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Molecular Diffusivities for Propene in 1-Butanol, Chlorobenzene, Ethylene Glycol, and *n*-Octane at Elevated Pressures

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Diffusivities of propene measured at 298.2-348.2 K and up to 6891 kPa are reported for the solvents 1-butanol, chlorobenzene, ethylene glycol, and *n*-octane. Measurements were made by means of the Taylor dispersion technique. The densities of the solvents at the experimental temperatures and up to 6891 kPa are also reported. It is found that the diffusivities are reduced in associating solvents. The effect of pressure on the diffusion coefficients is relatively small for pressures from 101.3 to 6891 kPa, and the effect of pressure on the diffusion coefficients becomes more significant at higher temperatures. The rough hard sphere theory successfully describes the experimental diffusivity data obtained in this study, and it is useful for interpolating or extrapolating the diffusivity data to different temperatures and pressures.

Introduction

The rate of molecular diffusion in liquids is often the rate-determining factor in chemical engineering operations involving mass transfer such as absorption, liquid extraction, and heterogeneous chemical reactions. Moreover, diffusion coefficients are useful for understanding the structure of liquids and in the development of theories of the liquid state. However, comparatively few diffusivity data have been published. In particular, there are few data at high temperatures and pressures because of the difficulties and the cost of experimentally determining them.

The most accurate measurements of the mutual diffusion coefficients of binary liquid mixtures have usually been measured by interferometric methods. However, it has proved exceedingly difficult to apply these techniques to conditions far removed from the ambient condition. Consequently, in order to provide experimental data over a wide range of thermodynamic states within reasonable experimental times, another technique, called the Taylor dispersion technique, is usually used for these measurements. The application of the Taylor dispersion technique to high temperatures and pressures has been demonstrated in a number of recent papers (*1*, *2-6*). In this work, diffusivities of propene gas were measured in the solvents 1-butanol, chlorobenzene, ethylene glycol, and *n*-octane at 298.2, 323.2, and 348.2 K and up to 6891 kPa by means of the Taylor dispersion technique. The theoretical basis for this technique was given by Taylor (*7*, *8*) and Aris (*9*). A rigorous evaluation of design criteria for the Taylor dispersion technique was given by Alizadeh et al. (*10*). The densities of the solvents for the experimental temperatures and up to 6891 kPa pressure were also measured in this work by using an Anton Paar high-pressure densitometer.

According to the rough hard sphere (RHS) theory (*11*), the mutual diffusion coefficient can be obtained from the following expression:

$$D_{AB} = D_{AB}^{HSG}\frac{1}{g(\sigma_{AB})}C(\sigma_A,\sigma_B,m_A,m_B,V)F \qquad (1)$$

The rough hard sphere approach begins with an analytical expression for diffusion in a dilute gas, scales this expression to the moderately dense region with the radial distribution function, $g(\sigma_{AB})$, and then applies two more correction terms, C and F, accounting for correlated motions and exchanges of rotational and kinetic energies. The quantity D_{AB}^{HSG} was derived by Chapman and Enskog (*12*) as

$$D_{AB}^{HSG} = \frac{3}{8n\sigma_{AB}^2}\left[\frac{kT}{2\pi}\left(\frac{m_A+m_B}{m_Am_B}\right)\right]^{1/2} \qquad (2)$$

In the above expression, n is the number density of the fluid, σ_{AB} is the average collision diameter of the solute and solvent molecules, and m_A and m_B are the molecular masses of solute and solvent. The radial distribution function, $g(\sigma_{AB})$, can be considered as a correction term relating diffusivities in dilute gas to that in moderately dense gas. This function depends on the composition and molar volume of the mixture and on the diameters of the constituent molecules. For an infinitely dilute solution, $g(\sigma_{AB})$ can be obtained by using the following expression (*13*):

$$g(\sigma_{AB}) = \frac{1}{1-\psi} + \frac{3\psi\sigma_A}{(1-\psi)^2(\sigma_A+\sigma_B)} + \frac{\psi^2\sigma_A}{2(1-\psi)^3\sigma_B} \qquad (3)$$

In the above expression, ψ is the packing factor for hard-sphere assemblies. For the infinitely dilute case ($n_A = 0$), ψ can be obtained by using the following expression (*13*):

$$\psi = \frac{\pi n_B\sigma_B^3}{6} \qquad (4)$$

The factor C takes into account the effects of dynamically correlated molecular collisions on diffusion. There are two classes of such collisions: the vortex motion, which enhances the diffusion rate, and the backscattering, which reduces the diffusion rate compared to the Enskog prediction. The factor C is defined as

$$C(\sigma_A,\sigma_B,m_A,m_B,V) = \frac{D_{AB}^{SHS}}{[D_{AB}^{HSG}/g(\sigma_{AB})]} \qquad (5)$$

