Tracer Diffusion of Carbon Tetrachloride, S-Trioxane, 12-Crown-4, 15-Crown-5, 18-Crown-6 in Acetonitrile, Benzene, and Chlorobenzene

Tracer diffusivities measured with the Taylor dispersion technique are reported for carbon tetrachloride, s-trioxane, 12-crown-4, 15-crown-5, and 18-crown-6 in acetonitrile, benzene, and chlorobenzene across ranges of temperature. It is demonstrated that Stokes' law corrected with a microfriction factor successfully accounts for the diffusion behavior of even disk-shaped crown ethers. Solute and solvent molecules being effectively spherical in the context of Stokes' law, the tracer diffusion of crown ethers is found to be satisfactorily represented by a rough-hard-sphere model for molecular diffusion. The degree of success increases with decreasing solvent polarity. The diffusion data for carbon tetrachloride are also used to extend the basis of the recently developed reduced equation for the tracer diffusion of nonelectrolytes in liquids over wide temperature ranges.

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SCOPE

In liquid membrane separation and solid-liquid-phase transfer catalysis employing crown ethers, the rate of involved transport processes is determined by the diffusivities of crown ethers. One of the objectives of this paper is to measure the tracer diffusivities of a series of crown ethers in practically important solvents including acetonitrile, benzene, and chlorobenzene as a function of temperature. The other objective is to investigate the diffusion behavior of disk-shaped molecules in terms of Stokes' law. To provide a basis for studying size and shape effects, quasispherical carbon tetrachloride is also included as one of the solutes. A rough-hard-sphere theory is then tested once it is established that crown ethers behave effectively as spheres. The applicability of the recently proposed generalized equation for nonelectrolyte diffusion in liquids is extended with the new data reported here.

CONCLUSIONS AND SIGNIFICANCE

The tracer diffusivities of carbon tetrachloride, s-trioxane, 12-crown-4, 15-crown-5, and 18-crown-6 in acetonitrile, benzene, and chlorobenzene can be quantitatively predicted from Stokes' law with a correction factor for microfriction. The failure of Stokes' law, often quoted, can be attributed solely to the neglect of size discrepancies between solute and solvent molecules. Even the disk-like crown ethers appear to be spherical due to rapid molecular rotation. This is further supported by the success of a rough-hard-sphere theory in describing the tracer diffusion of crown ethers. The theory is capable of predicting the observed diffusivities to within 6, 7 and 12% (absolute average deviations) in benzene, chlorobenzene, and acetonitrile; the less polar the solvent molecule, the more successful the RHS theory. The basis for applying Eq. 11 for predictive purposes has also been extended with additional binary interaction parameters for the new solute-solvent systems studied here.

INTRODUCTION

As part of our systematic studies of the diffusion of crown ethers in organic solvents, we have measured the tracer diffusivities of s-trioxane, 12-crown-4, 15-crown-5, and 18-crown-6 in acetonitrile, benzene, and chlorobenzene as a function of temperature using the Taylor dispersion technique (Chen et al., 1981). Being quasi-spherical in its molecular shape, carbon tetrachloride is also included as one of the solutes so that the shape effect on the molecular diffusion of disk-like crown ethers (Vogel and Weiss, 1981) can be investigated in the context of Stokes' law.

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Molecular diffusion has traditionally been discussed in terms of Stokes' law with the understanding that it was derived on the basis of continuum hydrodynamics. Even though it appears that the law is successful in describing self-diffusion in a number of liquids with slip boundary conditions, its failure for small solutes was rather dramatic (Evans et al., 1981). Observed deviations have been attributed to size and shape discrepancies (Tyrrell and Watkiss, 1979). Although the law has also provided the basis for developing empirical correlations (Hayduk and Cheng, 1971; Davis et al., 1980; Chen et al., 1982) for predictive purposes, there is as yet no unified treatment of the tracer diffusion across a substantial range of solute to solvent size ratios.

