more dilute regions would be likely to be reasonably accurate.

It is interesting to compare these results with those for the same *n*-alkane solutes with ethane as a common solvent (*6*). The pressures along the three-phase solid–liquid–vapor locus for all three of these binary systems are higher than the pressures for the comparable ethane binary systems. Also, the pressure maximum occurs at about the same temperature. The solid solubilities of the solute components are slightly less in ethylene than in ethane at the same temperatures and these solubility differences are more pronounced at the lower temperatures.

Glossary

R	universal gas law constant = 1.987 cal/(g-mol K)
T	temperature in K
T_T	triple point temperature in K: 216.38 K for *n*-octane, 243.51 K for *n*-decane, 263.61 K for *n*-dodecane
T^*	T/T_T
x	solute mole fraction
x_I	ideal solute mole fraction, computed from eq 1
γ	activity coefficient of solute $\equiv x_I/x$
ΔH_{FUS}	enthalpy of fusion of pure solute component, cal/g-mol

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Mutual Diffusion Coefficients in Binary Mixtures of Carbon Tetrachloride and Alcohols at 20 °C

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The mutual diffusion coefficients at 20 °C were measured for three associated binary mixtures: CCl_4–CH_3OH, CCl_4–*n*-C_3H_7OH, CCl_4–*n*-C_4H_9OH. A limited-diffusion method was used with concentration differences being measured by holographic interferometry. The experimental results are compared with values derived by various predictive methods.

In a previous article (*15*) we showed that the limited-diffusion method of Harned and French (*7*) could be adapted for measuring mutual diffusion coefficients in binary organic mixtures. This adaptation involved the use of holographic interferometry to measure the concentration differences. Since the results obtained were satisfactory, with an estimated error in the diffusion coefficient of 1.5%, we extended the work by applying the same method to mixtures of tetrachloromethane with a series of normal alcohols (methanol, 1-propanol, 1-butanol), at a temperature of 20 °C and throughout the entire range of concentration. The mixture tetrachloromethane–ethanol had been previously studied (*15*).

The diffusion coeficients measured in this work add new information to the values already existing in the literature (*1*, *9*, *11*), which were mostly obtained at other temperatures.

Numerous equations, either empirical or theoretical, have been proposed to predict diffusion coefficients in binary liquid mixtures throughout the whole range of composition (*5*, *10*, *13*, *18*). Most of these equations are applicable in the case of nearly ideal or regular mixtures. We ourselves, in a recent paper (*14*), have also proposed an empirical relationship that can be applied equally well to either regular or associated mixtures.

The second part of this work will be concerned with a comparison between the experimental results for a series of aliphatic alcohols from CH_3OH to C_4H_9OH in CCl_4 and the results calculated from these various equations. It is obvious that such a comparison is not entirely fair since most of the earlier equations were not originally intended to be applied to associated systems. However, there seems to be no alternative, since no other simple equations applicable to associated systems have yet been proposed.

Prediction of Diffusion Coefficients

The prediction of the variation with concentration of the mutual diffusion coefficient in binary liquid mixtures is a problem that has stimulated a great deal of interest, both theoretical and practical.

From a practical point of view the desired aim is to obtain a relationship giving the mutual diffusion coefficient at any chosen concentration as a function of system properties which are readily accessible. It is from this point that we shall approach the subject. On the basis of various theoretical equations so far proposed, none of which is entirely satisfactory for binary mixtures, a few empirical or semiempirical models have given rise to a number of equations intended for practical use.

