APPENDIX C

TABLE OF EXPERIMENTAL RUNS

Run	Experimental Conditions				
#	Experiment Type	From	To	Control Strategy	Graphical Record
1	Set Point Change in Top Products	x_{ov}: 0.7 x_{ss}: 0.53	0.65 0.45	PI + DC†	Figure 7, dashed lines
2	Set Point Change in Top Products	″	″	PI (parameters in Table 2)	Figure 7, solid lines
3	Set Point Change in Top Products	″	″	PI	Figure 8, solid lines
4	Set Point Change in Tray 19 Temp.	T_{19}: 92	97	PI + DC	Figure 10, dashed lines
5	Set Point Change in Tray 19 Temp.	T_{19}: 92	97	PI	Figure 10, solid lines
6	Set Point Change in Tray 19 Temp.	97	92	PI + DC	Figure 11, dashed lines
7	Set Point Change in Tray 19 Temp.	97	92	PI	Figure 11, solid lines
8	Disturbance in Feed Rate (Square pulse for	0.8 gpm	1.0 gm	PI + DC	Figure 12, dashed lines
9	Disturbance in Feed Rate one hour)	and return		PI	Figure 12, solid lines
10	Disturbance in Feed Temp.	78°	58°	PI + DC	Figure 14, dashed lines
11	Disturbance in Feed Temp.	78°	58°	PI	Figure 14, solid lines
12*	Set Point Change in Top Products	x_{ov}: 0.7 x_{22}: 0.5	0.65 0.42	PI + DC	Figure 16, dashed lines
13*	Set Point Change in Top Products	″	″		
		″	″	PI	Figure 16, solid lines
14*	Disturbance in Feed Rate	0.8 gpm (0.05 L/s)	1.0 gpm (0.06 L/s)	PI + DC	Figure 17, dashed lines
15*	Disturbance in Feed Rate	0.8 gpm (0.05 L/s)	1.0 gpm (0.06 L/s)	PI	Figure 17, solid lines

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* Experimental runs under drastically altered operating conditions.

† *Delay compensation.*

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Tracer Diffusion in Methanol, 1-Butanol and 1-Octanol from 298 to 433 K

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Diffusion coefficients of argon, krypton, xenon, methane, carbon tetrachloride and the tetraalkyltins (methyl through butyl) were measured in methanol, 1-butanol and 1-octanol over the temperature range 298 to 433 K. 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 diffusivity over the solvent density range in which hard-sphere computer simulations are available. The Wilke-Chang correlation predicts diffusion coefficients in the higher alcohols with an average error of 80% and a maximum error of 200%. A correlation of the form $D\mu p/T = A$ where p and A depend on solute and solvent size is more successful giving an average error of 7% and a maximum error of 24%.

SCOPE

There is as yet no adequate theory of tracer diffusion in alcohols and there is a dearth of experimental data at other than room temperature. This paper broadens the experimental data base to a wide range of temperatures (298 to 433 K) for argon, krypton, xenon, methane, carbon tetrachloride, and a series of tetraalkyltins (methyl through n-butyl) in methanol, 1-butanol and 1-octanol. A major aim of the paper is to extend to alcohols a rough-hard-sphere molecular theory and an empirical correlation scheme relating tracer diffusion, solvent viscosity and molecular sizes.

CONCLUSIONS AND SIGNIFICANCE

The Taylor dispersion technique has proven successful in providing experimental diffusivities over a wide temperature range, including temperatures above the normal boiling point of the liquid.

A rough-hard-sphere theory that has been successful for tracer diffusion in nonpolar fluids is found to work quite well for tracer diffusion in alcohols in the density range for which the inputs of the theory are available.

Two empirical correlations have been developed to predict tracer diffusion in aliphatic alcohols as a function of temperature using the tracer diffusivities reported here. One of them permits tracer diffusivities to be estimated to within 5% from the carbon number of solvent molecule, diffusivity at one temperature, solvent viscosity and solute size. The other which requires solute and solvent sizes as well as solvent viscosity performs as well as the Wilke-Chang equation in methanol. It is capable of predicting to within 7% tracer diffusion in alcohols higher than ethanol where the Wilke-Chang equation with Lusis and Ratcliff's association parameter was found inadequate.

