Figure 1. Dielectric constant of 3-methoxy-cis-4-cyclohexene-1,2-dicarboxylic anhydride in benzene at 25.00° C

The observed dipole moments in benzene at 25° C are presented in Table I along with the reported dipole moments of three other cyclic anhydrides (8). The value found for maleic anhydride agrees to $0.03D$ (0.8%) with the infinite dilution extrapolation of data in benzene at 25° C (3), and is within $0.01D$ of the value found in dioxane at 35° C (8).

From a comparison of the dipole moments of citraconic and succinic anhydrides with that for maleic anhydride, it appears that the methyl group at the double bond increases μ while the loss of the unsaturation decreases it. However, if the double bond is not conjugated, as in CDA, then a methyl group (MCDA) changes μ only very slightly. On the other hand, a methoxy group (MOCDA) increases μ dramatically, since the group moment contribution for the CH_3O-group is $1.22D$ (11) and the cyclohexene configuration is nonplanar. Greater unsaturation in the six-member ring, including conjugation with the carboxyl groups, in phthalic anhydride, gives a significantly higher μ than for CDA.

Recently the dipole moments of the two isomeric Diels-Alder bicyclo-adducts of cyclopentadiene to maleic anhydride have been measured in two solvents (1). The authors report for the exo and endo forms respectively, $\mu_X = 3.91D$ and $\mu_N = 4.32D$ in carbon tetrachloride, and μ_X $4.32D$ and $\mu_N = 4.46D$ in dioxane.

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Diffusion Coefficients of Ethylene Glycol and Cyclohexanol in the Solvents Ethylene Glycol, Diethylene Glycol, and Propylene Glycol as a Function of Temperature

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The binary molecular diffusion coefficients of the solutes ethylene glycol and cyclohexanol in the solvents ethylene glycol, diethylene glycol, and propylene glycol at various temperatures ranging from 25° to 50° C were measured in this work. This investigation extends the data previously obtained in this laboratory (6) at 30° C. The importance of these diffusivities is twofold. First, they are useful as experimental data in themselves, and second, they can be

used to test theories developed for estimating binary diffusion coefficients. For this second application, these data cover a range of solvent viscosities where there is a noticeable lack of experimental data—namely, about 7 to 43 centipoises. The self-diffusion coefficient of ethylene glycol was also determined as a function of temperature.

A modified absolute rate theory equation developed earlier in this laboratory (6) is used to estimate these diffusion coefficients. Also, the ability of this equation to account adequately for the effect of temperature is examined, with activation enthalpies of diffusion being calculated.

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Binary molecular diffusivities of the solutes ethylene glycol and cyclohexanol in dilute solutions of the solvents ethylene glycol, diethylene glycol, and propylene glycol were measured at temperatures ranging from 25° to 50° C. The self-diffusivity of ethylene glycol as a function of temperature was also measured. The variation of the diffusion coefficients with temperature was compared with a modification of the absolute rate theory developed earlier.

EXPERIMENTAL

An unsteady-state porous frit technique for determining binary diffusivities at low solute concentrations was developed for use in this work. Conventional steady-state methods for determining diffusivities were not considered practical because of the very slow rates of mass transfer encountered in high viscosity solvents. In addition, commonly used unsteady-state techniques generally either require relatively high initial solute concentrations—e.g., an interferometric technique—or are restricted to specialized solutes—e.g., a radiometric method with a strong gamma source as the solute. The technique and apparatus used in this work to determine binary molecular diffusivities have been described in detail (4).

Equipment and Procedure. The primary component of the diffusion apparatus is a porous ceramic frit about $2\frac{7}{8}$ inches square by $\frac{1}{4}$ inch thick. The edges of the porous frit were sealed with an epoxy resin, so that mass transfer in only one direction need be considered.