Among those equations requiring the fewest data, we find the following relationships, proposed respectively by Caldwell and Babb (*4*), Vignes (*18*), and Rathbun and Babb (*13*):

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$$D_{12}^{\text{id}} = (x_1 D_2^\circ + x_2 D_1^\circ) \tag{1}$$

$$D_{12} = (D_2^\circ)^{x_1} (D_1^\circ)^{x_2} \beta \tag{2}$$

$$D_{12} = (x_1 D_2^\circ + x_2 D_1^\circ) \beta^S \tag{3}$$

These relationships may be used to calculate the concentration dependence of the mutual diffusion coefficient by making use of the diffusion coefficients at infinite dilution D_i°, defined as

$$D_i^\circ = \lim_{x_i \to 0} D_{12}$$

together with the thermodynamic factor β

$$\beta = \frac{\partial \ln a_i}{\partial \ln x_i} \tag{4}$$

The exponent S in eq 3 serves to reduce the variation in the thermodynamic factor which is otherwise too great. The authors who suggested this equation gave the value $S = 0.6$ for systems showing positive deviations from Raoult's law and $S = 0.3$ for systems showing negative deviations. Equation 1, originally proposed for ideal systems, has here been modified, simply by multiplying by the thermodynamic factor, in order to account for the nonideality of the systems under consideration:

$$D_{12} = D_{12}^{\text{id}} \beta \tag{5}$$

Other equations used for predictive calculations involve extra data concerning the pure components and the mixtures, particularly the viscosity coefficients. We might give as examples the equations of Carman and Stein (*5*):

$$D_{12} = (x_1 D_2^\circ \eta_1 + x_2 D_1^\circ \eta_2)(\beta/\eta) \tag{6}$$

or of Leffler and Cullinan (*10*):

$$D_{12} = (D_2^\circ \eta_1)^{x_1} (D_1^\circ \eta_2)^{x_2} (\beta/\eta) \tag{7}$$

in which η_1, η_2, and η indicate respectively the viscosities of the pure components 1 and 2 of the mixture.

There exist other relationships not considered in this work, for example Darken's (*6*) equation which involves coefficients of self-diffusion of the constituents which are generally not available or the very recently published relationship of Kosanovitch and Cullinan (*8*) which requires a knowledge of the variation of the densities with temperature as well as viscosity data.

In a recent article, we showed that for many regular or associated mixtures the variation of $D_{12}/D_{12}^{\text{id}}$ as a function of β was approximated by a straight line passing through the point with coordinates (1,1). This led us to suggest the following correlation for the variation of the diffusion coefficient with liquid composition:

$$D_{12} = (x_1 D_{12}^\circ + x_2 D_1^\circ)(1 - m + m\beta) \tag{8}$$

a relationship in which m is the slope of the straight line passing through the point (1,1) and through the point with coordinates $(D_{12}/D_{12}^{\text{id}}, \beta)_{x_i}$.

Consequently this correlation requires, as well as the values D_1° and D_2°, another value of D_{12} to be determined experimentally. In order to have the most accurate value for m, x_i should be the concentration at which the curve $\beta = f(x_i)$ presents an extreme value.

Experimental Method

The method of analysis of limited diffusion and also the experimental apparatus used have been described previously (*15*). In the present case the cell used was of height 3 cm, width 1 cm, and optical path length 1 cm. It consists of a glass frame clamped between two metal walls the temperature being held constant at 20 ± 0.02 °C. We might recall that using this system the differential diffusion coefficient D_{12} is obtained from the relationship

Table I. Mutual Diffusion Coefficients at 20 °C

CH_3OH-CCl_4		n-C_3H_7OH-CCl_4		n-C_4H_9OH-CCl_4	
x, mol %	$10^5 D_{12}$, $cm^2\ s^{-1}$	x, mol %	$10^5 D_{12}$, $cm^2\ s^{-1}$	x, mol %	$10^5 D_{12}$, $cm^2\ s^{-1}$
0	2.1 ± 0.2	0	1.1 ± 0.1	0	0.8 ± 0.1
2	1.09	2	0.78	2	0.64
5	0.83	5	0.70	5	0.60
10	0.66	10	0.66	10	0.58
20	0.50	20	0.62	20	0.58
30	0.43	30	0.62	30	0.60
40	0.44	40	0.65	40	0.63
50	0.54	50	0.69	50	0.65
60	0.69	60	0.72	60	0.68
70	0.88	70	0.76	70	0.70
80	1.15	80	0.80	80	0.73
90	1.64	90	0.83	90	0.75
100	2.10	100	0.88	100	0.78

$$\Delta x = x\left(\frac{h}{6}\right) - x\left(\frac{5h}{6}\right) = 2B \exp\left(\frac{-D_{12} t \pi^2}{h^2}\right) \tag{9}$$

where t is the time and h is the cell height (3 cm).