In this work, we will account for the solute-solvent size discrepancy by empirically modifying the molecular theory of microfriction proposed by Gierer and Wirtz (1953). The microfriction factor will be developed as a function of solute-solvent size ratio using the tracer diffusion data for systems where both solute and solvent molecules are spherical or quasispherical in shape. Included in such development are the two limiting cases, one for Stokes' law recovery and the other for negligibly small solutes. We believe that with so chosen solute-solvent systems and the two limits considered, the empirical equation for microfriction factor is placed on a solid basis. Once the size effect is accounted for, the shape effect can then be revealed and rationalized in terms of Perrin's model (1936) for disk-shaped particles. This line of analysis will lead to a conclusion as to the effects of solute size and shape on molecular diffusion. The success of the Stokes-Wirtz equation will suggest that the tracer diffusion of crown ethers be investigated in terms of a rough-hard-sphere theory, which has recently been found to be successful in interpreting the diffusion of dissolved gases, such as methane and rare gases, carbon tetrachloride, and a series of tetraalkyltins in cyclohexane (Chen et al., 1981), long-chain hydrocarbons (Chen et al., 1982), and aliphatic alcohols (Chen et al., 1983).

When diffusion is considered an activated process, the Arrhenius-type equation has been found to correlate quite well the tracer diffusivities as a function of temperature. On the basis of this observation, we have recently developed a generalized equation for predicting tracer diffusion coefficients from solute and solvent critical temperatures and binary interaction parameters (Chen and Chen, 1983a). Its application will be extended with the new data reported here only for carbon tetrachloride for lack of the critical temperature data for s-trioxane and crown ethers.

EXPERIMENTAL

The Taylor dispersion apparatus for diffusion measurements and experimental procedures was as described by Chen et al. (1981). Acetonitrile (99 +%, b.p. 355 K), benzene (99 +%, b.p. 353 K), and chlorobenzene (99 +%, b.p. 405 K), all purchased from Aldrich Chemical Co., were filtered before usage with Teflon membrane (0.5 μm, Millipore) on all-glass filtration apparatus (Millipore). The solutes carbon tetrachloride (99 +%), s-trioxane (98%), 12-crown-4 (99 +%), 15-crown-5 (99%), and 18-crown-6 (99%) were all used as received from Aldrich. The bath temperatures were always controlled to within ±0.1 K. The concentration of injected solution is no higher than 1 mol %. Each reported diffusivity is the result from at least four measurements, the standard deviations being normally ±1%.

RESULTS AND DISCUSSION

Table 1 shows the tracer diffusivities of carbon tetrachloride, s-trioxane, 12-crown-4, 15-crown-5, and 18-crown-6 in acetonitrile, benzene, and chlorobenzene at temperatures as indicated and atmospheric pressure.

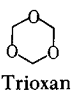
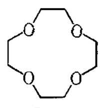
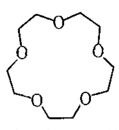
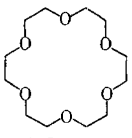
Stokes' law is valid for the movement of a large spherical particle in a continuous medium. The failure of the law in molecular diffusion is well documented, which can be attributed to the fact that the continuum theory breaks down at molecular dimensions. Taking account of the migration of the solute molecule into holes of the solvent and the finite thickness of the solvent layers which flow around a moving solute molecule, Gierer and Wirtz (1953) developed a molecular theory for microfriction in liquids. The theory has since been applied to interpret rotational diffusion in addition to magnetic relaxation phenomena. Its application to translational diffusion has largely been limited to self-diffusion. The only application to tracer diffusion (Spernol and Wirtz, 1953) demonstrated only the order-of-magnitude prediction using the Stokes-Wirtz theory.

In an effort to provide a basis for quantitative prediction, we have empirically modified Stokes' law based on the spirit of microfriction theory using the model systems for which diffusivities have been measured. We have selected systems in which both solute and solvent molecules are spherical or quasispherical in order to eliminate the complications arising from nonspherical molecular shape. The microfriction factor for translational motion of tracer solute in a solvent is calculated using the following formula:

$$f_t = \frac{kT}{6\pi r_1 \mu_2 D} \tag{1}$$

where k is Boltzmann's constant, T absolute temperature, r_1 van der Walls radius of the solute molecule (Bondi, 1964), μ_2 solvent viscosity, and D the measured tracer diffusivity. It has to be noted that self-diffusion (Jonas et al., 1980), and tracer diffusion (Chen et al., 1981) studies suggested that the cyclohexane molecule can be effectively treated as a sphere from a molecular theoretical standpoint, even though the two conformations, chair and boat

TABLE 1. TRACER DIFFUSIVITIES OF CARBON TETRACHLORIDE, S-TRIOXANE, 12-CROWN-4, 15-CROWN-5, AND 18-CROWN-6 IN ACETONITRILE, BENZENE, AND CHLOROBENZENE[a]