In the above expression, D_{AB}^{SHS} represents the diffusion coefficient of smooth hard spheres. The factor C depends on fluid density and solute-solvent mass and size ratios, but it cannot be obtained analytically. Chen et al. (*14*) reported the values of C for various solute-solvent mass and size ratios at various specific volumes by interpolating or extrapolating from existing computer simulation results for hard-sphere fluids. Finally, the quantity F accounts for the rotational contribution to diffusion. Baleiko and Davis (*15*) reported that the value of F ranges from 1.0 for perfectly smooth spheres to 0.7 for perfectly rough ones. Dymond (*16*) has shown that computer calculations for self-diffusion coefficients of hard-sphere molecules can be fitted accurately to the following expression:

$$D = \frac{2.306\times10^{-5}(T/M)^{1/2}}{V_0^{2/3}}(V-1.384V_0) \qquad (6)$$

In this equation, M is the molecular weight, V is the molar

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volume of the liquid solution, and V_0 is the closed-packed hard sphere volume defined as

$$V_0 = N\sigma_B^3/2^{1/2} \tag{7}$$

On the basis of the result of Dymond, Chen et al. (*17*) and Matthews (*5*) have introduced an expression that is equivalent to eq 1 in terms of the molar volume of the solution.

$$\frac{D_{AB}}{T^{1/2}} = \frac{\text{const}}{\sigma_{AB}^2}\left(\frac{m_A + m_B}{m_A m_B}\right)^{1/2}[a(V - bV_0)] = \gamma[V - V_D] \tag{8}$$

In the above expression, a is a constant for a given solute-solvent pair, and the constant b has been found empirically to be 1.358 (*11*). For diffusion coefficients at infinite dilution, the constant V_D should depend only on the solvent. The constant γ will depend on both the solute and the solvent and should be inversely proportional to the σ_{AB}^2 and the square root of the reduced mass, $(m_A + m_B)/m_A m_B$. In this work, it was found that the RHS theory could be successfully utilized to describe the experimental diffusivity data obtained in this study.

Experimental Section

The Taylor dispersion technique was employed to measure the diffusivities reported in this work. In this technique, a small sample of dilute solution is injected into a circular capillary tube in which the solvent is moving in laminar flow. According to Taylor's analysis (*7*, *8*), the combination of convection in the axial direction and molecular diffusion in the radial direction causes the injected pulse of solute to disperse axially to form a Gaussian concentration profile within the tube. At the end of the diffusion tube, the concentration $C(t)$ is recorded as the solute peak elutes through a detector. Taylor (*7*) has shown that for injection of material of mass m at a point $x = 0$ and at time zero, the concentration at the far-downstream end is given by

$$C = \frac{m}{2\pi R^2(\pi K t)^{1/2}} \exp\left[\frac{-(L - ut)^2}{4Kt}\right] \tag{9}$$

where

$$K = D_{AB} + \frac{R^2u^2}{48D_{AB}} \tag{10}$$

In the above equations, R is the tube radius, u the average solvent velocity, L the length of the dispersion column, and t the time. Equation 9 describes a Gaussian curve with a variance of $2Kt$. On the basis of the theories for chromatography, (*18*, *19*), the diffusion coefficient can be determined from the expression in terms of experimental data:

$$D_{AB} = 0.231\frac{R^2t_R}{W_{1/2}^2} \tag{11}$$

Here, t_R is the residence time of the solute in the dispersion column and $W_{1/2}$ the width at half-height of the eluted peak.

A schematic diagram of the Taylor dispersion apparatus constructed for this study is shown in Figure 1. The solvent was degassed by means of bubbling with helium gas inside the solvent holding tank. Then the degassed solvent was delivered at a low and steady flow rate (typically 1.3 × 10^{-9} m^3/s or about 0.25 cm/s) by a metering pump to the capillary tube. The metering pump was a Milton Roy Co., Model 396, pump, and it was specified to give a constant pumping rate to within ±0.3%. A pulse damper (SSI Model LP-21 LO-Pulse) was installed downstream of the pump to reduce any pressure pulsations from the pump. The solvent was directed through an injection valve, thence to a dispersion column consisting of a long capillary, a restricted passage, and then finally into the sample cell of the detector. The injection valve was a Rheodyne six-port valve and was suitable for injecting small quantities (2.0 × 10^{-8} m^3 or 20 μL) of sample into the system.