The clean, dry porous frit was first soaked in a binary solution with a known (C^{14}-tagged) solute concentration. Following this soaking period, the porous frit was fastened inside a $6 \times 3\frac{1}{2} \times 1\frac{1}{4}$ inch solvent box. A variable speed stirring mechanism which consisted of four horizontal blades that swept up and down very close to both surfaces of the porous frit was lowered around the plate and set in motion. The proper speed of this mechanism was determined to minimize the resistance to mass transfer outside of the porous frit, in preliminary experiments. The stirring assembly was activated immediately before the solvent bath was filled with 300 cc of pure solvent.

The solute inside the porous frit was transported by molecular diffusion through the pores to the surface of the plate and then transported to the bulk of the solvent in the solvent bath by convention. To determine the diffusivity, the concentration buildup in the solvent bath was measured as a function of time, by removing 1-ml samples from the bath at various time intervals during the run. About 12 samples were removed during each run and later analyzed, using a liquid scintillation counter. The radioactive samples were all counted for the same time period (typically 5 minutes for each sample), such that the total count was always more than 1000 for the lowest activity sample. Most of the samples had total sample counts of 2000 or more. Thus, the standard deviation for the worst conditions is less than 3% of the total count; for most samples, it is less than 2% of the count. Duplicate samples were reproducible to within the above-mentioned standard deviation.

The solutes consisted of a known mixture of radioactively tagged (C^{14}) solute and nontagged solute. The initial concentration of the solute ethylene glycol in the solvents propylene glycol and diethylene glycol inside the porous frit was $4.50 \times (10)^{-2}$ mole per liter. The initial concentration of cyclohexanol in all three glycols inside the porous frit was $2.41 \times (10)^{-2}$ mole per liter. The initial concentration of C^{14}-tagged ethylene glycol in normal ethylene glycol was $3.60 \times (10)^{-5}$ mole per liter.

The temperature in the solvent baths and, consequently, the porous frits was maintained to within $\pm 0.01°$ C by almost totally immersing the solvent bath in a constant temperature oil bath. The maximum change of viscosity with changing temperature of these systems is approximately 2.5 centipoises per centigrade degree.

Certain calibration parameters for the porous frits were determined during standarization runs, using the binary system sodium chloride in water at 25° C. Harned and Owen (3) give the diffusivity for this system as $1.61 \times (10)^{-5}$ sq cm per second. The initial concentration of sodium chloride (activated in the University of Missouri at Rolla Nuclear Reactor Facility) was 1.10×10^{-3} mole per liter. The activity and hence the concentration of sodium chloride samples were determined using a standard Geiger-Muller detector and a counter.

The activity data obtained for a standardization or diffusivity measurement were corrected only by subtracting the measured background. It was not necessary to correct for counting efficiency for the samples taken for the standardization runs, because the geometry for each count was the same. Correction for self-absorption of sodium chloride was negligible because of the very dilute solutions sampled. The decay of Na^{24} is sufficiently fast (half life of 15.0 hours) that it was necessary to allow for decay time. The radioactive decay was accounted for by multiplying the measured activity less the background by

$$\exp 0.693\, t/t_{1/2}$$

where t is the time elapsed from the beginning of the run to the time the sample was counted. The half life used for the decay correction ($t_{1/2} = 15.0$ hours) was measured, since it was possible, upon irradiation of the sodium chloride sample, to obtain radioactive species other than Na^{24}.

The viscosity data for each solvent used in this work were measured using a standard Canon-Fenske capillary tube viscometer from 20° to 50° C and the procedure outlined by Crosby (1). Likewise, the density data for each of these solvents were measured using a standard pycnometer and the procedure outlined by Daniels et al. (2).