		Carbon Tetrachloride	 s-Trioxane	 12-Crown-4	 15-Crown-5	 18-Crown-6
Acetonitrile	301.2 K	3.37 ± 0.04	3.42 ± 0.08	2.29 ± 0.07	2.02 ± 0.02	1.62 ± 0.01
	313.2	3.89 ± 0.09	4.00 ± 0.04	2.63 ± 0.02	2.37 ± 0.01	1.93 ± 0.01
	328.2	4.57 ± 0.03	4.74 ± 0.06	3.13 ± 0.07	2.79 ± 0.01	2.31 ± 0.01
	343.2	5.28 ± 0.04	5.38 ± 0.08	3.71 ± 0.05	3.31 ± 0.05	2.87 ± 0.01
Benzene	301.2	2.07 ± 0.03	2.27 ± 0.01	—[b]	1.23 ± 0.02	1.06 ± 0.01
	313.2	2.49 ± 0.01	2.69 ± 0.01	—	1.59 ± 0.03	1.39 ± 0.02
	328.2	3.07 ± 0.04	3.38 ± 0.05	—	1.93 ± 0.01	1.75 ± 0.03
	343.2	3.73 ± 0.04	4.05 ± 0.04	—	2.31 ± 0.02	2.16 ± 0.04
Chlorobenzene	301.2	1.85 ± 0.03	1.87 ± 0.02	1.33 ± 0.02	1.04 ± 0.01	0.91 ± 0.01
	313.2	2.15 ± 0.02	2.17 ± 0.03	1.57 ± 0.01	1.19 ± 0.01	1.06 ± 0.01
	343.2	3.05 ± 0.04	3.15 ± 0.04	2.35 ± 0.03	1.89 ± 0.02	1.76 ± 0.02
	373.2	4.22 ± 0.06	4.22 ± 0.05	3.27 ± 0.04	2.63 ± 0.02	2.43 ± 0.04

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[a] Diffusivities reported in $10^9 D$ m^2/s.

[b] Not measured because of limited solubility.

TABLE 2. SOLUTE-SOLVENT SYSTEMS SELECTED FOR DEVELOPING EQ. 3

Cyclohexane

Solute	r_1/r_2	f_t
Ar[a]	0.65	0.31 ± 0.04
Kr[a]	0.70	0.39 ± 0.05
Xe[a]	0.75	0.46 ± 0.07
CH_4[a]	0.66	0.35 ± 0.03
CCl_4[a]	0.95	0.62 ± 0.03
Me_4Sn[a]	1.06	0.59 ± 0.03
Et_4Sn[a]	1.23	0.66 ± 0.03
Pr_4Sn[a]	1.37	0.72 ± 0.02
Bu_4Sn[a]	1.48	0.78 ± 0.02
$C{-}C_6H_{12}$[b]	1	0.58 ± 0.01

Carbon Tetrachloride

Solute	r_1/r_2	f_t
Ar[c]	0.68	0.34
Kr[c]	0.73	0.42
Xe[c]	0.79	0.45
CH_4[c]	0.69	0.42
Me_4Sn[c]	1.11	0.66
Et_4Sn[c]	1.29	0.65
Pr_4Sn[c]	1.43	0.75
Bu_4Sn[c]	1.55	0.82
CCl_4[d]	1	0.68 ± 0.01
$C{-}C_6H_{12}$[e]	1.05	0.67 ± 0.02
CBr_4[f]	1.05	0.59

Sources of experimental diffusivities:

[a] S. H. Chen, H. T. Davis, and D. F. Evans, *J. Chem. Phys.*, **75**, 1422 (1981); 298–374 K.

[b] M. A. McCool and L. A. Woolf, *High Temp.-High Press.*, **4**, 85 (1972); 288–328 K.

[c] D. F. Evans, T. Tominaga, and H. T. Davis, *J. Chem. Phys.*, **74**, 1298 (1981); 298 K.

[d] M. A. McCool and L. A. Woolf, *J. Chem. Soc. Faraday Trans. I.*, **68**, 1971 (1972); 283–328 K.

[e] S. A. Sanni, C. J. D. Fell, and H. P. Hutchinson, *J. Chem. Eng. Data*, **16**, 424 (1971); 298–328 K.