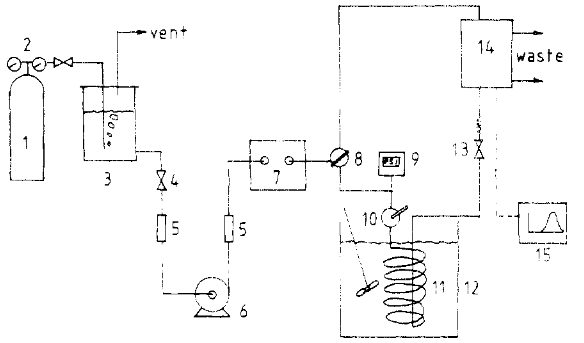

Figure 1. Schematic diagram of the Taylor dispersion apparatus: (1) helium gas cylinder; (2) regulator; (3) solvent holding tank; (4) shut-off valve; (5) filters; (6) metering pump; (7) pulse damper; (8) three-way valve; (9) pressure transducer; (10) injection valve; (11) dispersion column; (12) temperature bath; (13) restricted passage; (14) differential refractometer; (15) recorder.

The injection loop is of stainless steel tubing of about 10 cm in length and the same outside diameter as the dispersion tube. The internal diameter is approximately the same as that of the dispersion tube. Thus, there was only a small change in velocity for the flow through the injection loop and the dispersion column. Propene gas was bubbled through a sample of solvent at atmospheric pressure and at 25 °C. This saturated solvent, which contained a controlled amount of solute, was charged into the sample injection loop and subsequently into the dispersion column. The dispersion column is a 1.59 × 10^{-3} m outside diameter and 7.62 × 10^{-4} m inside diameter stainless steel capillary tube 68 m in length wound into a coil of 0.105-m radius. A displacement method was used to check the internal diameter of the capillary column. A volume of nonvolatile (*n*-butanol) solvent, initially deaerated by bubbling with helium, was infused into a syringe. The syringe was initially weighed full of solvent, after which the solvent was slowly injected into the washed and dried capillary tube. A provision was made to collect the few drops of solvent that came out of the end of the tube when it became filled, in a weighed vial. From the mass of solvent left in the syringe and in the vial, the mass of solvent required to fill the tube was determined. Since some 25–30 g of solvent were required for this purpose, an accurate determination of the internal tube diameter was possible based on a knowledge of the length of the tube and the solvent density. The internal diameter was found to be within 0.2% of the manufacturer's value. The capillary column was submerged in a constant-temperature bath (Tamson bath) that maintained a constant temperature to within ±0.01 K. After several hours, the fluid, containing the injected pulse of solute, passed through a restricted passage that consisted of a fine metering valve and a short section of small-diameter capillary tube (i.e. = 0.000 18 m); this restricted passage provided a resistance to flow and hence controlled the pressure inside the capillary to approximately 6900 kPa by viscous friction. The fluid pressure was reduced to essentially 101.3 kPa before the fluid went into the sample cell of the detector. The tube length for pressure reduction was less than 1% of that of the dispersion column. The detector utilized was a Waters R401 differential refractometer, which was used to monitor the axial solute concentration profile within the capillary. The concentration profile was recorded. A pressure transducer was installed upstream of the injection valve to measure the system pressure, which was also recorded. Usually a series of solute pulses was injected in sequence so that several response curves were obtained after the peaks eventually reached the detector. This resulted in a more rapid rate of accumulation of the data.

Questions may be raised as to the feasibility of coiling the dispersion tube and of reducing the pressure upstream of the detector. It is recognized that secondary flow occurs when fluid passes through a curved tube. The secondary flow can reduce the degree of dispersion and hence affect the measured diffusivity. However, the secondary flow effect can be neglected if the ratio of the coil diameter to the tube inside diameter is large and the flow velocity is relatively low. Alizadeh et al. (*10*) recommended that if $De^2Sc \leq 20$, then the effect of secondary flow is negligible. De is the Dean number $[Re/(R_c/R)^{1/2}]$ and Sc is the Schmidt number $(\mu/\rho D_{AB})$. For the worst case in this study, the value of De^2Sc was about 16. Next, it has been reported that the perturbations due to a pressure reduction occurring within a short length between the dispersion column and detector are negligible, if the following condition is satisfied (*20*):

$$uL/K \geq 1000 \qquad (12)$$

In this work the lowest value obtained for uL/K was about 15 000.