INTRODUCTION

Diffusion plays a key role in many chemical processes and consequently remains a central focus in chemical engineering. The compilation of diffusion coefficients by Babb et al. (1956) and Dullien et al. (1973) shows that although a number of systems have been measured at 298 K for many typical solutes, there is a paucity of data over extended temperature ranges, and there is almost no information on the effect of pressure on diffusion. Consequently, it is difficult to test theories or generate empirical correlations for predicting the diffusion coefficient over a wide range of thermodynamic conditions and solute/solvent types.

In a recent series of papers, we reported the diffusion coefficients of spherical or symmetrical solutes in a variety of alcohol and hydrocarbon solvents at 298 K and in cyclohexane over the temperature range 298 to 416 K. We chose the rare gases, methane, carbon tetrachloride and the tetraalkyltins (methyl through butyl) so that we could study approximately spherical solutes over a wide range of sizes. In the first paper (Evans, Davis and Tominaga, 1981), experimental results for systems with solute to solvent mass and size ratios of 1:22 and 1:2 were used to test a hard-sphere-like theory. It was found that for compact solvent molecules like cyclohexane, carbon tetrachloride and hexane, a rough-hard-sphere theory provides a reliable (19%) way to predict diffusion coefficients at 298 K. It was also shown that the validity of Stokes' equation for small solutes is a coincidence resulting from the particular sizes and solvent densities employed in most experiments. For solutes which are small compared to the solvent, the prediction from Stokes' law can be incorrect by a factor of ten. In another paper (Chen, Davis and Evans, 1981), we studied the diffusion coefficients of the nearly spherical solutes in one solvent, cyclohexane, over an extended temperature range (298–416 K). The rough-hard-sphere theory fits the data very well (± 5%) and provides a tool for dissecting the experimentally determined activation energies into component parts ammenable to simple physical interpretation. In a more recent work (Chen, Davis and Evans, 1981) we have shown that at higher temperatures the rough-hard-sphere theory is accurate when the solvent is composed of non-compact normal alkanes.

It was also shown (Evans, Tominaga and Chan, 1979; Davis, Evans and Tominaga, 1980) that an empirical correlation originated by Hayduk and Cheng (1971) provides an accurate method for predicting tracer diffusivity from the solvent viscosity and the solute radius. The method is accurate even when the rough-hard-sphere theory and Stokes' law fail. To test this method further and to provide a firmer experimental basis for theory testing and correlation development, we have measured diffusion coefficients of several inert gas and symmetrical polyatomic solutes in methanol, 1-butanol and 1-octanol over the temperature range 298 to 433 K.

EXPERIMENTAL

The Taylor dispersion technique was employed to measure the diffusion coefficients reported here. In this method, a small sample of a dilute solution is injected into a solvent which undergoes laminar flow through a circular tube. According to Taylor's analysis (1953) for liquids, the combination of convection in the axial direction and molecular diffusion in the radial direction causes the injected pulse of solute to disperse axially. At far end of the tube, the concentration distribution along the tube is gaussian, the variance of which is inversely proportional to the diffusion coefficient of the solute in the given solvent.

In our experimental apparatus, 200 ft (61 m) of stainless steel capillary tube of 0.03 in I.D. is coiled in 18-in. (457-mm) diameter and thermostated in a silicone oil bath which can be heated to 160°C. The solvent is delivered at steady and low flow rate (0.05 ~ 0.15 mL/min) with a Cheminert metering pump (CMP-2V). 25 or 50 μL sample solution (1–3% by weight) is introduced into the flowing solvent with a chromatography injection value (Reodyne). The concentration at tube end is detected using the differential refractometer (Waters R401). The dissolved-gas solution is prepared by saturating, at room temperature, the solvent with the gases (Ar, Kr, Xe, CH_4) under pressure, 10–20 psig (69–138 kPa), in a mixing vessel.

For the measurements of liquid solutes (CCl_4, M_4Sn, En_4Sn, n-Pr_4Sn, n-Bu_4Sn) below the normal boiling point of the solvent, the procedures are the same as previous described (Evans, Tominaga and Chan, 1979). For measurements above the normal boiling point, the system pressure is increased by 2 ~ 3 atm. above the vapor pressure of the solvent at the bath temperature. This is achieved by constricting the capillary tube at the end of the dispersion column and by adjusting the pumping rate at the top of the column. In the case of dissolved-gas solution, extra pressurization of the system is required to prevent the dissolved gas from bubbling as the solution is injected and to compensate for the possible reduced solubility at the bath temperature.