[f] A. Spernol and K. Wirtz, Z. *Naturforsch*, 8a, 522 (1953); 280 K.

forms, exist in equilibrium. The selected solute-solvent model systems, the ratio of the van der Waals radii (Bondi, 1964) of solute to solvent molecules, the values of f_t calculated with Eq. 1 and the temperatures at which the diffusivities were measured are listed in Table 2. Theoretically, as the solute molecule becomes considerably larger than solvent molecule, the Stokes' limit is approached, namely, $f_t = 1$. On the other hand, $f_t = 0$ as the solute molecule is negligibly small in comparison to solvent, for the former is able to move freely in the interstitital volume of the latter. Keeping these two limits in mind, we have arrived at the following expression for f_t as a function of r_1/r_2 from the best fit of experimental data:

$$f_t^{-1} = 1 + 0.695(r_1/r_2)^{-2.234} \qquad (2)$$

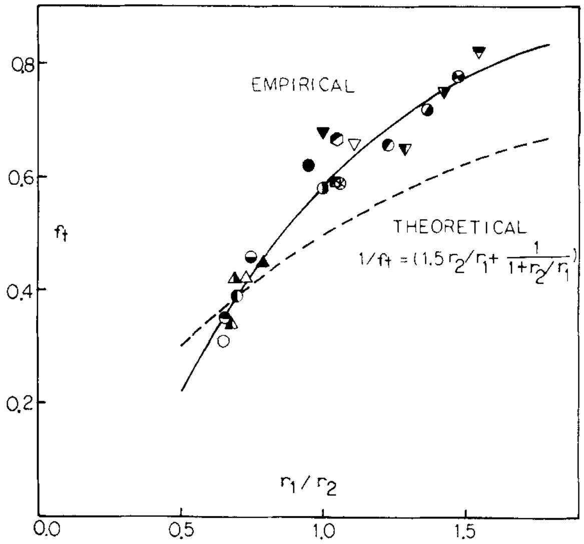

Figure 1. Microfriction factor f_t as a function of solute-solvent size ratios r_1/r_2. In $C{-}C_6H_{12}$ solvent: Ar, ○; CH_4, ◓; Kr, ◐; Xe, ◒; $C{-}C_6H_{12}$, ◐; CCl_4, ●; Me_4Sn, ⊗; Et_4Sn, ◐, Pr_4Sn, ◑; Bu_4Sn, ⊗; In CCl_4 solvent: Ar, △; CH_4, △; Kr, △; Xe, ▲; CCl_4, ▼; Me_4Sn, ▽; Et_4Sn, ▽; Pr_4Sn, ▽; Bu_4Sn, ▽; $C{-}C_6H_{12}$, ○; CBr_4, □.

which regenerates observed f_t values to within ±8% on the average. Both theoretical and empirical equations for f_t are plotted in Figure 1 as a function of r_1/r_2. We believe that the difference between theoretical and empirical equations for f_t arises from the simple geometrical consideration intrinsic to the theory of microfriction. With f_t evaluated from Eq. 2 the Stokes-Wirtz prediction of tracer diffusivity is simply

$$D_{S\text{-}W} = \frac{kT}{6\pi r_1 \mu_2 f_t} \qquad (3)$$

Before using Eq. 2 to examine the solute-solvent size discrepancy, it should be demonstrated that the deviations from Stokes' law arising from nonspherical nature of solute and/or solvent molecules are relatively small. First of all, the benzene molecule was treated effectively as a sphere in the interpretation of self-diffusion (Parkhurst and Jonas, 1975) and tracer diffusion of rare gases and methane (Evans et al., 1981) using rough-hard-sphere theories. When Eqs. 2 and 3 are used to calculate tracer diffusivities in benzene of carbon tetrachloride, s-trioxane, 15-crown-5, and 18-crown-6, Table 3, the agreement between prediction and experi-

TABLE 3. $D_{s\text{-}w}/D_{\text{expt.}}$ FOR TRACER DIFFUSION OF CARBON TETRACHLORIDE, S-TRIOXANE, 12-CROWN-4, 15-CROWN-5, AND 18-CROWN-6 IN ACETONITRILE, BENZENE, AND CHLOROBENZENE

Acetonitrile

			Temperature (K)			
	r_1/r_2	f_t	301.2	313.2	328.2	343.2
Carbon Tet.	1.23	0.69	0.96	0.96	0.97	0.96
s-Trioxane	1.18	0.67	0.91	0.93	0.93	0.92
12-Crown-4	1.54	0.79	0.93	0.93	0.94	0.96
15-Crown-5	1.65	0.82	0.91	0.93	0.94	0.96
18-Crown-6	1.76	0.84	0.86	0.83	0.84	0.90