The densities of the solvents at the elevated pressures were measured at 298.2, 323.2, and 348.2 K with an Anton Paar densitometer equipped with a high-pressure measuring cell. The densitometer consisted of two components. One was the high-pressure sensing unit DMA512, which contained a stainless steel sample tube connecting to a measuring oscillator. The other component was DMA60, which was a frequency counter and digital display component. The period of oscillation of the liquid or gas in the sample tube of the DMA512 was determined and displayed by means of this latter component. The densitometer is capable of providing densities of accuracy to ±0.0001 provided that the temperature is constant to within ±0.01 K. The densitometer was calibrated with use of the known densities of distilled water and nitrogen at the various pressures and temperatures. The calibration constant, A_p, was obtained from the fluid densities and corresponding vibration frequencies, Ω, according to the following equation:

$$A_p = \frac{\Omega_1^2 - \Omega_2^2}{\rho_1 - \rho_2} \qquad (13)$$

At a constant temperature, the value of the calibration constant, A_p, has been found to be pressure-independent (*21*). Therefore, the density of the sample, ρ, whose period of oscillation is read as Ω from the DMA60, is expressed by the following equation:

$$\rho = \frac{1}{A_p}(\Omega^2 - \Omega_2^2) + \rho_2 \qquad (14)$$

In the above equation, the period of oscillation for nitrogen, Ω_2, was found to be linearly correlated with the absolute pressure at any particular temperature:

$$\Omega_2 = k_1 + k_2P \qquad (15)$$

In this equation, k_1 and k_2 are temperature-dependent constants that were estimated by a linear regression for each temperature. Thus by substituting eq 15 into eq 14, the density of a sample is expressed as a function of pressure, P, and the period of the oscillation, Ω, as

$$\rho = \frac{1}{A_p}[\Omega^2 - (k_1 + k_2P)^2] + \frac{M_2}{V_2} \qquad (16)$$

Propene gas was purchased from Air Products at a specified minimum purity of 99.0%. The solvents were obtained from Aldrich Chemicals with specified minimum purities as follows: 1-butanol, chlorobenzene, and ethylene glycol, all 99.9%; *n*-octane, 99.0%.

Table I. Densities of 1-Butanol, Chlorobenzene, Ethylene Glycol, and *n*-Octane as a Function of Pressure and Temperature

		density/(kg/m^3)		
solvent	P/kPa	298.2 K	323.2 K	348.2 K
1-butanol	101.3	806.0	786.8	760.0
	689.1	806.2	787.1	760.7
	2067.3	806.7	788.1	762.1
	3445.6	807.2	788.9	763.5
	4823.8	807.8	789.8	764.9
	5512.9	808.1	790.2	765.6
	6891.2	808.7	791.0	766.6
chlorobenzene	101.3	1100.9	1073.0	1047.0
	689.1	1101.0	1073.9	1047.7
	2067.3	1101.7	1075.0	1049.3
	3445.6	1102.6	1076.3	1051.0
	4823.8	1103.6	1077.5	1052.4
	5512.9	1104.1	1078.2	1053.1
	6891.2	1105.2	1079.3	1054.6
ethylene glycol	101.3	1109.9	1092.3	1073.1
	689.1	1109.9	1092.5	1073.5
	2067.3	1109.9	1092.9	1074.2
	3445.6	1110.0	1093.2	1075.0
	4823.8	1110.2	1093.6	1075.7
	5512.9	1110.3	1093.8	1076.1
	6891.2	1110.5	1094.2	1076.9
n-octane	101.3	698.4	678.3	660.0
	689.1	698.6	678.8	660.7
	2067.3	699.3	679.9	662.6
	3445.6	700.1	681.1	664.3
	4823.8	700.8	682.2	666.0
	5512.9	701.2	682.8	666.9
	6891.2	702.0	683.9	668.6

Table II. Comparison of the Densities Measured in This Work with Values from the Literature at 101.3 kPa

		density/(kg/m^3)	
solvent	T/K	this work	literature
1-butanol	298.2	806.0	806.1 (*22*), 806.0 (*21*)
	323.2	786.8	786.6 (*21*), 786.7 (*23*)
	348.2	760.0	
chlorobenzene	298.2	1100.9	1100.8 (*21*), 1100.9 (*24*)
	323.2	1073.0	1073.3 (*21*), 1074.0 (*24*)
	348.2	1047.0	1047.0 (*24*)
ethylene glycol	298.2	1109.9	1109.9, 1110.0 (*24*)
	323.2	1092.3	
	348.2	1073.1	
n-octane	298.2	698.4	698.7 (*21*), 698.5 (*24*)
	323.2	678.3	678.1 (*21, 24*)
	348.2	660.0	

