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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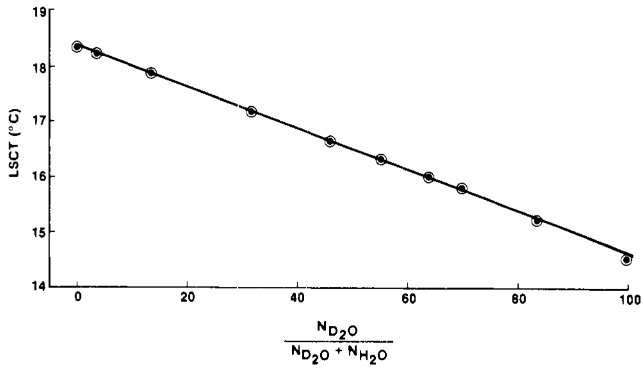

Figure 1. LCST as a function of D_2O composition.

of hydrate compounds in which the amine is surrounded by a hydrogen bonded water cage. Analogous transient structures might be expected to exist in solution as well. If this view of the solution is adopted, then it can be argued that there is a "structural" contribution to ΔS_a which is negative and which results from the greater ordering imposed upon water molecules when they are "diluted" by TEA and become incorporated into these cagelike frameworks. Because of the greater strength of the D-O-D bond as compared with H-O-H (see ref 1 for a discussion of this subject), the entropy of dilution would be more negative in the D_2O/TEA system, for this reason alone. Again, this would lead to the expectation of a lower LCST for D_2O/TEA.

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Heat Capacity and Enthalpy of the Ternary System Ferrous Sulfate Heptahydrate, Sulfuric Acid, and Water

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Heat capacity and enthalpy for the ternary system of ferrous sulfate heptahydrate, sulfuric acid, and water have been reported for the temperature range 0-60 °C. The temperature dependence of the heat capacities of the ternary mixtures of different compositions and the integral heats of solution of the heptahydrate in mixtures of sulfuric acid and water were determined calorimetrically. Heat capacity constants *a* and *b* and enthalpy at 0 °C for 18 different compositions (up to a maximum of 25% sulfuric acid) of the ternary mixture have been presented. Other terms involved in the enthalpy equation for the purpose have been derived from literature. The temperature-dependent enthalpy equations can now be set and enthalpy-concentration plots made with varying enthalpy and heptahydrate concentration against fixed concentrations of sulfuric acid.

Introduction

It is very useful to have the enthalpy-concentration diagrams for binary or ternary systems in view of their relevance to the phenomena of refrigeration, crystallization, evaporation, etc. Of particular importance is the ternary system of ferrous sulfate heptahydrate, sulfuric acid, and water since the knowledge of enthalpies here is relevant to the recovery of waste pickle liquor. The present paper reports the enthalpy for the ternary system for which calorimetric experiments have been carried out with 18 different mixtures. The various mixtures studied have a maximum sulfuric acid content of 25%, as above this the solubility of the heptahydrate becomes very low at the experimental temperatures. The experimental work carried out here can be divided into two sections, viz., (i) determination of temperature dependence of heat capacities of the ternary mixtures of various compositions and (ii) determination of the integral heats of solution of the heptahydrate in mixtures of sulfuric acid and water such that the values for required compositions are obtained. Experiments have been carried out for the temperature range of 10-60 °C. The previous heat capacity data for the ternary mixture reported by Agde and Holtmann (*1*) were considered inadequate as these were mean heat capacities in the temperature range 25-45 °C.

Enthalpy Calculations

All enthalpy calculations were based upon the assumption of zero enthalpy for liquid water, liquid sulfuric acid, and crystalline anhydrous ferrous sulfate at 0 °C. This reference state is the same as that used in the steam tables (*2*) and in the enthalpy-concentration diagram for sulfuric acid-water (*3*). The effect of pressure on the enthalpies of solid and liquid phases was neglected.

Heat capacity of a solution may be defined as

$$C_p = a + bt = (\partial H_t/\partial t)_p \qquad (1)$$

so that

$$H_t = (H_0)_{sol} + at + (b/2)t^2 \qquad (2)$$

In order to determine H_t, $(H_0)_{sol}$ is to be determined which can be done by knowing H at a particular temperature (say, H_{25}), a, and b; H_{25} on the other hand can be calculated from the relation as derived below.

One gram of the ternary solution at 25 °C can be obtained by addition of m_1 grams of the heptahydrate and m_2 grams of sulfuric acid to $(1 - m_1 - m_2)$ grams of liquid water at that temperature. Considering the heat changes involved in the process, the enthalpy per gram of the solution at 25 °C, i.e., H_{25}, would be given by the expression

$$H_{25} = m_1(C_p)_7(25 - 0) + m_1(H_0)_7 + m_2(C_p)_A(25 - 0) + m_2(H_0)_A + (1 - m_1 - m_2)(C_p)_w(25 - 0) + (1 - m_1 - m_2)(H_0)_w + m_1(\Delta H_s)_7 + m_2(\Delta H_s)_A \qquad (3)$$

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