Since the differential refractometer cannot be used at temperatures higher than 348 K and pressures higher than 90 psig (620 kPa) the temperature and pressure of the fluid is lowered to 298 K and atmospheric prior to its entrance to the detector. The perturbations on the measured diffusivity due to temperature and pressure reduction is negligible if the following condition reduced from van der Laan's solution (1958) to the dispersion equation is satisfied,

$$8D_T L/ua^2 \gg (D_T/D_{298.2K})^2$$

where D_T is the diffusion coefficient at temperature T.

The tracer diffusion of dissolved-gas and liquid solutes have been measured over 298 ~ 433 K. The precision of these measurements is normally ± 1% over the entire temperature range. The apparatus is designed to minimize the effects on diffusion due to tube coiling, temperature and pressure difference between the dispersion column and the differential refractometer. From the normal concentration distribution, the tracer diffusivity can be calculated from the expression

$$D_{12} = 0.2310a^2 t_R/w_{1/2}^2$$

The solvents methanol (99.8%, Fisher certified ACS), 1-butanol (99%, Aldrich), and 1-octanol (99%+, Aldrich) were filtered (Millipore, 0.5 μm) before usage. The source and purity of the solutes were described previously (Evans, Tominaga and Chan, 1979).

RESULTS AND DISCUSSION

We report the diffusion coefficients of Ar, CH_4, Kr, Xe, CCl_4 and a series of tetraalkyltins (R_4Sn, R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9) in methanol, 1-butanol and 1-octanol over 298 to 433 K. The entries shown in Table 1 are the average of five diffusion mea-

TABLE 1. TRACER DIFFUSIVITIES IN ALCOHOLS[a,b]

T(K)	Solute Solvent	Ar	CH_4	Kr	Xe	CCl_4	Me_4Sn	Et_4Sn	Pr_4Sn	Bu_4Sn
283[d]	MeOH	—	—	—	—	1.76_2	1.62_2	1.27_2	1.05_1	0.89_1
	BuOH	—	—	—	—	0.591_2	0.487_2	0.333_6	0.260_1	0.212_2
	OcOH	—	—	—	—	0.237_2	0.208_3	0.156_1	0.106_2	0.084_1
298	MeOH	[c]6.43_4	5.81_7	5.10_3	3.97_3	2.25_2	2.06_2	1.66_4	1.38_1	1.18_1
	BuOH	3.31_1	2.66_4	2.19_5	1.62_3	0.843_4	0.700_3	0.490_3	0.391_1	0.324_3
	OcOH	1.86_1	1.45_2	1.19_2	0.845_7	0.381_2	0.331_2	0.240_4	0.176_2	0.137_1
313	MeOH	7.6_1	7.05_6	6.06_6	4.65_6	2.85_2	2.60_2	2.13_2	1.74_2	1.48_1
	OcOH	2.48_6	2.12_3	1.73_4	1.28_2	0.576_6	0.519_9	0.371_2	0.276_3	0.222_3
333	MeOH	9.4_1	8.85_8	7.52_4	5.85_5	3.82_3	3.50_3	2.80_2	2.26_2	1.92_1
	BuOH	5.38_2	4.94_4	4.10_2	3.14_4	1.67_2	$1.41n1$	1.07_1	0.835_7	0.706_6
353	MeOH	—	—	—	—	5.03_4	4.61_3	3.69_1	3.04_1	2.64_2
	OCOH	4.87_4	4.4_1	3.72_2	2.76_5	1.48_1	1.26_1	0.948_5	0.762_3	0.626_2
373	BuOH	9.2_1	8.70_5	7.1_1	5.60_4	3.30_1	2.90_2	2.31_1	1.79_1	1.55_2
383	MeOH	15.3_1	14.9_1	12.4_1	9.82_4	7.06_3	6.32_9	5.16_8	4.34_2	3.79_3
391	OcOH	7.8_1	7.50_9	6.01_7	4.77_6	2.75_2	2.71_1	1.86_2	1.59_1	1.31_2
430	OcOH	11.4_2	10.7_3	8.9_1	7.25_8	—	3.85_6	3.02_4	2.63_2	2.36_3
433	BuOH	17.2_1	16.8_1	13.4_4	11.4_1	—	6.08_5	5.47_4	4.61_3	3.82_3

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[a] MeOH = methanol, BuOH - 1-butanol, and OcOH = 1-octanol.