Results and Discussion

The densities of the solvents 1-butanol, chlorobenzene, ethylene glycol, and *n*-octane were measured at 298.2, 323.2, and 348.2 K and at pressures up to 6891 kPa by using the Anton Paar densitometer equipped with a high-pressure measuring cell. The experimental results are shown in Table I and the maximum experimental error for the densities has been estimated to be ±0.05%. To verify the consistency of the high-pressure densitometer, the densities of the four solvents are compared at 101.3 kPa with those reported in the literature in Table II, and good agreement is obtained in all cases. On the basis of the observation of the density data, the effect of pressure on the density is relatively small, and the changes of density with increasing pressure are more significant at higher temperature.

As a confirmation of the proper design of the Taylor dispersion apparatus, a comparison of some of the diffusivities measured by the Taylor dispersion technique is made with values measured by the steady-state capillary cell method reported elsewhere (*22*) as shown in Table III. The agreement is generally very good, and the maximum difference is 2.0%.

Table III. Comparison of Results for 101.3-kPa Pressure for Two Different Methods for Measuring Diffusivities of Propene Gas

		diffusivity/10^{-9} m^2/s	
solvent	T/K	steady-state capillary cell method (*25*)	Taylor disperion technique
1-butanol	298.2	1.34 ± 0.02	1.35 ± 0.01
	323.2	2.37 ± 0.02	2.40 ± 0.04
chlorobenzene	298.2	2.40 ± 0.09	2.44 ± 0.01
	323.2	3.37 ± 0.06	3.40 ± 0.01
n-octane	298.2	3.40 ± 0.09	3.42 ± 0.00
	323.2	4.77 ± 0.07	4.78 ± 0.05

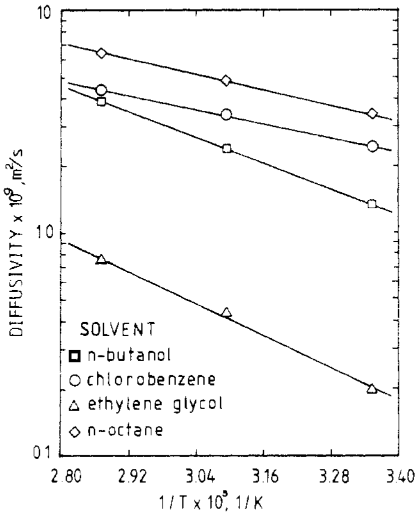

Figure 2. Plot of ln $D°_{AB}$ versus $1/T$ for propene in 1-butanol, chlorobenzene, ethylene glycol, and *n*-octane for atmospheric pressure.

Therefore, it is considered that both measurement methods can produce reliable results since it is unlikely that similar results could be coincidentally obtained by those two totally different experimental techniques. The average values of at least three experimental diffusivities of propene in 1-butanol, chlorobenzene, ethylene glycol, and *n*-octane at different temperatures and pressures are shown in Table IV. The uncertainties indicated in the table correspond to 1 standard deviation of the multiple runs. On this basis, it is considered that the accuracy of the diffusivity data is at least ±2.0%. It is evident that the diffusivity decreases with increasing pressure. However, the effect of pressure on the diffusion coefficients is relatively small for pressures from 101.3 to 6891 kPa. On the basis of observations of the results obtained, it may be stated that the effect of pressure on the diffusion coefficients becomes more significant at higher temperatures. This phenomenon is similar to the effect of pressure on densities. Since the density increases with increasing pressure, it may be considered that the free space between the liquid molecules, through which diffusion occurs, is decreased; thus it is considered that the rate of diffusion will also decrease because the space for diffusion is reduced.

It has been found that the polarity of the solvent and the tendency for self-association of the solvent molecules affect the diffusion process. In Figure 2, the diffusivities of propene in 1-butanol, chlorobenzene, ethylene glycol, and *n*-octane at atmospheric pressure are compared. It is shown that the diffusivities of propene in *n*-octane are the highest, followed by chlorobenzene and 1-butanol, and the diffusivities of propene in ethylene glycol are the lowest among those solvents. *n*-Octane is nonpolar and nonassociating, chlorobenzene is slightly polar but nonassociating, 1-butanol is highly polar and associating, and ethylene glycol is even more polar and strongly associating due to its two hydroxyl groups. These solvents show a typical effect; that is, the higher the degree of molecular association in the solvent, the greater the reduction in diffusivity of the dissolved gases.