Analysis of Data. The molecular diffusion coefficients were determined from the data for the bath solute concentration vs. time. The following relations describe the solute concentration inside the porous frit as long as the solute concentration in the center of the frit—i.e., $L_{eff} \rightarrow \infty$—is approximately equal to the initial solute concentration in the plate:

$$\frac{\partial C}{\partial t} = D_{AB} \frac{\partial^2 C}{\partial x^2} \tag{1a}$$

$$C(x, 0) = C_o \tag{1b}$$

$$C(\infty, t) = C_o \tag{1c}$$

$$C(0, t) = C_f(t) \tag{1d}$$

A material balance for the solute gives the solute concentration in the solvent bath as

$$\frac{V_f dC_f}{dt} = 2D_{AB}A_T \frac{\partial C(0, t)}{\partial x} \tag{2a}$$

$$C_f(0) = C_f^o \tag{2b}$$

Solving Equations 1 and 2 simultaneously gives the following expression for the solute concentration in the solvent bath

$$\frac{C_f - C_\infty}{C_f^0 - C_0} = \exp{(K^2 t)} \cdot [1 - \mathrm{erf}\,(Kt^{-2})]$$ (3a)

where

$$K = 2A_T(D_{AB})^{1/2}/V_f$$ (3b)

The solvent bath volume, V_f, is assumed to be constant during the entire run, even though it changes slightly. The average solvent bath volume is used and is approximated by

$$V_f = 300 - n/2$$ (4)

The number of samples withdrawn is n.

As previously stated, Equation 1 and, hence, Equation 3 are valid only if the solute concentration in the center of the porous frit is approximately equal to the initial solute concentration in the porous frit. This restricts the sampling times to less than $0.30\ L_{eff}^2/D_{AB}$, where L_{eff} is the effective length of the pores. The above criterion was obtained by assuming that the time required for the concentration at L_{eff} to be reduced by 1% of its initial value was the time limit for the application of the slight penetration assumption (Equation 1c) and using a model for the diffusion process which assumed that the change in bulk composition can be ignored in Equation 1d (4). This is a conservative criterion. Typically, about 12 samples were withdrawn before this time limit. Approximate values of L_{eff} were determined in a separate investigation (7) and varied from 0.38 to 0.58 cm for one half of the frit thickness.

Before the molecular diffusion coefficients could be determined from a knowledge of the concentration of the solute in the fluid surrounding the frit, C_f vs. time, the porous plate area parameter, A_T, had to be determined using a binary system with a known diffusivity. The data were then analyzed to determine A_T or D_{AB} by a nonlinear least-square curve fit of Equation 3 to the experimental data. To consider any possible initial solute concentration, C_f^0 also had to be regarded as a curve-fitting parameter, because some of the solute is adsorbed onto the outside surfaces of the porous plate as it is transferred from the initial soaking solution to the solvent bath. The iterative, non-linear, least-squares technique is described in detail elsewhere (4).

The porous plates were calibrated at the beginning of the study and recalibrated following their use in diffusivity determinations. There were no consistent trends in the values of A_T. This indicates that foreign particles probably did not accumulate in the pores of the frits during the study. The cleaning of the porous plates is described elsewhere (4). The average absolute percent precision of the determination of A_T is about 6%.

RESULTS AND DISCUSSION

The experimentally measured diffusivities are shown in Table I and plotted as discrete points in Figures 1 and 2 as a function of temperature.

The activation enthalpy for the diffusion coefficients was determined from the absolute rate theory, by first evaluating the activation free energy from the equation

$$\Delta F_{D_{AB}} = -RT \ln \left\{ \frac{D_{AB}\xi h}{kT} \left[\frac{N}{(2)^{1/2}\bar{V}_B} \right]^{2/3} \right\}$$ (5)

The diffusion activation enthalpies were then determined as

$$\Delta H_{D_{AB}} = \partial \left(\frac{\Delta F_{D_{AB}}}{T}\right) / \partial \left(\frac{1}{T}\right)$$ (6)

