

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231539509>

Enthalpy composition diagram and other data for the hexamine–water system

ARTICLE *in* JOURNAL OF CHEMICAL & ENGINEERING DATA · JULY 1967

Impact Factor: 2.04 · DOI: 10.1021/je60034a001

CITATIONS

15

READS

26

1 AUTHOR:



Edward Thomas White

University of Queensland

108 PUBLICATIONS 1,110 CITATIONS

SEE PROFILE

Enthalpy Composition Diagram and Other Data for the Hexamine-Water System

E. T. WHITE¹

Chemical Engineering Department, Imperial College, London, S.W.7, England

Values of the solubilities, boiling points, freezing points, heat capacities, densities, refractive indices, heats of solution, viscosities, and surface tensions of aqueous hexamine solutions were measured. By using certain of these data, an enthalpy-composition chart for the hexamine-water system was constructed. The effect of methanol, ethanol, and ammonia on the solubility of hexamine in aqueous solution was also investigated.

ALTHOUGH hexamine (hexamethylenetetramine, $C_6H_{12}N_4$), an organic chemical used extensively in the explosives and plastics industries (8), is prepared in, and recovered from, aqueous solution, the amount of physical data available on the hexamine-water system is small. The available data have been reviewed by Beilstein (2) and Walker (24). Additional data determined by the author in the course of studies on the crystallization of hexamine (27) are presented below.

EXPERIMENTAL

The experimental methods used were, for the most part, based on those described by Weissberger (26). Solutions were prepared from doubly recrystallized hexamine and deaerated distilled solvents. The composition of the prepared solutions were checked by the usual analytical technique employing excess sulfuric acid, and back-titration with sodium hydroxide after 7 hours of boiling.

Measurements were made in a constant temperature water bath maintained at $25.00^\circ \pm 0.02^\circ C$, or $\pm 0.05^\circ C$ of any other temperature quoted. N.P.L. certified thermometers were used for all temperature measurements.

Density. Densities were measured using 25-ml. density bottles calibrated with distilled water. The density of hexamine crystals was measured by immersion in a petroleum solvent saturated with hexamine.

Refractive Index. A precision Abbé refractometer, periodically calibrated with deaerated distilled water and benzene, was used.

Viscosity. Viscosities were measured using a standard U-tube viscometer in accordance with British Standard B.S. 188:1929. The viscometer was calibrated using deaerated distilled water.

Surface Tension. A capillary tube tensiometer was constructed from a carefully selected piece of capillary tubing, and calibrated with distilled water. It was cleaned with hot chromic acid. Liquid heights were measured with a traveling microscope.

Solubility. Solubilities were measured directly by the analysis of solutions stored over excess crystal for prolonged periods of time. For aqueous solutions, a second method was used giving results in excellent agreement with the first. In this method the temperature at which a prepared solution became saturated was determined by observing

the Schlieren patterns about a single crystal placed in the solution. With hexamine in aqueous ammonia solutions the usual analytical method gave the combined hexamine plus ammonia content. The ammonia content could be estimated separately by the Nessler method.

Boiling Point Elevation. Two standard ebulliometers were used: one containing the prepared solution, the other distilled water. Both were interconnected and connected to the same vacuum system. The difference in temperature between the two gave the boiling point elevation.

Freezing Point. Prepared solutions were placed in thin sample tubes attached to a thermometer bulb and placed in a freezing bath in which the temperature slowly rose. Temperatures were measured at the initial and final stages of the phase change.

Analysis of Hydrate. Crystals of the hydrate were prepared by freezing saturated aqueous solutions, filtering off the crystals, and drying them over silica gel at temperatures below $13^\circ C$. for several weeks. The composition of the hydrate was determined by analysis and its decomposition temperature by the method used for freezing points.

Thermodynamic Properties. All measurements were made using a water-jacketed copper calorimeter with manual agitation.

The temperature rise on solution was determined by adding a known mass of crystal to known quantities of water both initially at $25.00^\circ C$. and measuring the temperature rise. Corrections were applied for the water equivalent of the calorimeter and stirrer (obtained by previous calibrations with water) and for heat losses (by extrapolation to zero time).

Heat capacities of solutions were measured by electrically heating the solutions and measuring the temperature rise. The quantity of energy added was measured by a calibrated wattmeter and a stopwatch. Measurements with water gave excellent agreement with published values. The heat of decomposition of the hydrate was measured in a similar manner.

RESULTS

The properties measured are indicated in Table I. Their significance in relation to the construction of an enthalpy composition diagram will be discussed initially.