Benzene

			Temperature (K)			
	r_1/r_2	f_t	301.2	313.2	328.2	343.2
Carbon Tet.	1.03	0.60	0.91	0.91	0.84	0.88
s-Trioxane	0.99	0.58	0.93	0.91	0.85	0.89
15-Crown-5	1.38	0.75	0.91	0.97	0.88	0.91
18-Crown-6	1.47	0.77	0.86	0.93	0.87	0.94

Chlorobenzene

			Temperature (K)			
	r_1/r_2	f_t	301.2	313.2	343.2	373.2
Carbon Tet.	0.97	0.57	1.05	1.07	1.11	1.12
s-Trioxane	0.93	0.55	0.89	0.87	0.91	0.82
12-Crown-4	1.21	0.69	1.04	1.03	1.10	1.04
15-Crown-5	1.30	0.72	0.91	0.88	1.00	0.95
18-Crown-6	1.39	0.75	0.88	0.86	1.03	0.96

ment is reasonably good considering the uncertainty associated with Eq. 2. Secondly, the prediction errors are fairly uniform among all four solutes, which suggests that the nonspherical nature of crown ethers is averaged out by rapid molecular rotation. In consequence, the microfriction factor (f_t), which accounts for solute-solvent size discrepancy, is adequate for elucidating the deviations from Stokes' law. Predicted diffusivities in acetonitrile and chlorobenzene are also compared to experimental data in Table 3. Again, the microfriction factor consistently improves Stokes' prediction. The fact that prediction errors are fairly uniform for all the systems of interest in the present work simply suggests that all the solute and solvent molecules involved behave as effective spheres. In other words, within the error of Eq. 2 apparent molecular shape has no contribution to the deviations from the Stokesian behavior.

The fact that the solute and solvent molecules under investigation behave effectively as spheres has prompted the testing of a rough-hard-sphere (RHS) model for molecular diffusion. In a recent series of papers (Chen et al., 1981, 1983), it has been demonstrated that the tracer diffusion of spherical and quasispherical solutes in hydrocarbon and hydrogen-bonding solvents across a wide temperature range are fairly well described by the RHS theory. In the following it will be shown that the tracer diffusion of apparently disk-like crown ethers, which behave as effective spheres in the context of Stokes' law, is successfully represented by the RHS model.

According to the RHS theory, the self- and binary diffusivities can be predicted from the following equation:

$$D_{RHS} = D_{12}^{E}(D_{12}^{SHS}/D_{12}^{E})h_{12} \tag{4}$$

In this equation D_{12}^{E} is the diffusivity given by Enskog's dense gas theory as follows:

$$D_{12}^{E} = \frac{3}{8n\sigma_{12}^{2}g(\sigma_{12})}\left(\frac{kT}{2\pi m_{12}}\right)^{1/2} \tag{5}$$

where n is the number density, k Boltzmann's constant, T absolute temeprature, m_{12} reduced mass of the solute-solvent pair, σ_{12} the mean of the solute and solvent effective hard-sphere diameters, and $g(\sigma_{12})$ the contact value of the solute-solvent pair correlation function evaluated from the following expression (Chen et al., 1981):

$$g(\sigma_{12}) = \frac{1}{1-\eta} + \frac{3\eta\sigma_1}{(1-\eta)^2(\sigma_1+\sigma_2)} + \frac{\eta^2\sigma_1}{2(1-\eta)^3\sigma_2} \tag{6}$$

In Eq. 6 $\eta = \pi n_2\sigma_2^3/6$ is the packing efficiency. In the case of self-diffusion, $\sigma_1 = \sigma_2$ is substituted in Eq. 6 to obtain $g(\sigma_1)$. Since the Enskog dense gas theory was developed on the basis of smooth hard spheres undergoing binary uncorrelated collisions, it applies to the diffusion of monatomics over a limited density range. The RHS theory essentially extends the Enskog theory to the diffusion of polyatomics over a wider density range where dynamic correlation of molecular collisions is important. For monatomics the mass is concentrated almost at a point in space (i.e., nucleus). Hence, there will be no angular momentum associated with molecular motion while the finite effective size arises from internuclear repulsion when they collide into each other. In the case of polyatomics, the molecular mass is distributed in space and there will be translation-rotational coupling of molecular motion. The angular momentum transfer upon collision results in a diffusivity which is reduced by 30% according to Baleiko and Davis' theory for rough spehres (Baleiko and Davis, 1974). The roughness factor, $h_{12} = 0.70$ in Eq. 4, accounts for this molecular phenomenon.

