nometer reading error is about 0.1 torr. Thus, the overall uncertainty of the high-temperature vapor pressures is estimated to be 1% plus 0.1 torr.

The specificity of the analytical method obviates spuriously high low-temperature vapor pressures owing to low-boiling contaminants. This, together with the high purity of the compound, tends to keep errors from impurities to at most 1 or 2%. Errors owing to the spectrophotometric analysis are expected to be of similar magnitude. Deviations from ideal gas behavior are negligible at the low partial pressures. Errors in the nitrogen volume, as judged by fluctuations in the rotameter calibrations, might be as high as 2-4%. Thus, the uncertainty of the low-temperature vapor pressures should be well under 10%.

Results

In gas saturation measurements, one expects a decrease in apparent vapor pressure as the nitrogen flow rate is increased beyond the point where the residence time in the saturator is sufficient for vapor-liquid equilibration. But on the contrary, the apparent vapor pressure rose to a limiting value as the nitrogen flow rates, whether of the main stream or of the diluting stream, were increased (Figure 2). In spite of the many precautions taken, such as rigorous water removal, installation of the glass-wool plug, and long-term conditioning of the apparatus, this effect persisted. As shown in Figure 2, the same limiting value is obtained over a decade of residence times (or flow rates), and this was taken to be the true vapor pressure. The attainment of such a limiting value also demonstrates that saturation was complete and that entrained droplets, if any, were effectively removed by the glass-wool plug.

The low apparent vapor pressure at residence times above two seconds points to an isocyanate-consuming chemical reaction. The most obvious possibility is the reaction with water to form amine and/or urea. However, 1 mole of water reacts with at most 1 mole of diisocyanate, so that the water present (0.25 millitorr or less) can account for at most a 2.5% decrease in the vapor pressure, while a decrease of about 40% was observed for the longest residence time (Figure 2). Some other isocyanate-consuming reaction must, therefore, be involved. One might conjecture that dimerization or trimerization, both known reactions under base catalysis, might occur, possibly on the glass surface. However, the identification of this reaction is not essential for the present purpose, since its effects were circumvented by keeping the residence time short enough.

Vapor pressures obtained by both methods are given in Table I. They were fitted by regression to a single Kirchhoff equation, valid from 20° to 170°C:

$$\log_{10} p = 38.179 - 4821/T - 9.612 \log_{10} T \qquad (1)$$

where p is the vapor pressure in torr, and T the absolute temperature in kelvins. Equation 1 predicts the vapor pressures from 120° to 170° to within less than 1% of the observed values and the others to within 6% or less, as shown in the last column of Table I.

Differentiation of Equation 1 gives the enthalpy of vaporization (ΔH_v in cal/mol) for the same temperature range:

$$\Delta H_v = 22060 - 19.10\,T \qquad (2)$$

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Solubility and Diffusivity of Hexamethylene Tetramine in Ethanol

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The solubility and diffusivity of hexamethylene tetramine (HMT) in ethyl alcohol were accurately measured in the range 10-40°C. No accurate data were previously available for HMT in nonaqueous solvents.

During studies on the growth of hexamethylene tetramine [$(CH_2)_6N_4$] (HMT) crystals from solution, reliable data were required for the solubility and diffusivity of HMT in ethanol. Despite previous reports of the growth of HMT from alcoholic solution (*2*, *4*), no data were available on the diffusion of HMT in ethanol, and only one value [2.89 g/100 ml ethanol at room temperature (*6*)] could be found for its solubility. Fairly extensive data are, however, available for aqueous HMT solutions (*1*, *8*).

Experimental

Starting materials. All solutions were prepared from pharmaceutical grade HMT (subsequently doubly recrystallized from methanol) and 99.8 vol % ethanol as supplied by Fluka AG (Switzerland). Contamination of the HMT by water vapor was prevented by storage over silica

Table I. Solubility of HMT in Ethanol (Water Content, 0.04 Vol %)

Temp, °C ± 0.02	Solubility, g HMT/100 g solution
15.04	2.606 ± 0.008
20.34	2.941 ± 0.003
25.28	3.298 ± 0.008
30.25	3.696 ± 0.005
39.76	4.569 ± 0.005

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Table II. Diffusion Coefficient of HMT in Ethanol (Water Content, 0.04 Vol %)