ENTHALPY COMPOSITION DIAGRAM

For the construction of the enthalpy composition diagram a knowledge of the properties of the pure components is

¹ Present address: Department of Chemical Engineering, University of Queensland, Brisbane, Australia

Table I. Properties Measured for Hexamine-Water System

System	Property	Value
Hexamine (cryst.)	Density at 25.0° C.	1.335 g./ml.
Hexamine + water	Density	Equation 3 (± 0.00015 gram/ml.)
	Depression of freezing point	Figure 3
	Enthalpy	Figures 5 and 6
	Elevation of boiling point	Equation 1 ($\pm 0.2^\circ$ C.)
	Eutectic composition and temperature	0.292 ± 0.004 ; $-10.2 \pm 0.5^\circ$ C.
	Heat capacity	Equation 2 (± 0.015 cal./gram $^\circ$ C.)
	Heat of solution	Figure 4
	Hydrate composition	$C_6H_{12}N_4 \cdot 6H_2O$
	Hydrate decomposition temperature	$13.5 \pm 0.5^\circ$ C.
	Hydrate heat of decomposition at 13.5° C.	$\Delta H = 5.0 \pm 0.5$ kcal./g.-mole
	Refractive index	Equation 4 (± 0.0002 unit)
	Solubility	Figure 2
	Surface tension	See text
	Viscosity	Figure 7 ($\pm 2\%$)
Hx + H ₂ O + ammonia	Solubility	Figure 8
Hx + H ₂ O + ethanol	Solubility	Figure 8
Hx + H ₂ O + methanol	Solubility	Figure 8

quired, together with the phase equilibria data for the system and thermal data for the mixtures (6).

Pure Components. Hexamine belongs to the cubic system and crystallizes as colorless, rhombic dodecahedral crystals [density at 25° C., 1.335 grams per ml., refractive index at 23.7° C., $n_D = 1.5892$ (12)]. The molecular structure of this material has been studied extensively (1, 25), and accurate measurements of the thermodynamic properties are available (4). At ordinary pressures, solid hexamine sublimes; vapor pressure data for the solid are available (22). The corresponding enthalpy change on sublimation is 18.0 kcal. per gram mole.

Properties for pure water were taken from the steam tables (17).

Phase Equilibria Data. The phase diagram for the hexamine-water system is shown in Figure 1. Hexamine

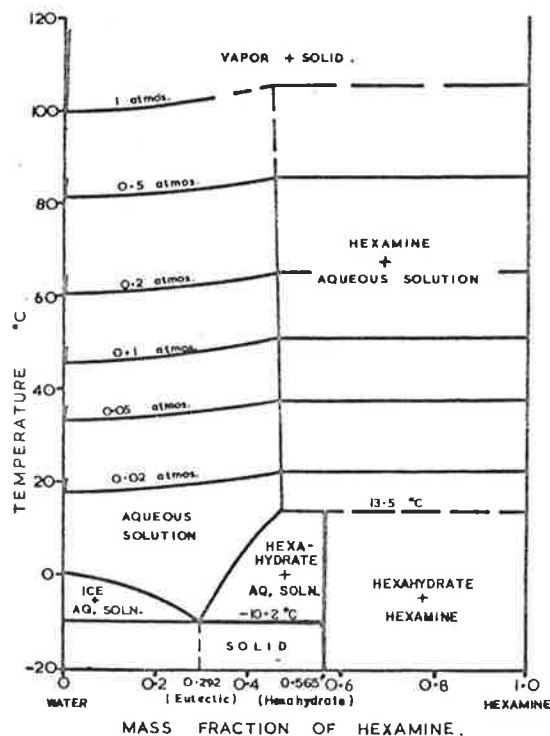


Figure 1. Phase diagram for hexamine-water system

The almost vertical lines along the water axis represent the beginnings of the vapor composition curves