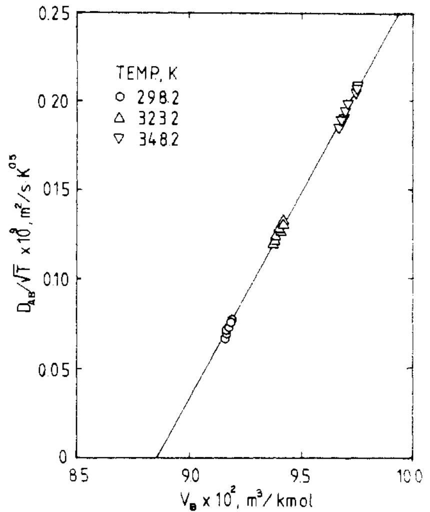

Figure 3. Plot of $D°_{AB}/T^{1/2}$ versus V_B for propene in 1-butanol at different temperatures and pressures.

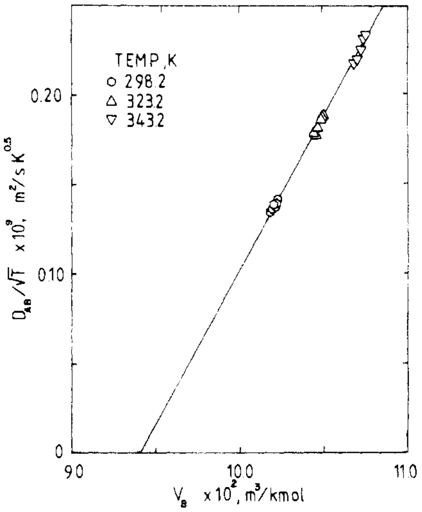

Figure 4. Plot of $D°_{AB}/T^{1/2}$ versus V_B for propene in chlorobenzene at different temperatures and pressures.

Chen et al. (*17*) and Matthews (*5*) have introduced a simplified expression for the rough hard sphere theory in terms of the molar volume of the solution. For dilute solution

$$\frac{D°_{AB}}{T^{1/2}} = \gamma[V_B - V_D] \tag{17}$$

If this relationship is valid, then it would be possible to predict the diffusivity at infinite dilution for a given solute–solvent system by using one physical property (the solvent molar volume, V_B) and two parameters, γ and V_D. Figures 3–6 are the plots of $D°_{AB}/T^{1/2}$ versus the solvent molar volume, V_B, for propene in the four solvents studied in this investigation at different temperatures and pressures. The figures show linear relationships between $D°_{AB}/T^{1/2}$ and V_B. Thus, it appears that eq 17 can be used to successfully describe the diffusivities measured in the ranges of temperature and pressure utilized in this work. The parameters γ and V_D were determined by linear regression of the experimental results for each system, and the values are given in Table V. It was found that the value of V_D increased in a regular way with increasing solvent critical volume, V_{CB}. The ratios of V_D to V_{CB} for the four systems in this work are also shown in Table V. The ratios are from 0.296 to 0.329 and are on the average 0.309. The relationship between V_D and V_{CB} obtained in this work is slightly different from

Table IV. Diffusivities of Propene in 1-Butanol, Chlorobenzene, Ethylene Glycol, and *n*-Octane at Elevated Pressures

