These data are consistent with the measurements of Carmichael et al. (*4*) on the two isotherms where the measurements are reported at nearly the same temperature. The negative slope of the ammonia viscosity with density observed at low temperature and reported by Carmichael et al. at about 473 K was not observed in these measurements. This effect is small and very careful experiments must be done to observe it.

Glossary

a	capillary tube radius
L	length of the capillary tube
m	Hagenbach factor
n	Couette factor
p_1	pressure at inlet of the capillary tube
p_2	pressure at outlet of the capillary tube
Δp	$p_1 - p_2$, pressure drop across the capillary tube
Q_e	volumetric flow rate at the inlet of the capillary tube
T	temperature
ΔT	temperature at experimental conditions minus T = 298.15 K
X	term defined by eq 4

Greek Symbols

α	linear thermal expansion coefficient for the capillary tube material
η_0	viscosity at low density
η_p	Poiseuille's law viscosity defined by eq 3
ξ	viscous slip coefficient
ρ	gas density

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Vapor Pressure of 3,4-Diethyl-3,4-hexanediol

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The vapor pressure of 3,4-diethyl-3,4-hexanediol was determined for a wide range of temperatures. The temperature dependence of the vapor pressure was expressed by an Antoine equation of the form ln P/torr = −4215.352/(189.301 + t/°C) + 16.5993.

The literature dealing with the vapor pressures of organic compounds is extensive (*1–6*). However, for the larger diols, there is very little information available. The only literature source (*7*) for the 3,4-diethyl-3,4-hexanediol provides insufficient, unreliable information. To deal with some hydrogen bonding problems, we needed accurate vapor pressure data for the 3,4-diethyl-3,4-hexanediol in a wider temperature range than was available and so we determined it experimentally.

Experimental Section

The 3,4-diethyl-3,4-hexanediol was synthesized in our laboratory by a pinacol reaction of 3-pentanone with magnesium in a solvent. The product was purified repeatedly by vacuum distillation and crystallization until gas chromatographic analysis failed to show any significant impurities. The small difference between the boiling point and condensation temperatures, 0.003 °C, measured in a differential ebulliometer (*8*, *9*) at a pressure of 10 torr, indicated that the sample did not contain sufficient impurities of different volatility to have any significant effect on the vapor pressure measurement. The physical constants of the pure substances were found to be the following: d_4^{25} = 0.94350 g cm^{-3}, normal boiling point 233.7 °C, and freezing point 25–26 °C.

The vapor pressures were measured by a dynamic method using two ebulliometers connected in parallel to a pressure controlling system (*4*). One of the ebulliometers contained deionized, twice distilled water and the other was filled with the organic substance. From the boiling point of water, the corresponding pressure in the system was determined with an accuracy of better than 0.1 torr. The boiling points of water and the organic substance, respectively, were measured simultaneously with two 25-Ω platinum resistance thermometers in a Mueller bridge circuit (Leeds and Northrup) with an accuracy of better than 0.01 °C for water but only ±0.03 °C for the diol. The temperature of the water remained constant during the measurement while the temperature of the diol (a very viscous liquid) fluctuated within ±0.03 °C under the same conditions. Since the resistance thermometers were fully immersed in both liquids, it is our opinion that the fluctuation was caused by small temperature differences in the boiling diol due to its poor heat conductance. Both thermometers had been recently calibrated by the National Bureau of Standards.

Results and Discussion

The experimental data listed in Table I were fitted by the least-squares method to an Antoine equation of the form

$$\ln P/\text{torr} = -\frac{4215.352}{189.301 + t/{}^\circ\text{C}} + 16.5993$$

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Table I. Vapor Pressure of 3,4-Diethyl-3,4-hexanediol as a Function of Temperature

T/K	P/torr	T/K	P/torr
405.29	32.6	457.42	203.3
410.98	41.0	460.68	224.3
414.61	47.0	464.91	253.9
418.52	54.9	465.95	261.7
423.30	65.5	469.71	291.4
431.00	86.4	476.37	350.8
434.07	95.6	479.39	380.7
437.37	107.3	482.19	410.5
441.20	121.9	488.21	480.2
445.82	141.7	493.08	543.8
448.89	156.4	501.96	676.8
451.36	169.0	504.08	712.1
453.61	181.1	507.09	764.8
455.42	191.6		

This equation reproduced the experimental data within the limits of experimental error. Because of the fluctuation in the boiling point of the diol, the standard deviation and the maximum percent deviation, ±0.4 torr and 0.35%, respectively, were larger than is usual for accurate vapor pressure measurements.