The difference in concentration Δx between the points $h/6$ and $5h/6$ was determined by real-time holographic interferometry, the reference state recorded in the hologram being the same cell filled with a mixture of uniform concentration. The number of fringes k observed between two points is related to the difference in refractive index in the liquid Δn between these two points

$$k = e\Delta n/\lambda$$

where e is the optical path length, in this case 1 cm, and λ is the wavelength of the light source (λ 6328 Å).

The variation of the refractive index with the composition was determined for each mixture at the temperature in question and at the wavelength of the laser light. Considering the slight difference in concentration between the two superposed liquids (mostly less than 1 mol %), it may be assumed that in this case there is a linear relationship between the refractive index and the concentration. Taking this into account eq 9 may be written

$$k = C \exp(-D_{12} t \pi^2/h^2) \tag{10}$$

where C is a constant, and the diffusion coefficient may be determined from a graph of ln k against time.

Results

The values obtained for the differential mutual diffusion coefficients are shown in Table I. These values were derived by graphical interpolation from the actual experimental points.

In order that the error in the value for D_{12} should be no greater than 1.5%, it is necessary to work with solutions between which the initial difference in concentration corresponds to a k value of the order of ten fringes. Under these conditions the required difference Δx in concentration between the two superposed mixtures is always about 1 mol % for the mixtures CCl_4–C_3H_7OH and CCl_4–C_4H_9OH, while for the mixture CCl_4–CH_3OH it was about 0.5 mol %, except in the range of concentrations weak in alcohol where the variation in refractive index with concentration is much smaller. As this mixture approaches the condition of pure CCl_4, the difference in concentration can hardly be made less than 1.5 mol %. It is precisely in this range of concentrations that the diffusion coefficient increases steeply, making it very hard to extrapolate to infinite dilution. At the other

Table II. Data Required for the Predictive Calculation

System	$D_1°$	m	Data references η	Data references β
CH_3OH-CCl_4	1.9	0.81		
	2.1	0.83	2	16
	2.3	0.85		
C_2H_5OH-CCl_4	1.6	0.78		
	1.75	0.80	2	3
	1.9	0.82		
n-C_3H_7OH-CCl_4	1.0	0.50		
	1.1	0.55	2	12
	1.2	0.62		
n-C_4H_9OH-CCl_4	0.7	0.26		
	0.8	0.35	2	17
	0.9	0.44		

limit of the concentration scale the extrapolation is much easier.

The values were obtained for other concentrations by graphical interpolation, there being no analytical function to describe the variation of the diffusion coefficient with concentration. For the mixtures n-C_3H_7OH–CCl_4 and n-C_4H_9OH–CCl_4, seven experimental points were available; for the mixture CH_3OH–CCl_4, there were ten experimental points. The mean deviations of the points from the smoothed curves are never greater than 1.5% and so remain within the limits of experimental error.

Predictive Calculations

The eq 2, 3, 5, 6, 7, and 8 have been used to carry out predictive calculations for the three systems studied in this work, as for the system CCl_4–C_2H_5OH, the results for which were published previously (*15*). In each case the values of the diffusion coefficients at infinite dilution were obtained by extrapolation of the experimental curves. The extrapolation becomes very difficult as one approaches pure CCl_4, particularly for the first two alcohols, and this may result in significant error (Table I). At the other limit of the plot the extrapolation presents no difficulty. The sources used for the other data (η and β) are given in Table II.