		diffusivity/10^{-9} m^2/s		
solvent	P/kPa	298.2 K	323.2 K	348.2 K
1-butanol	137.8	1.35 ± 0.01		3.89 ± 0.03
	172.3		2.40 ± 0.04	
	468.6			3.86 ± 0.07
	1722.8	1.31 ± 0.01		
	2411.9		2.30 ± 0.04	
	3376.7			3.69 ± 0.04
	3790.1	1.24 ± 0.03	2.24 ± 0.05	
	5444.0			3.53 ± 0.05
	5512.9	1.21 ± 0.02	2.19 ± 0.02	
	6546.6		2.16 ± 0.02	
	6822.2			3.45 ± 0.04
	6891.2	1.17 ± 0.03		
chlorobenzene	117.2		3.40 ± 0.01	4.35 ± 0.05
	124.0	2.44 ± 0.01		
	1033.7	2.42 ± 0.01		
	1378.2			4.29 ± 0.07
	1585.0		3.33 ± 0.03	
	2480.8			4.19 ± 0.03
	3445.6	2.40 ± 0.01		
	4272.5		3.24 ± 0.02	
	4582.6			4.09 ± 0.04
	5857.5		3.19 ± 0.02	
	6202.0	2.33 ± 0.02		
	6271.0			4.03 ± 0.02
ethylene glycol	344.6			0.756 ± 0.003
	379.0		0.437 ± 0.003	
	447.9	0.203 ± 0.001		
	1378.2		0.433 ± 0.002	0.750 ± 0.002
	2687.6		0.431 ± 0.002	
	2894.3			0.740 ± 0.008
	3424.9	0.202 ± 0.001		
	3721.2	0.189 ± 0.001		
	4134.7		0.426 ± 0.005	0.721 ± 0.008
	6753.3	0.188 ± 0.001		0.692 ± 0.001
	6891.2		0.419 ± 0.002	
n-octane	103.4	3.42 ± 0.00	4.78 ± 0.05	
	137.8			6.41 ± 0.06
	1447.1			6.26 ± 0.08
	2274.1	3.21 ± 0.03	4.67 ± 0.05	6.16 ± 0.02
	3101.0	3.18 ± 0.02	4.60 ± 0.04	
	3514.5			6.01 ± 0.06
	4444.8		4.52 ± 0.04	
	5099.5	3.07 ± 0.03		
	5685.2		4.43 ± 0.04	
	5995.3			5.71 ± 0.04
	6202.0	3.01 ± 0.03		
	6753.3			5.63 ± 0.05
	6856.7		4.32 ± 0.01	

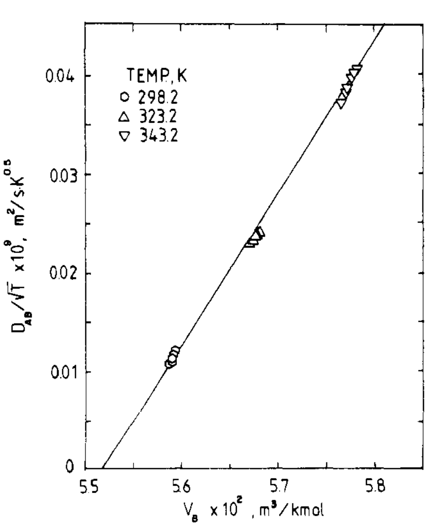

Figure 5. Plot of $D°_{AB}/T^{1/2}$ versus V_B for propene in ethylene glycol at different temperatures and pressures.

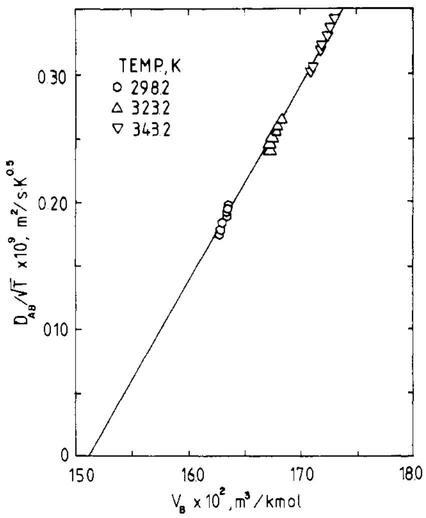

Figure 6. Plot of $D°_{AB}/T^{1/2}$ versus V_B for propene in n-octane at different temperatures and pressures.

Table V. Values of V_{CB}, γ, and V_D for Propene in the Four Solvents

solvent	V_{CB}/(m^3/kmol)	$\gamma/10^{-9}$ kmol/(m s $K^{0.5}$)	V_D/(m^3/kmol)	V_D/V_{CB}
1-butanol	0.274	23.14	0.090	0.329
chlorobenzene	0.308	17.30	0.094	0.305
ethylene glycol	0.186	15.14	0.055	0.296
n-octane	0.492	15.47	0.151	0.307