Both the experimentally determined diffusivities and the activation enthalpies were then compared to those calculated from the following modified form of the absolute rate theory equation (5):

$$D_{AB} = \frac{kT}{\xi h} \left[\frac{(2)^{1/2}\bar{V}_B}{N} \right]^{2/3} \cdot \exp\left(\frac{-\Delta F_{D_{AB}}}{RT}\right)$$ (7a)

where

$$\Delta F_{D_{AB}} = f\Delta F_{D_{BB}} - (1-f) \left\{ \Delta F_{D_{BB}} \left(\frac{\bar{V}_A}{\bar{V}_B}\right) - 2\bar{V}_A \left[\left(\frac{\Delta F_{D_{AA}}}{\bar{V}_A}\right) \left(\frac{-\Delta F_{D_{BB}}}{\bar{V}_B}\right) \right]^{1/2} \right\}$$ (7b)

The diffusivities predicted by Equation 7 are shown in Table I and are plotted in Figures 1 and 2 as curves. The activation enthalpies calculated from the activation free energies in Equation 7b are also given in Table I. Activation energies calculated from Equation 5 are defined here as "experimental values," while those calculated from Equations 7a and 7b are defined as the "theoretical" activation energies.

Equation 7, which was used for the prediction of the activation free energy, was developed through the use of regular solution theory by relating the bond-breaking energy of the jump step in the diffusion mechanism to the bond-breaking energy in vaporization. The complete details of this development are given by Mitchell (4).

The values of parameters ξ and f used in these calculations were 5.6 and 0.775, respectively (4). The activation free energies for self-diffusion of the solute (A) and the solvent (B) were assumed equal to the activation free energies for viscosity of the pure components. These activation free energies for viscosity were obtained from viscosity and molar volume data and the equation

$$\Delta F_{D_{XX}} = \Delta F_{\eta_X} = RT \ln \left(\frac{\eta_X \bar{V}_X (2)^{1/2}}{hN} \right)$$ (8)

Table I. Experimental and Predicted Diffusivities and Activation Enthalpies

Solvent[a]	Solute[a]	Temp, °C	D_{AB}, 10^{-6} cm²/sec	$\hat{D}_{AB}$, 10^{-6} cm²/sec	$\Delta H_{D_{AB}}$, kcal/mole	$\Delta \hat{H}_{D_{AB}}$
EG	EG	25.0	0.961	0.872	5.07	6.72
		30.0	1.136	1.085		
		40.0	1.509	1.610		
		50.0	2.067	2.305		
DEG	EG	25.0	0.558	0.598	6.58	7.37
		30.0	0.650	0.757		
		40.0	0.996	1.164		
PG	EC	25.0	0.482	0.416	7.07	8.67
		30.0	0.532	0.568		
		40.0	0.924	0.909		
		50.0	1.259	1.369		
EG	C	26.6	0.608	0.689	7.68	7.87
		30.0	0.636	0.836		
		39.9	1.072	1.307		
DEG	C	26.6	0.460	0.403	7.84	8.51
		30.0	0.496	0.480		
		39.9	0.827	0.774		
PG	C	26.6	0.259	0.310	10.51	9.94
		30.0	0.310	0.380		
		39.9	0.572	0.663		

