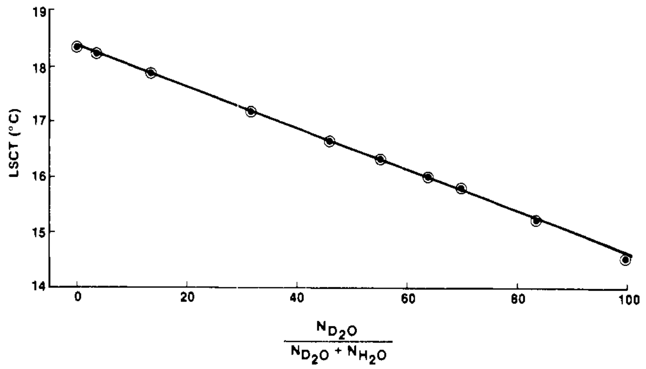

Figure 1. LCST as a function of D_2O composition.

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

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

In order to determine H_t, $(H_0)_{\text{sol}}$ 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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Table I. Heat Capacity Constants, Integral Heats of Solution at 25 °C, and Enthalpies at 0 and 25 °C for Ternary Mixtures of Various Compositions

	system[a]		constants in the eq $C_p = a + bt$; C_p, cal/(g °C)		ΔH_s/g at 25 °C, cal/g	$(H_0)_{sol}$/g at 0 °C, cal/g	H_{25}/g at 25 °C, cal/g
no.	$FeSO_4 \cdot 7H_2O$, %	H_2SO_4, %	a	$10^4 b$			
1	5	5	0.898	8.0	+16.79	−11.71	+10.98
2	10	5	0.884	6.0	+16.50	−13.42	+7.76
3	15	5	0.870	4.0	+13.35	−17.78	+4.08
4	20	5	0.854	3.0	+15.40	−20.31	+1.13
5	25	5	0.834	1.0	+16.10	−22.83	−1.95
6	5	10	0.890	6.0	+13.40	−21.63	+1.05
7	10	10	0.878	5.0	+17.10	−23.98	−1.88
8	15	10	0.866	2.0	+19.13	−26.97	−4.70
9	20	10	0.845	0.0	+20.30	−28.64	−7.51
10	5	15	0.857	3.0	+19.30	−29.50	−7.99
11	10	15	0.852	2.0	+17.05	−32.46	−11.10
12	15	15	0.835	0.0	+17.73	−34.95	−14.08
13	20	15	0.808	0.0	+18.30	−37.24	−17.04
14	5	20	0.830	0.0	+19.37	−37.47	−16.72
15	10	20	0.818	0.0	+20.70	−39.54	−19.09
16	15	20	0.806	−1.5	+21.32	−41.53	−21.43
17	5	25	0.795	−1.5	+21.34	−43.55	−23.72
18	10	25	0.778	−3.0	+21.53	−45.57	−26.21

[a] In water.

From definition $(H_0)_A$ and $(H_0)_w$ are taken as zero. The literature data are available for $(C_p)_7$ (*4*), $(H_0)_7$ (*5*), $(C_p)_A$ (*6*, *7*), and $(C_p)_w$ (*8*). $(\Delta H_s)_7$ was experimentally determined. $(\Delta H_s)_A$ was determined from the graphical plots for the same (*3*) and the standard integral heat of solution at 25 °C reported in literature (*9*).

In order to determine a and b (in the heat capacity equation) one has to know the temperature dependence of the heat capacities of the different mixtures. For this, ternary mixtures of different compositions were prepared and their heat capacities at different temperatures (viz. 10, 20, 30, 40, 50, and 60 °C) were determined calorimetrically. In selecting the experimental temperature care was taken regarding the mutual solubility (*10*) of the ternary system so that some of the mixtures, where the mutual amounts of the heptahydrate and sulfuric acid were higher, were studied starting from a higher temperature. The heat capacities were calculated from the relation

$$(TC + ms)\Delta t = i^2RT/J \qquad (4)$$

When m and s were values for water, one could readily obtain the TC. Two independent heat capacity experiments were carried out for each composition of the ternary mixture over the same temperature range. For the two sets, heat capacities were determined at almost the same temperatures. The data for each composition, with a pair of points near a single temperature, were plotted graphically and the intercept and slope, a and b, were actually read out from the plots as they appear in Figure 1. The extent of scatter of the points was small and the standard deviation for a plot of any composition never exceeded 0.6%. It is apparent that the plots are linear within our experimental range of temperatures. Table I gives the values of a and b.