[b] Number given in 10^9 m^2/s.

[c] $6.43_4 = 6.43 \pm 0.04$.

[d] Data taken from D. F. Evans, T. Tominaga, and C. Chan, *J. Solution Chem.*, 8, 461 (1979).

surements on each solute. The precision of these measurements is ± 1% across the entire temperature range.

As Stokes' law provides the simplest possible connection between diffusion, solute size, and solvent viscosity, we compare the results at 298 and 433 K with the prediction of this law. As can be seen from Figure 1, the diffusion constants approach the Stokes' law limit as the solute becomes large; however, for the smallest solutes the deviations from the predicted results are spectacular. In addition, the solute methane shows consistent deviation from a smooth curve drawn through all the rest of the data. Since Stokes' law was derived under the condition that the solute molecule is so large that the solvent can be treated as continuum, it is not surprising that it fails for small solute molecules. This failure and its relation to solute/solvent size effects have been pointed out previously (Hildebrand and Ross, 1964; Evans, Tominaga and Chan, 1979; Evans, Davis and Tominaga, 1981).

Wilke and Chang (1955) modified Stokes' law empirically and obtained significant improvement in estimation of diffusivity. Their equation is

$$D_{12} = 1.17 \times 10^{-16} \left[(\phi M_2)^{1/2} \frac{T}{\mu V_1^{0.6}}\right] \cdot \qquad (1)$$

The recommended values of the association parameter ϕ for several solvents are: 2.6, water; 1.9, methanol; 1.5, ethanol; 1.0, unassociated solvents in general. Lusis and Ratcliff (1971) recommended that $\phi = 3.3$ for methanol and ethanol and $\phi = 5.1$ for higher alcohols as solvents.

The Wilke-Chang equation predicts measured diffusivities in methanol from 283 to 383 K with an average error of 16% and maximum error 39%. With Lusis and Ratcliff's value $\phi = 3.3$ there is 16% average error and 65% maximum error, no improvement over $\phi = 1.9$. Wilke and Chang did not attempt to apply their equation for alcohols other than methanol and ethanol, and with Lusis and Ratcliff's association parameter for 1-butanol and 1-octanol ($\phi = 5.1$) the equation does not perform satisfactorily, predicting diffusivity with 79% average error and over 200% maximum error. We also note in passing that the free-volume equations of Batschinski (1913) fail to correlate the fluidity and tracer diffusivities in 1-butanol and 1-octanol (Chen 1981) as was pointed out by Hildebrand (1971).

An alternative approach to correlate diffusion data is based on the systematic deviation from the Stokes' law as the solute size is varied. This approach has recently been shown to be quite successful (Davis, Evans, and Tominaga, 1980). The nature of the correlation is indicated by Figure 2, in which log (D_{12}/T) is plotted against log μ, where μ is the solvent viscosity, for tracer diffusion of the nine solutes in 1-butanol over 283 ~ 433 K. Stokes' law predicts that all these straight lines for different solutes should be parallel to each other with a slope of −1. As can be seen from the figure, there is a systematic deviation from the law as the solute size decreases in the sequence Bu_4Sn to Ar. The following equation summarizes the trends indicated by Figure 2,

$$10^9 D_{12}(10^3 \mu)^p = AT \qquad (2)$$

Furthermore, it has been found that the parameters p and A can be evaluated from the solute size alone. Solute size r_1 is determined following Bondi's procedure (1964). Thus, although Stokes' law fails