Table VI. Comparison of Molecular Diameters Calculated on the Basis of a Rough Hard Sphere (RHS) and a van der Waals (vdW) Molecular Model

solvent	$\sigma_B/10^{-10}$ m	$\sigma_{vdW}/10^{-10}$ m
1-butanol	5.35	5.46
chlorobenzene	5.46	5.66
ethylene glycol	4.57	4.78
n-octane	6.39	6.56

the result reported by Matthews (*5*), who stated that V_D/V_{CB} is 0.302 for the gaseous solutes. Physically, V_D can be considered to be the hypothetical solvent molar volume at which the diffusion coefficient goes to zero. The physical meaning of V_D can be checked by calculating the hard-sphere diameter, σ_B, based on the value of V_D calculated from the experimental data with use of the following expression:

$$V_D = bV_0 = bN\sigma_B^{\,3}/2^{1/2} \qquad (18)$$

In the equation above, the constant b has been found empirically to be 1.358 (*11*). The calculated values of the diameter, σ_B, are compared with the predicted values of diameter, σ_{vdW}, based on the van der Waals volume in Table VI. The van der Waals volumes are calculated from the group contribution method of Bondi (*26*). From Table VI, it is shown that there is relatively good agreement between the two diameter values. The ratio of σ_B to σ_{vdW} is found on the average to be 0.969. The above finding is consistent with the result reported by Matthews (*5*), for which it was reported that σ_B/σ_{vdW} is 0.974 for n-alkane systems.

In this work, it is found that the diffusivities are reduced in associating solvents, and the effect of pressure on the diffusion coefficients is relatively small for pressures ranging from 101.3 to 6891 kPa. The simplified form of the RHS theory successfully describes the experimental diffusivity data obtained in this study, and it is useful for interpolating or extrapolating the diffusivity data to different temperatures and pressures.

Glossary

A_p	calibration constant for the densitometer
a,b	constants in eq 8
C	concentration of solute (mass/volume)

$C(...)$	correction term in eq 1
D_{AB}	mutual diffusion coefficient (m^2/s)
D_{AB}^{SHS}	mutual diffusion coefficient for smooth hard spheres
D_{AB}^{HSG}	mutual diffusion coefficient for a low-density hard sphere gas
D°_{AB}	mutual diffusion coefficient at infinite dilution
De	Dean number
F	correction term in eq 1
$g(\sigma_{AB})$	radial distribution function
L	length of the dispersion column
k	Boltzmann constant
k_1,k_2	calibration constants in eq 15
K	Taylor diffusion coefficient
m	mass of solute in the sample injected
m_A,m_B	molecular masses of solute and solvent
M	molecular weight
n	number density (molecules/volume)
n_A,n_B	number densities of solute and solvent
N	Avogadro number
P	pressure
R	radius of the tube
R_c	helix radius
Re	Reynolds number
Sc	Schmidt number
t	time
t_R	residence time
T	absolute temperature (K)
u	velocity at x frame of reference
V	molar volume
V_D	molar volume at which the diffusion is frozen
V_0	closed-packed hard-sphere volume
$W_{1/2}$	the width at half the peak height
x	axial coordinate

Greek Letters

γ	constant in eq 8
μ	viscosity of solution
ρ	density
σ_A,σ_B	molecular diameters of solute and solvent
σ_{AB}	average collision diameter of the solute and solvent molecules
ψ	packing factor for hard-sphere assemblies
Ω	period of oscillation

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Excess Properties for 1-Butanethiol + *n*-Heptane, Cyclohexane, Benzene, and Toluene. 1. Excess Molar Volumes at 283.15 and 298.15 K

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This paper reports densities and excess molar volumes at 283.15 and 298.15 K, at atmospheric pressure, for binary mixtures of 1-butanethiol + *n*-heptane, cyclohexane, benzene, and toluene. The excess molar volumes are less than 0.607 $cm^3\ mol^{-1}$, or 0.56% of the mixture molar volume. The excess molar volumes increase with increasing temperature for 1-butanethiol + *n*-heptane; they decrease with increasing temperature for the other three systems. Excess molar volumes for 1-butanethiol + aromatic systems are smaller than for paraffinic systems, with the maximum values for toluene being 0.007 $cm^3\ mol^{-1}$.

Introduction

Sulfur compounds, and their behavior with hydrocarbons, are important in the petroleum and chemical industries. An understanding of mixture nonidealities is needed to design processes to remove sulfur compounds from petroleum, to purify sulfur compounds for use as chemical intermediates, and to solve environmental problems. Excess molar volumes, together with excess enthalpies and activity coefficients, when used to develop and evaluate molecular models, help us to understand the effects of molecular size and molecular interactions as the basis of nonideal mixing behavior. This understanding, together with experimental data, is required for the development of practical models and correlations for design calculations.

We know of no published density data for binary mixtures of thiols (mercaptans) with hydrocarbons. Here we present den-

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