The integral heats of solution of the heptahydrate in mixtures of sulfuric acid and water were determined by adding known portions of the solid heptahydrate to a fixed composition of the mixture of water and sulfuric acid taken in the calorimeter. Time–temperature readings were taken with each addition and additions were made in such a fashion that the desired composition was reached after the final portion of the heptahydrate had been added. The total amount of heptahydrate to be added during each run was usually divided into three nearly equal portions. Integral heat of solution per gram of the heptahydrate was determined along with the percentage of heptahydrate in solution for each portion added. From a graphical plot of ΔH_s/g against percentage of heptahydrate, the value of ΔH_s/g for the required percentage could readily be obtained. ΔH_s on the other hand, could be calculated from the relation

$$\Delta H_s = ms(\Delta t) + (TC)\Delta t - m_7 s_7 (t_r - t_m) \qquad (5)$$

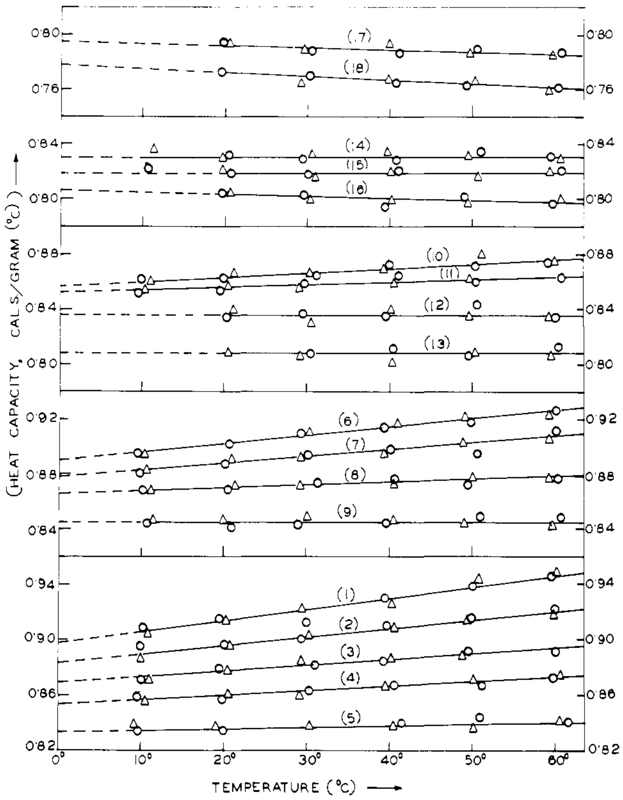

Figure 1. Heat capacity variation with temperature for the ternary system of ferrous sulfate heptahydrate, sulfuric acid, and water: O and Δ denote the points corresponding to two independent experiments. Bold lines indicate the experimental parts and broken lines indicate the extrapolated parts. Curve numbers indicate the systems as numbered in Table I.

Enthalpy–Concentration Plots

A knowledge of H_{25} (eq 3) and a and b (eq 2) enables one to know $(H_0)_{sol}$ and to set the temperature-dependent enthalpy equation for any particular composition. Table I gives the values for $(H_0)_{sol}$, a, and b. Enthalpy–concentration diagrams may be drawn by plotting enthalpies against percentage of heptahydrate, keeping the concentration of sulfuric acid fixed. The zero heptahydrate concentration then corresponds to the binary system of sulfuric acid and water and if the enthalpies are plotted on the basis of the values derived from the enthalpy–concentration diagram for the system of sulfuric acid and water as reported by Hougen and Watson (*3*), they fit the curves with unimpaired continuity.

Experimental Section

In order to measure the heat capacities of the ternary solution, a calorimeter similar to that described by Kobe and Anderson (*11*), Kobe and Sheehy (*12*), and Kobe and Couch (*5*) was constructed. The calorimetric vessel was a glass Dewar properly insulated and placed within an outer container. Through the lid of the Dewar passed the two heaters, stirrer, and a thermometer graduated upto 0.1°. The Dewar and its lid were covered by an outer insulating lid fixed with the outer container. This entire arrangement was suspended in a water thermostat, the temperature of which could be maintained within 0.02 °C. The stirrer was driven by a constant speed motor. The calorimeter heating elements were of manganin wire, suitably encapsulated in order to protect them from direct contact with the solution. A constant background temperature was maintained by the outer thermostatic bath.