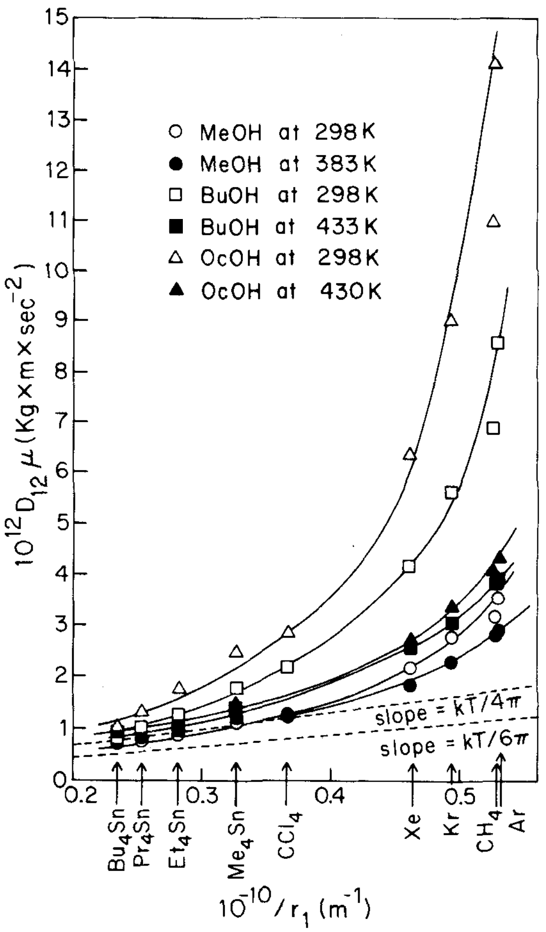

Figure 1. Comparison to Stokes' law of tracer diffusion in methanol, 1-butanol and 1-octanol.

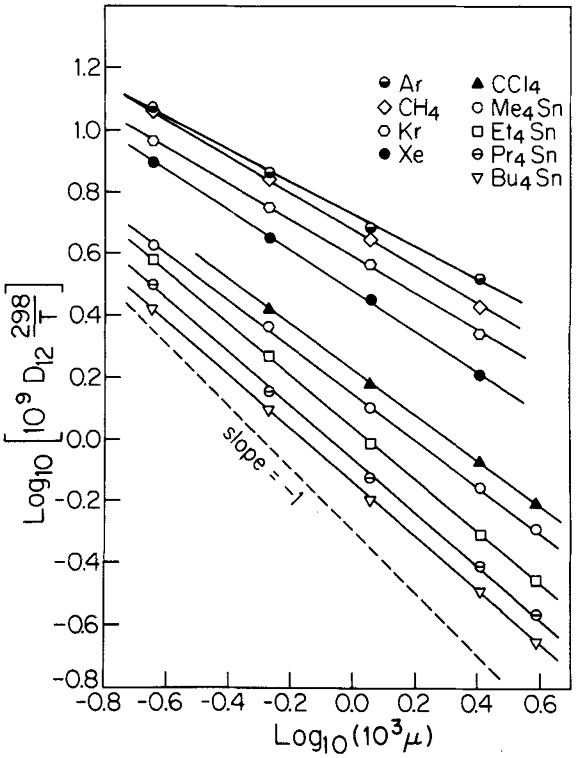

Figure 2. Tracer diffusion in 1-butanol over 283–433 K.

TABLE 2. COMPARISON OF PREDICTION TO EXPERIMENT[a]

System	T°K	$10^9 D_{pred}$ (m²/s)	$10^9 D_{expt}$ (m²/s)	% Error[b]
C_6H_6/CH_3OH	300	2.93	2.76[c]	6
$C_6H_5CH_3/CH_3OH$	298	2.44	2.56[d]	−5
$CHCl_3/C_2H_5OH$	288	1.47	1.63[f]	−10
C_6H_6/C_2H_5OH	298	1.61	1.81[e]	−10
CCl_4/C_2H_5OH	298	1.54	1.50[g]	3
Me_4Sn/C_2H_5OH	298	1.23	1.25[h]	−2
Et_4Sn/C_2H_5OH	298	0.932	0.950[h]	−2
CO_2/C_2H_5OH	298	3.41	3.42[m]	0
H_2/C_2H_5OH	293	14.8	14.9[n]	−1
He/C_2H_5OH	293	13.9	14.3[p]	−3
H_2/1-C_3H_7OH	298	12.38	12.84[j]	−4
CCl_4/2-C_3H_7OH	283	0.644	0.629[h]	2
Pr_4Sn/2-C_3H_7OH	298	0.460	0.458[h]	0
Bu_4Sn/2-C_3H_7OH	298	0.406	0.394[h]	3
C_6H_6/1-C_4H_9OH	298	0.87	0.99[i]	−12
CO_2/1-$C_7H_{15}OH$	298	1.60	1.80[l]	−11
C_3H_8/1-$C_7H_{15}OH$	298	0.78	0.88[l]	−11
CO_2/1-$C_8H_{17}OH$	298	1.45	1.46[k]	−1

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[a] Predictions made with Eqs. 2, 7 and 8.