The other aspect of the RHS theory, which applies both to monatomics and polyatomics, pertains to the dynamically correlated molecular encounters. For instance, the "vortex formation" enhances whereas backscattering reduces diffusive motion of the solute molecule relative to the prediction using the Enskog dense gas theory, Eq. 5. The ratio of smooth-hard-sphere to Enskog diffusivity, D_{12}^{SHS}/D_{12}^{E}, generated by molecular dynamics computation, reflects the relative importance of the two competing factors for a given set of solute to solvent mass and size ratios and the fluid molar volume reduced with that of the close-packed hard-sphere system. The values of D_{12}^{SHS}/D_{12}^{E} were compiled and employed to successfully interpret the tracer diffusion of methane, rare gases, carbon tetrachloride, and a series of tetraalkyltins in cyclohexane (Chen et al., 1981).

In the present work, Eq. 4 is used to calculate the solvent diameter, σ_2, from the self-diffusivities of benzene (McCool et al., 1972), acetonitrile (Hurle and Woolf, 1982), and chlorobenzene (Ertl and Dullien, 1973) as a function of temperature:

$$10^{10}\sigma_2(m) = 5.83 - 2.544 \times 10^{-3}\mathrm{T(K)}, \text{ benzene} \tag{7}$$

TABLE 4. COMPARISON OF RHS THEORY TO EXPERIMENT, $D_{RHS}/D_{\mathrm{expt}}$

	T (K)	$10^{10}\sigma_2$ (m)	Carbon Tet.[a] ($10^{10}\sigma_1 = 5.28$ m)	s-Trioxane[b] ($10^{10}\sigma_1 = 4.98$ m)	12-Crown-4[b] ($10^{10}\sigma_1 = 6.15$ m)	15-Crown-5[b] ($10^{10}\sigma_1 = 6.68$ m)	18-Crown-6[b] ($10^{10}\sigma_1 = 7.26$ m)
Benzene	301.2	5.07	0.94	1.03	—	1.09	1.12
	313.2	5.04	0.97	1.06	—	1.04	1.04
	328.2	4.99	1.01	1.05	—	1.09	1.04
	343.2	4.96	1.03	1.08	—	1.13	1.04
Chlorobenzene	301.2	5.33	0.98	1.12	0.95	1.08	1.08
	313.2	5.31	0.99	1.14	0.98	1.16	1.14
	343.2	5.24	0.99	1.12	1.01	1.13	1.05
	373.2	5.18	1.01	1.14	1.01	1.11	1.04
Acetonitrile	301.2	4.11	0.82	0.94	0.94	0.92	0.99
	313.2	4.09	0.80	0.90	0.93	0.88	0.94
	328.2	4.07	0.78	0.88	0.90	0.87	0.90
	343.2	4.05	0.78	0.89	0.87	0.84	0.84

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[a] The value of σ_1 taken from S. H. Chen, H. T. Davis, and D. F. Evans, *J. Chem. Phys.*, **75**, 1422 (1981).

[b] The values of σ_1's taken from H. C. Chen and S. H. Chen, *Chem. Eng. Sci.* (1983).

TABLE 5. VALUES OF E_D AND A FROM THE FIT OF EXPERIMENTAL DATA TO EQ. 10

Solvent		Carbon Tet.	s-Trioxane	12-Crown-4	15-Crown-5	18-Crown-6
Acetonitrile	E_D (kJ/kmol)	6,506	6,644	7,251	7,339	8,874
	$10^{10}A$ (m^2/sec·K)	1.52	1.63	1.37	1.27	1.85
Benzene	E_D	9,368	9,301	—	9,941	11,820
	$10^{10}A$	2.90	3.08	—	2.22	4.04
Chlorobenzene	E_D	7,912	7,853	8,979	9,548	10,340
	$10^{10}A$	1.44	1.43	1.59	1.54	1.85