Temp, °C ± 0.05	Diffusion coefficient measured by porous disc method			Diffusion coefficient measured by rotating disc method		
	cm²/sec·10⁵	c_P, wt %	c_B, wt %	cm²/sec·10⁵	c_S, wt %	c_B, wt %
10	0.71 ± 0.01	0	1.80			
15				0.79 ± 0.01	2.60	0
20	0.89 ± 0.05	1.80	0			
25	0.97 ± 0.02	0	1.87	0.95 ± 0.02	3.28	0
30	1.08 ± 0.05	1.87	3.68			
30.3				1.03 ± 0.02	3.70	0

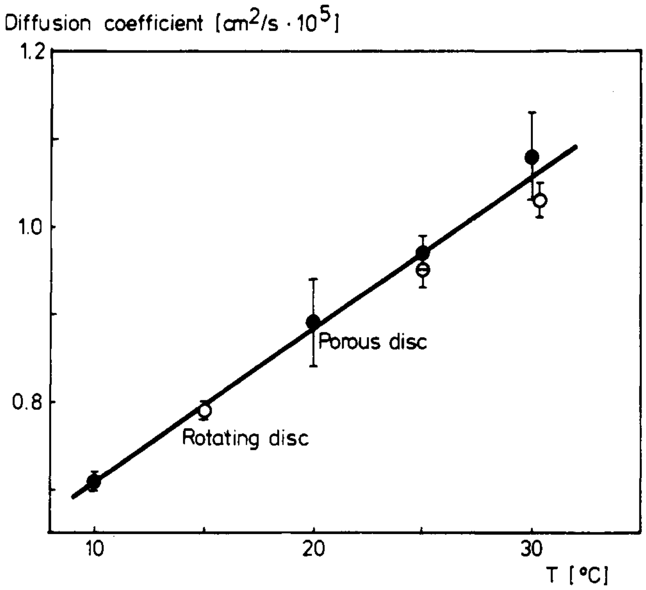

Figure 1. Diffusivity of HMT in ethanol (water content, 0.04 vol %)

gel. No special drying procedures were used to remove water from the ethanol. However, owing to the high solubility of HMT in water, it was clearly important that the water content of the ethanol should be known. Karl-Fischer titrations showed that the water content was constant at 0.04 vol %.

Measurement of solubility. Saturated solutions, prepared from ethanol and excess HMT, were sealed and stirred continuously in 500-ml flasks for approximately 14 days. A new solution was prepared for each temperature studied, and solution temperatures were measured to an accuracy of ±0.02°C.

Solution samples were drawn through a sintered glass filter (pore size 15–40 μm), and the concentration of HMT was determined by reaction with excess 0.1*N* sulfuric acid and subsequent back titration, as discussed by Walker (*6*) and Slowick and Kelly (*5*).

Measurement of diffusivity. Diffusion coefficients were measured by two methods: by following the diffusion into and out of porous clay discs with a technique described fully by both Wall et al. (*7*) and Bourne and Trivedi (*1*); and from the measured rate of dissolution of a rotating disc of compressed HMT by the method described by Gros (*3*) and Bourne and Trivedi (*1*).

The use of large solution volumes (~5 liters) insured that no significant changes in solution concentration occurred during experiments.

Results

Solubility. The measured data for the solubility of HMT in ethanol are given in Table I. The error limits quoted indicate the measured variation (over a minimum of six determinations at each temperature) encountered by two workers in this laboratory and, therefore, include the inaccuracies owing to both systematic instrument errors and random experimenter errors.

The data were correlated by a nonlinear regression and fit the equation:

$$c_S = 1.899\ (\pm 0.008) + 0.0347\ (\pm 6 \cdot 10^{-4})\ T + 0.00082\ (\pm 10^{-5})\ T^2$$

where c_S is the saturation concentration of HMT in g HMT/100 g solution, and T is the temperature in °C.

Diffusivity. Table II gives the values of the diffusion coefficient of HMT in ethanol as measured by the porous and rotating disc methods, respectively. For the porous disc the values of c_P, the concentration of solution in the disc, and c_B, the external bulk concentration, are given, and for the rotating disc the concentration c_S at the dissolving interface, being the saturation concentration, is also stated. For the rotating disc all measurements were made in pure ethanol, so that c_B is zero. No significant effect of solution concentration on the diffusion coefficient could be detected in these measurements.

Figure 1 shows the data graphically, illustrating the good agreement between values measured by the two techniques.

The activation energy for diffusion was calculated, from an Arrhenius correlation of the data, to be 3.4 ± 0.6 kcal/mol. At 25°C the Wilke-Chang prediction gave $0.81 \cdot 10^{-5}$ cm²/sec, which may compare with the measured diffusivity of $0.97 \cdot 10^{-5}$ cm²/sec.

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