[b] % error = $(D_{pred} - D_{expt})D_{expt} \times 100$.

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to describe the diffusion behavior, Eq. 2 provides an empirical basis for estimating diffusion from solvent viscosity and solute size. Equation 2 also correlates quite well diffusion in methanol and 1-octanol over the temperature range studied. The p and A values were found by fitting data to the solute-solvent pair.

Two correlations result from different approaches to generalize Eq. 2 with respect to the solvents. These are as follows:

a) A correlation characterizing solvents with the number of carbon atoms, n.

The p values are related to r_1^{-1}, r_1 in 10^{-10} m, as follows:

$$p = -1.0486\, r_1^{-1} + 1.1546, \text{ methanol} \tag{3}$$

$$p = -1.0352\, r_1^{-1} + 1.1128, \text{ 1-butanol} \tag{4}$$

$$p = -0.9928\, r_1^{-1} + 1.0518, \text{ 1-octanol} \tag{5}$$

Assuming that for tracer diffusion in aliphatic alcohols, $C_nH_{2n+1}OH$, p is of the form

$$p = -s r_1^{-1} + b \tag{6}$$

where m and b are linear functions of carbon number n and found from least-squares fit to be

$$s = -0.008141n + 1.06069$$
$$b = -0.01472n + 1.17017$$

Unfortunately we have found no simple way to generalize the lnA vs. r_1^{-1} correlation among the three solvents, although lnA is a linear function of r_1^{-1} in each solvent. Thus, Eq. 2 has to be used along with diffusivity at one temperature to evaluate A for a given solute-solvent pair. The result is that tracer diffusion can be predicted as a function of temperature from p, determined with Eq. 6, and A, determined from the diffusivity at one temperature, both p and A being temperature-independent.

As a test of the reliability of this scheme, the tracer diffusivities in the three solvents from 283 to 433 K are calculated from p and A (determined with diffusivity at 298 K) and compared to the experimental results. The average error of prediction is 5%, and the maximum error is 10%. Thus, this scheme allows one to predict tracer diffusion as a function of temperature from the carbon number of the solvent, and the diffusivity at one temperature in a specific solvent. To relieve the need for an experimental diffusivity, a second scheme was devised.

b) A correlation characterizing a solvent by its van der Waals radius, r_2.

The three almost parallel lines given by Eqs. 3–5 can be collapsed and data points spread by plotting $(1 - p)^{-1}$ against r_1/r_2. r_2 is the van der Waals radius of the solvent molecule, determined also by Bondi's procedure. lnA for each solute in the three solvents being more or less constant (to within ± 3%), an average is taken among the solvents and is again correlated with r_1^{-1} in order to remove the association between lnA and the solvent. The results for aliphatic alcohols are the correlation formulas

$$\frac{1}{1-p} = 4.740\left(\frac{r_1}{r_2}\right) - 0.88064 \tag{7}$$

$$lnA = 6.060\, r_1^{-1} - 7.408. \tag{8}$$

For diffusion in methanol, Eqs. 2, 7 and 8 perform comparably to the Wilke-Chang equation, 12% average error and 37% maximum error. But the same set of equations predicts diffusion in 1-butanol and 1-octanol with an average error of 7% and maximum error 24%, as opposed to 79% and over 200% obtained with the Wilke-Chang equation with the Lusis-Ratcliff association parameter.

Equations 7 and 8 were further tested by application to tracer diffusion results measured previously in alcohols. Table 2 reveals reasonably good agreement between the prediction and experiment.