The power supply to the heating elements was made from two 6-V storage batteries and the current through the heating wires was measured by a LN K2 potentiometer–galvanometer arrangement. The length of the heating period was noted by a stop clock readable up to 0.05 s. The calorimeter temperature was measured by means of a thermometer graduated at 0.1 °C intervals. Distilled water was used as the calorimeter fluid in determining the thermal capacity of the calorimeter and all the heat capacity determinations were carried out at 10–60 °C, in intervals of 10 °C. A determination consisted of making time–temperature readings before and after a heating period during which a known amount of fluid was heated through a temperature rise of about 3–5 °C. Sufficient time was allowed to obtain the steady baseline before and after the passage of current, and the temperature change was determined by a graphical plot with necessary heat loss corrections.

For the experiments on determination of the integral heats of solution a slight modification was made in the aforesaid calorimeter. A funnel-shaped inlet device made of glass was introduced through the lid of the Dewar, its long stem dipping into the liquid within the Dewar and the funnel remaining outside raised above the lid. Through this funnel, samples of solid heptahydrate, obtained as fine crystals of small mesh size, were added to the liquid at fixed intervals of time. All other arrangements remained the same as above.

The ferrous sulfate heptahydrate used was of BDH-analyzed certified quality. Sulfuric acid used was of CP grade and was purified in the manner proposed by Randall and Taylor (*13*). Strengths of the sulfuric acid solutions were determined by acidimetric titrations with standard alkali solution. In order to avoid oxidation of the solutions, boiled distilled water, through which nitrogen was bubbled during cooling and storage, was used. All containers for solutions were flushed with nitrogen and the solutions kept in a nitrogen atmosphere. A fresh solution was prepared immediately before each calorimetric determination.

Considering the various measurable quantities and the experimental setup in our calorimetric experiments on heat capacity and integral heat of solution, we estimate our experimental inaccuracy to be less than 1%. It is not, however, convenient to estimate the inaccuracy of the integral heat of solution and enthalpy, particularly the latter data, given in Table I, as they have been computed by taking help of literature values for certain terms most of whose uncertainties are not well defined.

Results and Discussion

From the plots of the heat capacities of the ternary mixtures with respect to temperature (Figure 1), certain regularities are observed. With low concentration of both sulfuric acid and the heptahydrate, there is a tendency for the heat capacities to rise very slowly with temperature. For a particular concentration of the acid, the heat capacities at a particular temperature decrease with increasing heptahydrate concentration and this is expected if one is considering the relative decrease in water (with higher specific heat) and increase in heptahydrate (with lower specific heat). At higher concentrations of the solutes, the heat capacity curves have a general tendency to fall very slowly with rise in temperature and at intermediate concentrations the curves are almost parallel to the temperature axis. It is to be pointed out that mean specific heats in the temperature range 25–45 °C calculated from our data agree well with the mean specific heats for the ternary mixtures determined by Agde and Holtmann (*1*). The change in integral heats of solution with change in composition is somewhat less marked and at several points no definite trend is observable which may be due to the complex nature of the ternary system.

The enthalpy data given in Table I have a general trend and the values decrease with increasing sulfuric acid concentration. With a fixed sulfuric acid concentration, there is a regular approach toward more negative values with increased heptahydrate concentration. Zero heptahydrate concentration points (leading to the binary system of sulfuric acid–water) obtained from Hougen and Watson (*3*) maintain the smooth nature of the curves unimpaired.

Acknowledgment

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Glossary

a, b	empirical constants in the heat capacity equation
C_p	heat capacity at constant pressure, cal/(g °C)
$(C_p)_A$	mean heat capacity for sulfuric acid between 0 and 25 °C, cal/(g °C)
$(C_p)_w$	mean heat capacity for liquid water between 0 and 25 °C, cal/(g °C)
$(C_p)_7$	mean heat capacity for solid heptahydrate between 0 and 25 °C, cal/(g °C)
H_t	enthalpy of a solution at t °C, cal/g
$(H_0)_A$	enthalpy at 0 °C of liquid sulfuric acid, cal/g
$(H_0)_7$	enthalpy at 0 °C of the solid heptahydrate, cal/g
i	current passed through the heater, A
J	Joule's constant, J/cal
m	mass of the ternary mixture, g
$m_1(\Delta H_s)_7$	integral heat of solution of m_1 grams of heptahydrate in a solution of m_2 grams of sulfuric acid and $(1 - m_1 - m_2)$ grams of water, cal
$m_2(\Delta H_s)_A$	integral heat of solution of m_2 grams of sulfuric acid in $(1 - m_1 - m_2)$ grams of water, cal
m_7	mass of the heptahydrate added, g
R	resistance of the heating element, Ω
s	heat capacity of the ternary mixture, cal/(g °C)
s_7	heat capacity of the heptahydrate at the mean temperature of experiment, cal/(g °C)
t	temperature, °C
t_m	mean temperature of the contents of the calorimeter during each experimental run, °C
t_r	room temperature at the time of experiment, °C
TC	thermal capacity of the calorimeter, cal/°C