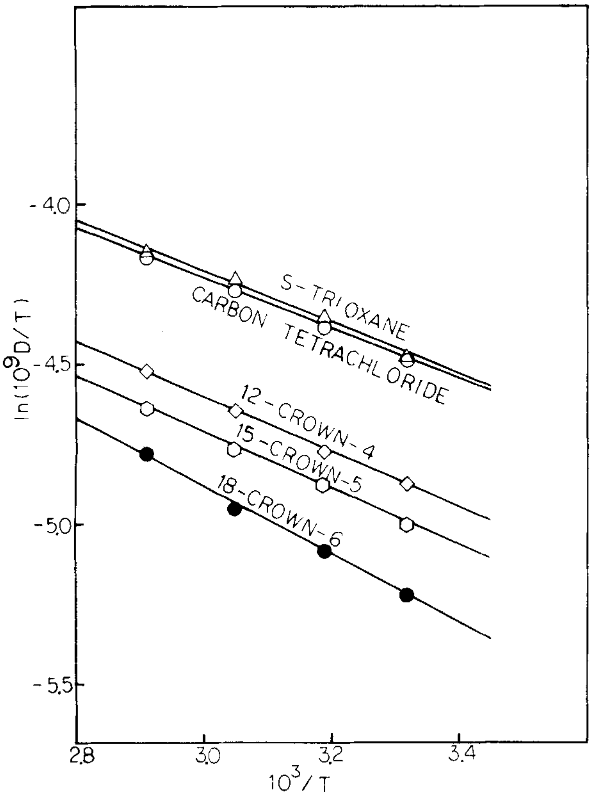

Figure 2. Arrhenius plot for tracer diffusion of carbon tetrachloride, s-trioxane, 12-crown-4, 15-crown-5, and 18-crown-6 in acetonitrile.

$$10^{10}\sigma_2(m) = 4.55 - 1.447 \times 10^{-3}T(K), \text{ acetonitrile} \quad (8)$$

$$10^{10}\sigma_2(m) = 5.94 - 2.022 \times 10^{-3}T(K), \text{ chlorobenzene} \quad (9)$$

Since the small variations of effective solute diameters with temperature have little effect on the predicted tracer diffusivity using Eq. 4, we consistently employ the formerly calculated values (Chen et al., 1981; Chen and Chen, 1983b) in applying the RHS theory. The value of h_{12} is set constant at 0.70, and that of D_{12}^{SHS}/D_{12}^{E} interpolated or extrapolated using the graphs prepared from computer simulation results for hard-sphere fluids (Chen, 1981). From the comparison made in Table 4, the RHS theory predicts to within 6, 7 and 12% for the tracer diffusion in benzene, chlorobenzene, and acetonitrile, respectively. It seems to us that the more polar the solvent molecule, the less successful the hard-sphere theory. This is anticipated in view of the fact that long-range dipole interactions, as opposed to impulsive repulsion at the contact of hard spheres, parallel the dipole moments of the solvent molecules: 0 for benzene, 1.69 for chlorobenzene, and 3.92 debye for acetonitrile.

Viewed as an activated process, the tracer diffusion across a range of temperature can be described by the Arrhenius equation

$$D/T = A \exp(-E_D/RT) \quad (10)$$

in which A is the preexponential factor and E_D the activation energy of diffusion. As an example, the tracer diffusion in aceonitrile is plotted in Fig. 2. The values of A and E_D obtained from the fit to Eq. 10 of experimental data in Table 1 are given in Table 5. It is of interest to extend the applicability of the recently formulated reduced equation for the tracer diffusion of nonelectrolyte in the liquid state. Using the experimental diffusivities of rare gases, methane, carbon tetrachloride, and tetramethyltin in cyclohexane, normal alkanes and aliphatic alcohols, we found that the reduced equation (Chen and Chen, 1983a).

$$\ln\left(\frac{D_r}{T_r}\right) = 2.80\left(1.00 - \frac{1}{T_r}\right) \quad (11)$$