In their study of self-diffusion in liquid methanol, Jonas and Akai (1977) rationalized the temperature and pressure dependence with a rough-hard-sphere (RHS) model which corrects the smooth-hard-sphere diffusivity for the retarding effect of intermolecular hydrogen bonding. The value of this correction factor varies from 0 to 1 monotonically as the temperature is raised. This is consistent with spectroscopic observation (Sakai, Sadaoka and Yamamoto, 1973) that hydrogen bonding is disrupted by thermal agitation. In the present work, the solute molecules do not hydrogen bond, and so we have not tried to introduce hydrogen bonding corrections. Rather we have tested the version of the RHS theory formerly applied (Evans, Davis and Tominaga, 1981; Chen, Davis and

TABLE 3. COMPARISON BETWEEN THE RHS THEORY AND EXPERIMENT[a]

T(K)	$n \times 10^{-24}$ (m^{-3})	$10^{10}\ \sigma_2$ (m)	Ar	CH_4	Kr	Xe	CCl_4	Me_4Sn	Et_4Sn	Pr_4Sn	Bu_4Sn
				Methanol							
283	15.06[c]	3.83	—	—	—	—	1.00	—	—	—	—
298	14.79[c]	3.76	0.94	0.92	0.99	1.09	1.10	—	—	—	—
313	14.55[c]	3.71	0.97	0.91	1.01	1.13	1.06	—	—	—	—
333	14.20[c]	3.65	0.98	0.94	1.03	1.14	1.01	—	—	—	—
353	13.83[c]	3.58	—	—	—	—	0.95	—	—	—	—
383	13.20[c]	3.49	0.99	0.92	1.00	1.10	0.90	—	—	—	—
				1-Butanol							
373	5.917[b]	5.22	0.94	0.90	0.91	0.93	0.93	1.07	1.13	1.18	1.15
433	5.344[b]	5.06	1.00	1.00	0.97	0.96	—	1.13	1.05	1.00	1.02
				1-Octanol							
391	3.495[b]	6.42	0.94	0.92	0.98	1.00	0.92	0.93	.11	0.99	1.00
430	3.348[b]	6.34	1.00	0.98	1.01	1.01	—	1.04	1.10	1.01	0.96
$10^{10}\ \sigma_1$ (m)			3.37	3.61	3.61	3.90	5.28	5.20	5.80	6.65	7.40

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[a] The comparison made in terms of D_{pred}/D_{expt}; D_{pred} calculated from Eq. 9.

[b] Determined with Benson's equation for liquid molar volume at normal boiling point and Mathias' equation for liquid density: R. C. Reid and T. K. Sherwood, "The Properties of Gases and Liquids," 2nd ed., McGraw-Hill, New York, 1966.

[c] Densities taken from: J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Interscience, New York, 1956.

Evans, 1981) to diffusion in nonpolar, polyatomic liquids.

According to the rough-hard-sphere (RHS) theory, the diffusion coefficient in the liquid state can be predicted from the expression (Chandler, 1974, 1975; Jonas and Parkhurst, Jr., 1975; Bertucci and Flygare, 1975; Evans, Davis and Tominaga, 1981; Chen, Davis and Evans, 1981),

$$D_{12} = h_{12}(D_{12}^{SHS}/D_{12}^{E})D_{12}^{E}, \tag{9}$$

where h_{12} is the rotational factor accounting for angular momentum transfer upon collision, $(D_{12}^{SHS}/D_{12}^{E})$, 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 Enskog diffusivity in the dense gas region.

As was done previously (Evans, Davis and Tominaga, 1981), h_{12} was set equal to 0.78 for monatomic solutes and 0.7 for polyatomic solutes at all temperatures, and the ratio $(D_{12}^{SHS}/D_{12}^{E})$ 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 (Chen, 1981). The parameter D_{12}^{E} is given by

$$D_{12}^{E} = \frac{3}{8n\sigma_{12}^{2}g_{12}(\sigma)}\left(\frac{kT}{2\pi m_{12}}\right)^{1/2}, \tag{10}$$

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} 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 ($n_1 \simeq 0$) or self-diffusion were computed from the formula

$$g_{12}(\sigma) = \frac{1}{1-\eta} + \frac{3\eta\sigma_1}{(1-\eta)^2(\sigma_1+\sigma_2)} + \frac{\eta^2\sigma_1}{2(1-\eta)^3\sigma_2} \tag{11}$$

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 demonstrated (Alder, Alley and Dymond, 1974) to be accurate for hard-sphere fluids.