For the sake of these calculations, the experimental value for D_{12} chosen to calcuate m in eq 8 was the one corresponding to the minimum in the curve $\beta = f(x)$. For this equation (3), three predictive calculations were carried out with three different values for $D_1°$: one most probable value and two other values within the limits of extrapolation error, one on either side (Table II). As might be expected, the value for m varies with the value given to $D_1°$ (Table II).

The calculations were performed for each mole fraction increment of 0.1 (i.e., 0.1, 0.2, ..., 0.9). For each system the mean deviations were calculated using the formula

$$E = \frac{1}{9} \sum_{i=1}^{9} \frac{|D_{12}^{\text{calcd}} - D_{12}|_i}{D_{12}} 100\%$$

The results appear in Table III. It may be noted that the best results are obtained with eq 8 for which the maximum error is of the order of 4%. The error is hardly affected by the value chosen for $D_1°$ since any possible deviations are largely corrected by the change in the parameter m.

After eq 8, the one giving the most acceptable results is eq 3. It this case, however, the successfulness of the calculation depends greatly on the value assigned to $D_1°$.

All the other equations give rather poor results for associated mixtures, the mean deviations being between 30 and 50%.

Conclusion

The limited diffusion method used in this work is perfectly suited to measurements of diffusion coefficients in mixtures such as those studied here. Nevertheless, for low alcohol concentrations the accuracy achieved is not sufficient to allow a clear determination of the diffusion coefficient at infinite dilution.

At first sight, it might seem that this problem could be overcome by using an observation cell with a longer optical path length. It is true that this would allow a smaller difference in concentration to be used without reducing the number of fringes visible, but the superposition of the two liquids is already a delicate operation, the difference in density between the two layers being very slight, and use of a wider cell and a smaller difference in density would encourage convection currents and so make measurements unreliable. Yet the values obtained so far are sufficient in any case to give good accuracy in predictive calculations when eq 8 is used. This equation is well suited to such associated systems. The one extra experimental point necessary for the calculation may be rapidly determined using an experimental method such as the one used in this work.

Glossary

a_i	activity of component i
D_{12}	mutual diffusion coefficient, cm^2 s^{-1}
$D_i°$	diffusion coefficient at infinite dilution, cm^2 s^{-1}
h	height of the cell, cm
k	number of interference fringes between the points $h/6$ and $5h/6$
n	refractive index of the mixture
t	time, s
x_i	mole fraction of component i
β	thermodynamic factor
η	viscosity, cP
λ	wavelength of laser light, cm

Table III. Mean Deviations between Experimental and Calculated Results

Eq	CH_3OH-CCl_4 $10^5D_1°$, cm^2 s^{-1}	CH_3OH-CCl_4 E, %	C_2H_5OH-CCl_4 $10^5D_1°$, cm^2 s^{-1}	C_2H_5OH-CCl_4 E, %	n-C_3H_7OH-CCl_4 $10^5D_1°$, cm^2 s^{-1}	n-C_3H_7OH-CCl_4 E, %	n-C_4H_9OH-CCl_4 $10^5D_1°$, cm^2 s^{-1}	n-C_4H_9OH-CCl_4 E, %
8	1.9	2.2	1.60	4.3	1.0	2.6	0.7	2.4
	2.1	1.8	1.75	3.8	1.1	2.8	0.8	2.5
	2.3	2.1	1.90	3.6	1.2	3.4	0.9	3.1
3	1.9	12.3	1.60	3.2	1.0	16.4	0.7	27.1
	2.1	13.6	1.75	5.0	1.1	12.3	0.8	22.8
	2.3	14.7	1.90	9.8	1.2	8.4	0.9	18.2
5	2.1	45.0	1.75	33.0	1.1	34.9	0.8	40.7
2	2.1	45.0	1.75	33.0	1.1	35.3	0.8	40.7
6	2.1	51.2	1.75	32.1	1.1	32.8	0.8	40.2
7	2.1	50.4	1.75	32.9	1.1	30.8	0.8	34.8

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Compressibility, Second and Third Virial Coefficients, and Interaction Second Virial Coefficients of Mixtures of Propane–Helium and Propene–Helium

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Compressibility factors, the second and the third virial coefficients of mixtures, and the interaction second virial coefficients of propane + helium and propene + helium systems have been determined by the Burnett method at 393.2, 407.5, 423.0 K in the pressure range from 425 to 6870 kPa.

