However, we feel it is more appropriate to develop an empirical correlation from readily available data, such as densities, which are inputs for Bondi's radii. A least squares fit of p and $\ln A$ to all the diffusion data in Table I yields

$$p = -0.8365r_1^{-1} + 1.0741, \quad (13)$$

$$A = \exp(5.9734r_1^{-1} - 7.3401). \quad (14)$$

With these formulas, Eq. (12) reproduces the tracer diffusion data in Table I with an average absolute error of 7% and maximum absolute error of 19%. As previously noted,⁴ Eqs. (12), (13), and (14) provide, in the spirit but not the form of Stokes' law, a correlation between tracer diffusivity, solvent viscosity, and solute radius. In alcohols¹³ it was found expedient to introduce the solvent radius as an added correlation parameter.

The $D\mu^p$ -correlation becomes Stokes' law in the special case $p=1$. For solutes small in size compared to the solvent molecules, it is now well-established that Stokes' law fails.^{1,11,12,13} If in Eqs. (8) and (9) the characteristic volumes \bar{V}_μ and \bar{V}_D were identical for any solute, the Stokes' law correlation ($p=1$) would be valid for all solutes. Thus the fact that the \bar{V}_D values are slightly solute dependent is a reflection through the free-volume model of the fact that Stokes' law is not valid for solutes small compared to the solvent molecules. The more direct manifestation of this in the $D\mu^p$ -correlation is that p is less than 1 and decreases with decreasing

solute radius. Consistency between the $D\mu^p$ -correlation and the free-volume Eqs. (8) and (9) is that the ratio $(V - \bar{V}_D)/(V - \bar{V}_\mu)^p$ be independent of temperature for a given solvent-solute pair. This ratio is constant within $\pm 3\%$ for *n*-octane, *n*-decane, *n*-tetradecane, and cyclohexane in the temperature range 25 to 160 °C.

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