In the study of tracer diffusion in cyclohexane as a function of temperature (Chen, Davis and Evans, 1981) the temperature-dependent σ_2 was determined by fitting the RHS theory to self-diffusion data at different temperatures. Since the predicted tracer diffusivity is insensitive to small variations in σ_1, the value of σ_1 at 298 K found by Evans, Davis and Tominaga (1981) was used for all temperatures. In the present work, the same set of σ_1's was used, whereas σ_2 for each solvent was determined by fitting to the RHS theory the measured tracer diffusivity of one of the solutes at each temperature. 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 3 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 methanol across the entire temperature range. The average error of prediction is 6%, the maximum error is 14%. Additionally, the value of σ_2 fixed from tracer diffusion at 298 K (3.76 Å) is close to the value (3.69 Å) calculated from the solubility of rare gases in methanol at same temperature using the scaled particle theory (Wilhelm, 1973). For solutes Me_4Sn through Bu_4Sn the solute-solvent mass ratios are all greater than 5, and hence there are no existing computer results which can provide reliable estimate of the ratio D_{12}^{SHS}/D_{12}^{E}. For solvents 1-butanol and 1-octanol the model performs equally well at temperatures where $V/Vo \geqslant 1.5$ (Chen, Evans and Davis, 1981) and so D_{12}^{SHS}/D_{12}^{E} can be estimated from computer results.

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Variable Volume Enzyme Reactor with Ultrafiltration Swing: A Theoretical Study on CSTR Case

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A new membrane enzyme reactor system is proposed, and its performance is analytically and numerically examined by operational modes. This membrane-separated, two-compartmental reactor is operated in a cyclic manner such that ultrafiltration swing is induced either by a pulsatile flow or by an alternating pressure difference. Substrate and product solutions are permeable to the membrane while enzyme is impermeable. In one reservoir, enzyme solution is stored into which substrate is supplied by diffusion-coupled ultrafiltration and product is removed by the same mechanism into the substrate compartment, which is similar to CSTR in view of fluid mixing and continuous inlet-outlet flows, but differs from CSTR in a sense that reaction takes place only in the enzyme compartment.

The governing model equations are derived and their analytical solutions are obtained for fast reaction and high ultrafiltration with first-order kinetics. In addition, nonlinear Michaelis-Menten kinetics problem is solved numerically. As a result, we have found that the system can increase the conversion substantially compared with previous diffusion-moderated enzyme reactors where diffusion very often can limit the extent of conversion.

SCOPE

In the last decade, several membrane devices have been considered for an immobilized enzyme reactor where soluble form of enzymes can be retained. This effort stems from the fact that insolubilization of enzymes requires chemical modification of supports and purification of enzymes to such extent that sometimes the whole process may become uneconomical. Despite these troublesome procedures, the recovery of the original enzyme activity is very often minimal. For this reason physical immobilization technique will be favorably sought if we have a method to keep a native enzyme stable in a soluble form (Schmid, 1979).

Hollow-fiber devices are used to retain an enzyme solution in the shell or lumen and a substrate solution flows in the opposite side (Waterland et al., 1974; Rony, 1971). On the other hand, ultrafiltration cells are used as CSTR where substrates and enzymes are mixed to react and only the product is removed through the membrane by ultrafiltration (Butterworth et al., 1970), or substrate passes through the immobilized enzyme membrane (Alfani et al., 1979). In spite of the promising role of these membrane devices as immobilized enzyme reactor a certain aspects of operational limitations are unavoidable. In the hollow-fiber reactor, the flow rate has to be low to achieve a considerable conversion since diffusion often limits the conversion. Besides, washing-out of enzymes from the sponge region of the fiber frequently happens to cause unequal distribution of enzymes along the fiber. The water flux in the ultrafiltration cell is also limited owing to the concentration polarization near the membrane surface.

In this study we propose a new membrane enzyme reactor having operational flexibility by combining the features of hollow-fiber device and ultrafiltration cell. This reactor is operated with ultrafiltration of an alternating direction which is induced either by an alternating pressure difference or by a pulsatile flow at the inlet or outlet of the substrate compartment. For the systematic investigation a theoretical model was developed to evaluate the performance of the new variable volume membrane enzyme reactor system by its various operational modes.

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