[a] EG ethylene glycol. DEG, diethylene glycol. PG, propylene glycol. C, cyclohexanol.
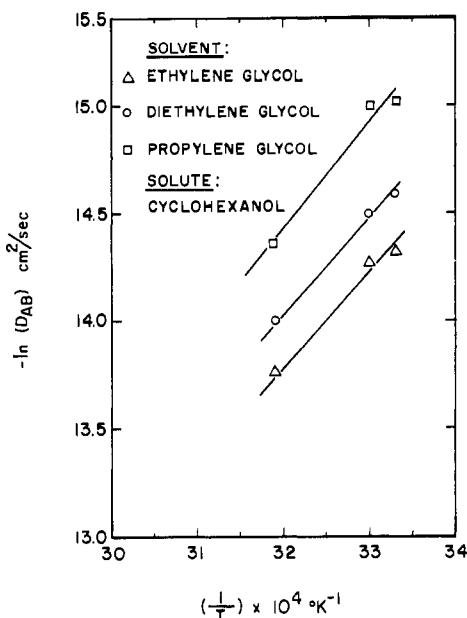
Figure 1. Diffusivity as a function of temperature
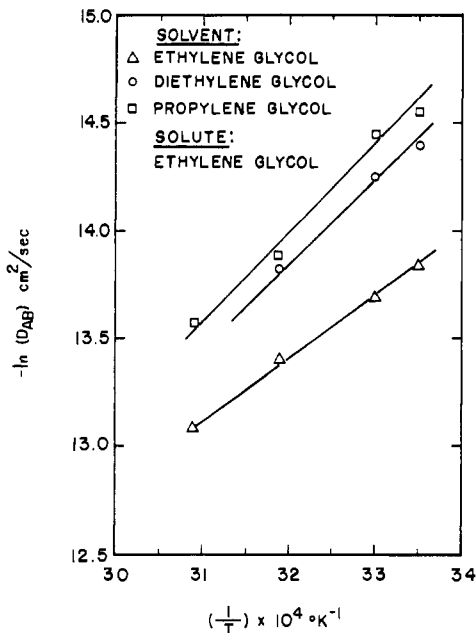Cyclohexanol as solute. Comparison between Equation 7 and data

Figure 2. Diffusivity as a function of temperature
Ethylene glycol as solute. Comparison between Equation 7 and data

The self-diffusion coefficient of ethylene glycol in pure ethylene glycol was predicted by Equation 7a, where the activation free energy for self-diffusion was substituted for that for binary diffusion. Equation 8 was used to evaluate the activation free energy for self-diffusion.

The results in Table I show that Equation 7 can be used to predict the diffusivities to within a maximum deviation of about 30%. (The average absolute deviation is 12.5%.)

In addition, the effect of temperature is accurately predicted by this modified absolute rate theory equation. This is evidenced by the fact that the calculated diffusivities

are approximately equal to the measured diffusivities at all temperatures. The activation enthalpies are less accurately predicted than the actual diffusivities, with the maximum deviation being approximately 35% and the average absolute percent deviation being 14.0%. The one case where the maximum deviation is excessively high for both the diffusivity and the activation enthalpy is for the self-diffusion coefficient of ethylene glycol in pure ethylene glycol. A constant value of ξ—viz., 5.6—obtained from self-diffusion data for other systems was used in all of the predictions.

NOMENCLATURE

A_T = effective mass transfer area on surface of porous frit, sq cm

C, C_f = solute concentration in porous frit and solvent bath, respectively, moles per liter

D_{XX} = molecular diffusion coefficient, sq cm per second

f = ratio of activation free energy due to hole formation to total activation free energy

$\Delta F_{D_{XX}}$ = activation free energy for diffusion of component X in component X, kcal per mole

$\Delta F_{\eta X}$ = activation free energy for viscous flow of component X, kcal per mole

h = Planck's constant = 6.6242 × 10^{-27} erg per second

$\Delta H_{D_{XX}}$ = enthalpy of activation for diffusion, kcal per mole

k = Boltzman constant = 1.3805 × 10^{-16} erg per °K

K = $2 A_T (D_{XX})^{1/2} / V_f$, sec$^{-1/2}$

L_{eff} = effective pore length to center of porous frit, cm

n = number of samples removed from solvent bath

N = Avogadro number = 6.023 × 10^{23} molecules per mole

R = universal gas constant = 1.987 × 10^{-3} kcal per mole °K

T = temperature, °K

t = time, seconds

V = molar volume, cm^3 per mole

x = length, cm

Greek Letters

η = viscosity, centipoises

ξ = lattice parameter in rate theory equation

Subscripts

o = initial value

A, B, X = components

Superscripts

0 = initial value

$—$ = calculated value

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