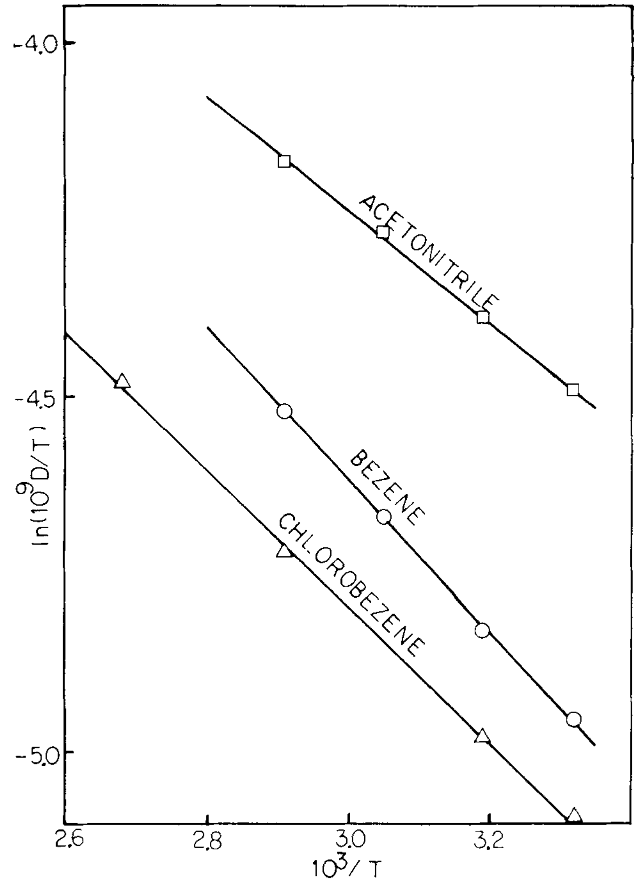

Figure 3. Arrhenius plot for tracer diffusion of carbon tetrachloride in acetonitrile, benzene, and chlorobenzene.

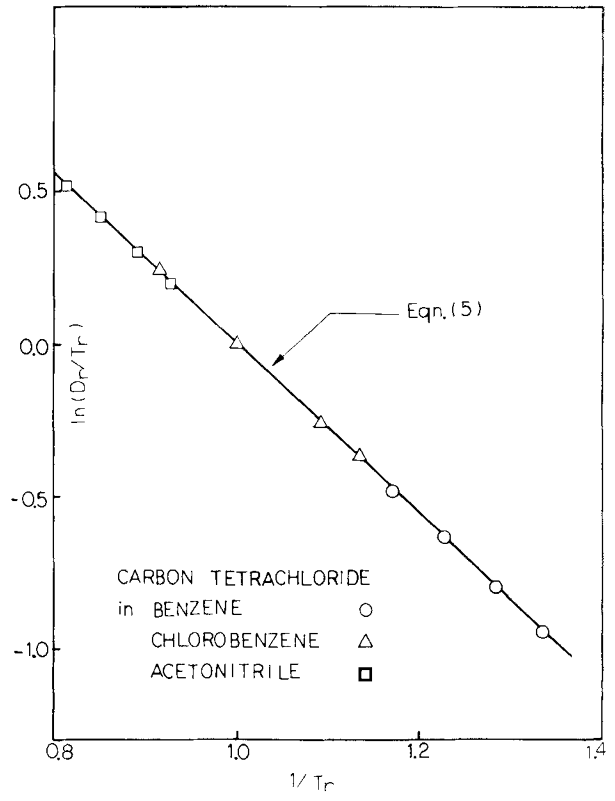

Figure 4. Reduced Arrhenius plot of Figure 3 with α = 0.506, 0.720, and 0.576 for acetonitrile, benzene, and chlorobenzene, respectively.

agrees with observed values to within ±5% over extended temperature ranges. In Eq. 11 $D_r = D/D_R$ and $T_r = T/T_R$, where D_R is evaluated at T_R using Eq. 10 and T_R is defined as the geometric mean of solute and solvent critical temperatures scaled with a parameter α:

$$T_R = \alpha(T_{C1}T_{C2})^{1/2} \tag{12}$$

where T_{C1} and T_{C2} are the solute and solvent critical temperatures, respectively. The idea originated from the notion that E_D may be directly proportional to the solute-solvent attractive potential with α accounting for the variation from system to system of the associated proportionality constant. In essence, α is a binary interaction parameter. For carbon tetrachloride solute we found that with α values 0.506, 0.720, and 0.576 for acetonitrile, benzene, and chlorbenzene, respectively, Eq. 11 is capable of collapsing the three straight lines shown in Figure 3 into a single straight line in Figure 4. As a result, the basis for applying Eq. 11 for predictive purposes has been extended with additional binary interaction parameters for new solute-solvent systems.

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NOTATION

D = tracer diffusivity
E = activation energy of diffusion
f = microfriction factor
g = pair correlation function
h = molecular roughness factor
k = Boltzmann's constant
m = molecular mass
n = fluid number density
R = ideal gas constant
r = van der Waals radius
T = absolute temperature

Superscripts

E = Enskog value
SHS = smooth-hard-sphere value

Subscripts

1 = solute
2 = solvent
12 = diffusion of 1 in 2
c = critical property
D = diffusion
R = reference property
r = reduced property
RHS = rough-hard-sphere theoretical prediction
S-W = Stokes-Wirtz prediction
t = translational motion

Greek Letters

α = binary interaction parameter, Eq. 12
μ = viscosity
η = packing efficiency
σ = effective hard-sphere diameter

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