1. Introduction

The compressibility factor Z of real gases describes deviations from ideal gas properties. It is convenient to express the compressibility factor by the virial equation of state

$$Z = P/\zeta RT = 1 + B(T)\zeta + C(T)\zeta^2 + \ldots \tag{1}$$

where P is gas pressure, ζ is density, R is gas constant, T is absolute temperature, and $B(T)$, $C(T)$, ..., are virial coefficients. Virial coefficients have a firm basis in theory and are derived from the knowledge of the potential energy of molecular interaction by means of statistical thermodynamics of the gas phase.

In this work, the Burnett method (*1*) has been employed for the investigation of mixtures. In contrast with other *PVT* methods, that of Burnett does not require the knowledge of mass or volume.

Up to now a correlation for hydrocarbon + helium mixtures does not exist, and our knowledge about their molecular interactions is very meager (*6*).

2. Experimental Section

Purity of Substances. The purity of helium used for the experiments was 99.995 vol %. Propane and propene were stored in the commercial pressure cylinder of Fluka A.G. Chemische Fabrik. The purity of 99.9% given by the manufacturer was confirmed by the GLC method.

Description of the Method of Measurements. The scheme of the apparatus is shown in Figure 1. A more detailed description of the method and apparatus can be found elsewhere (*7–9*) along with the details of the calibration of the dead weight gauge. The temperature was measured with a Tinsley Pt thermometer (5187SA) calibrated at the National Physical Laboratory, Teddington Middlesex, England.

The experiment is based on temperature and pressure measurements in a series of isothermal gas expansions from V_{I} (volume limited by valves 1 and 4 and the membrane of the differential pressure indicator III) to the volume $V_{\mathrm{I}} + V_{\mathrm{II}}$ (volume V_{II} being included between valves 1 and 2). Each expansion follows evacuation of the gases from the volume V_{II}. The series of measured pressures P_1, P_2, ..., P_r in the isothermal experiment is called an expansion run. The following equations can be derived for the Burnett method

$$\frac{\zeta_{r-1}}{\zeta_r} = AN_r = AN_\infty \xi_r = AN_\infty \left[\frac{1 + a10^{-6}P_r}{1 + b10^{-6}P_{r-1}}\right] \tag{2}$$

$$\zeta_1 = \zeta_r AN_\infty{}^{r-1} \prod_{i=1}^{r-1} \xi_i \tag{3}$$

where AN_∞ is the apparatus constant and ξ_r is the correction for the isothermal pressure deformation of the apparatus. The constants a and b are given elsewhere (*7, 8*).

The method makes possible the preparation of mixtures by condensation of one component directly in the apparatus. A sample of propane or propene of known mass, sealed in a glass ampole, was placed in crushing chamber IV. After evacuation of the volumes $V_{\mathrm{I}} + V_{\mathrm{III}}$ (volume V_{III} is a part of a chamber limited by valve 4), valve 1 was shut and reservoir I was frozen with liquid nitrogen in a Dewar flask. Then, the ampole was crushed by means of a special valve in the heated chamber IV.

After complete condensation of the hydrocarbon, valve 4 was shut and the Burnett apparatus was heated to working temperatures between 393 and 423 K. The pressure P_{01} of propane or propene in volume V_{I} was measured after thermal equilibrium had been achieved. Then expansion reservoir I was cooled again with liquid nitrogen. In the meantime, the volume contained between valves 1 and 3 after its previous evacuation to pressures of the order of 5×10^{-4} Torr was filled with helium. The quantity of helium was roughly estimated from the valve of volume V_{II} and the pressure measured with a Bourdon-type manometer, V. Helium was then forced into reservoir I by a rapid opening of valve 1. Pressure was measured again when

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