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Effect of D_2O on the Lower Critical Solution Temperature of Triethylamine in Water

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Data are presented showing the effect of D_2O on the lower critical solution temperature (LCST) of triethylamine (TEA) in water. The lower value of the LCST in the system D_2O/TEA is explained in terms of entropy effects arising from the greater strength of the deuterated bond.

The effect of replacing H_2O by D_2O on the lower critical solution temperature of triethylamine–water mixtures has been examined. The ten solutions studied all had a mole fraction amine of 0.0805 but varied in D_2O composition $[n_{D_2O}/(n_{D_2O} + n_{H_2O})]$ from 0 to 100%.

Materials were purified as in ref 3; D_2O (99.9%) was obtained from Mallinckrodt and used directly. The experimental apparatus consisted of a well-insulated 3-L beaker filled with water, whose temperature could be changed slowly (0.02 °C min^{-1}) by either heating or cooling. The solution under study was contained in a 100-mL flask suspended in the beaker. Both the bath water and the solution were vigorously stirred magnetically.

The phase change was detected by shining a laser beam (1 mW, He–Ne) through the solution. The critical point was taken as the point of maximum opalescence, i.e., when the emergent beam could no longer be detected visually on a sheet of filter paper. The relative temperature of the phase change was read from a Beckmann thermometer immersed in the bath water. For all solutions, the critical point was approached from both above and below and it was found that the difference in these readings, once good equilibrium between the bath water and the solution had been attained, in no case exceeded 0.032 °C.

The data are presented in Table I and are shown graphically in Figure 1. The temperature at which opalescence was observed for the 0.0805 TEA/H_2O solution, a composition very close to the critical composition, is in excellent agreement with the measurement of Hales et al.[3] but different from early results of Timmermans and Poppe.[6]

Table I. Critical Solution Temperatures for TEA (0.0805) in H_2O/D_2O Mixtures

$n_{D_2O}/(n_{H_2O} + n_{D_2O})$	temp, °C	$n_{D_2O}/(n_{H_2O} + n_{D_2O})$	temp, °C
0	18.35	55.25	16.33
3.350	18.24	63.75	16.00
13.12	17.89	69.95	15.77
31.49	17.21	83.39	15.24
45.96	16.65	99.80	14.55

It is interesting to speculate why D_2O should have such a pronounced effect on the LCST. One plausible explanation follows from Rice's[5] thermodynamic discussion of the LCST. For a lower critical solution temperature, ΔS_a (here $\Delta S_a = \bar{S}_a'' - \bar{S}_a'$, where $\bar{S}_a''$ is the partial molal entropy of component a in one of the phases and $\bar{S}_a'$ is the partial molal entropy of a in the other phase; ΔS_a can be viewed as the entropy of transfer for a between the two phases), or the entropy of dilution across the coexistence curve, must be zero at the critical point but negative just above it. This indicates that there is an attraction between molecules of the two components, in this case through a protiated or deuterated bond between water and the amine nitrogen. It is known that deuterated methanol, for example, forms a stronger bond with water than protiated methanol,[2] and it is probably true here that the deuterated bond between water and TEA is somewhat stronger than the protiated bond. The entropy of dilution, ΔS_a, should therefore be more negative for D_2O/TEA, and the critical temperature should be correspondingly lower.

In addition, it seems likely that water structural effects may also come into play here. This possibility is suggested by Jeffrey's[4] crystallographic observations that amines form a class

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