Δt change in temperature of the mixture, °C
T time through which the current is passed, s

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Three-Phase Solid–Liquid–Vapor Equilibria of the Systems Ethylene–Cyclohexane, Ethylene–*trans*-Decalin, Ethylene–Benzene, and Ethylene–2-Methylnaphthalene

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Pressure, temperature, liquid-phase molar volumes, and liquid-phase compositions are presented along the solid–liquid–vapor loci for four ringed hydrocarbon solutes with ethylene as a common solvent. The data were taken employing cryoscopic techniques over a liquid compositional range from solute-rich solutions to very dilute solute solutions. The data are pictorialized as the logarithm of composition vs. T_T/T to elucidate the nonideality of the liquid phase. The standard deviations of the liquid compositional data are 0.93% for cyclohexane, 1.08% for *trans*-decalin, 1.34% for benzene, and 2.10% for 2-methylnaphthalene.

Introduction

Three-phase, solid–liquid–vapor, solubility data of hydrocarbon components in low molecular weight solvents are important for use in the design of liquefaction, vaporization, and transport systems for liquefied ethylene as well as liquefied natural gas (LNG) and liquefied petroleum gas (LPG). The authors are engaged in an extended program of obtaining such data and recently reported solid–liquid–vapor data for three ethylene–*n*-alkane binary systems (*5*). In an earlier paper, Liu et al. (*4*) studied the solubility of three of these same solutes studied here with ethane as a common solvent by cryoscopic means. The ethane–2-methylnaphthalene system has been investigated and the data are reported in ref 6. In the same spirit as ref 4, we have undertaken the present study to add to existing knowledge of the solubility behavior of aromatic and naphthenic hydrocarbon species in light liquid hydrocarbon solvents. These data will serve as an interesting basis for comparison of ethylene to other solvents, especially ethane, over a wide range of temperatures and solute compositions.

As the U.S. production of ethylene is fifth of all chemicals and first of all petrochemicals, this paper provides useful design data. These binary data not only are readily applicable but also form a basis from which the solubility of hydrocarbons in multicomponent systems with ethylene can be predicted.

Experimental Section

The ethylene used in this study was Matheson CP grade with a minimum purity of 99% and was identical with that used in the previous study (*5*). The cyclohexane used was an Eastman Reagent "ACS" Grade chemical. The benzene was a Mallinckrodt "Spectrar" spectrophotometric grade chemical. The 2-methylnaphthalene was supplied by Aldrich Chemical Co., Inc., with a stated purity of 99+%. The *trans*-decalin was supplied by Columbia Organic Chemicals Co., Inc., and is at least 99% pure. The purity of these hydrocarbons was further checked by a Bausch and Lomb ABBE-3L refractometer and by measuring the freezing point of each of the four compounds. The refractive indices of the hydrocarbons agreed with literature values within the accuracy of the instrument (±0.0001) at 20 °C (at 40 °C for 2-methylnaphthalene). The freezing points measured agreed well with literature values. All four hydrocarbon solutes were used without further purification. The apparatus and procedures used in this study were identical with that reported by Lee and Kohn (*3*) which was used in other cryoscopic studies (*1*, *2*, *4*).

Table I. Solid-Liquid-Vapor Three-Phase Smoothed Data: Ethylene-Cyclohexane Binary System

temp, K	pressure, atm	liquid-phase compn (mole fraction cyclohexane)	liquid-phase molar volume, mL/g-mol
270	1.68	0.9706	104.6
260	3.09	0.9347	101.5
250	3.83	0.8941	98.4
240	4.09	0.8508	95.3
230	4.00	0.8068	92.1
220	3.66	0.7602	89.0
210	3.10	0.7127	85.8
200	2.38	0.6629	82.5
190	1.80	0.6103	79.2
180	1.33	0.4063	69.0
170	0.90	0.1761	58.0
160	0.56	0.07955	52.7
150	0.35	0.03963	50.0
140	0.30	0.02170	48.4

Results

Tables I and II present the smoothed experimental data for the two naphthenic solute systems studied and Tables III and IV present the smoothed experimental data for the two aromatic solute systems studied. The pressures are precise to ±0.1 atm, the temperatures to ±0.2 °C, and the liquid molar volume to

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