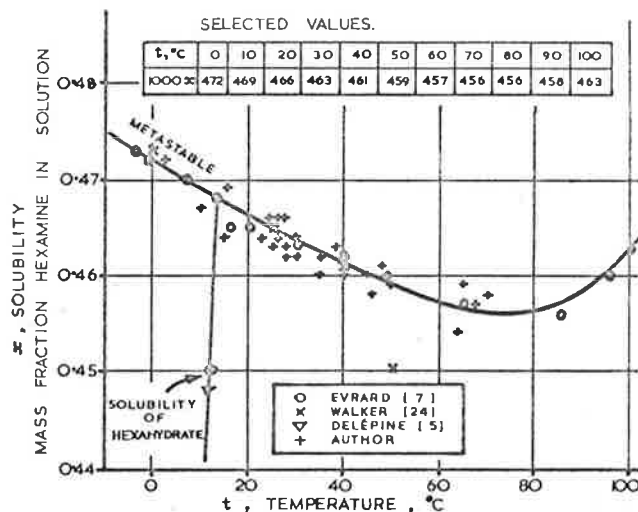


Figure 2. Solubility of hexamine in water

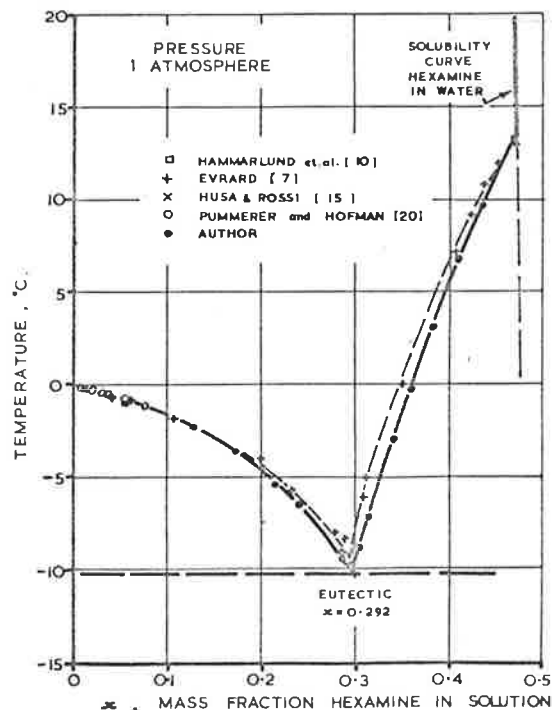


Figure 3. Freezing point diagram for aqueous hexamine solutions

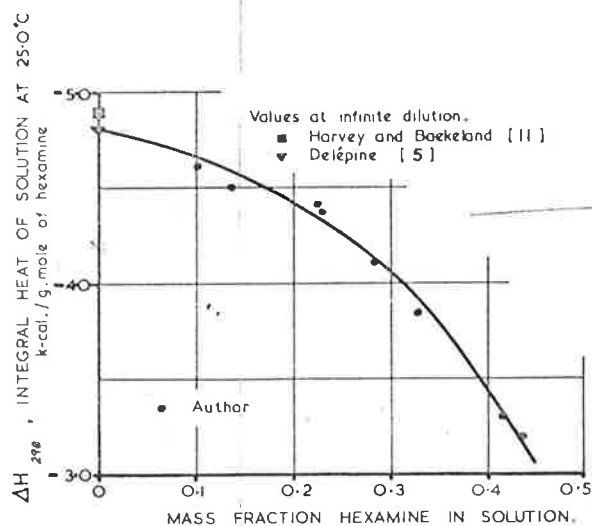


Figure 4. Integral heats of solution at 25.0°C. for hexamine in water

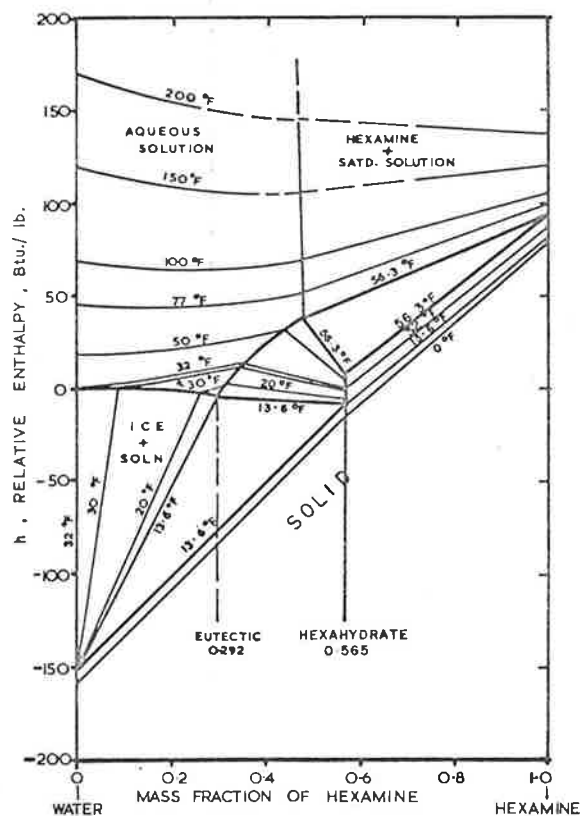


Figure 5. Enthalpy composition diagram for the hexamine-water system

Enthalpy datum: $h = 0$ for liquid water 32° F.,
 $h = 100$ B.t.u./lb. for solid hexamine at 77° F.

forms the hydrate $C_6H_{12}N_4 \cdot 6H_2O$ (5, 16). This hydrate is stable below $13.5^\circ \pm 0.5^\circ C.$ ($56.3^\circ \pm 1^\circ F.$) (7, 27) and crystallizes from solution as long needles. At $13.5^\circ \pm 0.5^\circ C.$, the hydrate decomposes endothermically into anhydrous crystal and saturated solution, for which $\Delta H = 5.0 \pm 0.5$ kcal. per gram mole of hydrate.

The solubility of hexamine in water is shown on an enlarged scale in Figure 2. The much-neglected data of Evrard (7) are plotted together with values determined by the author by several different methods. Below $13.5^\circ C.$, the hydrate is the stable form, but metastable solutions

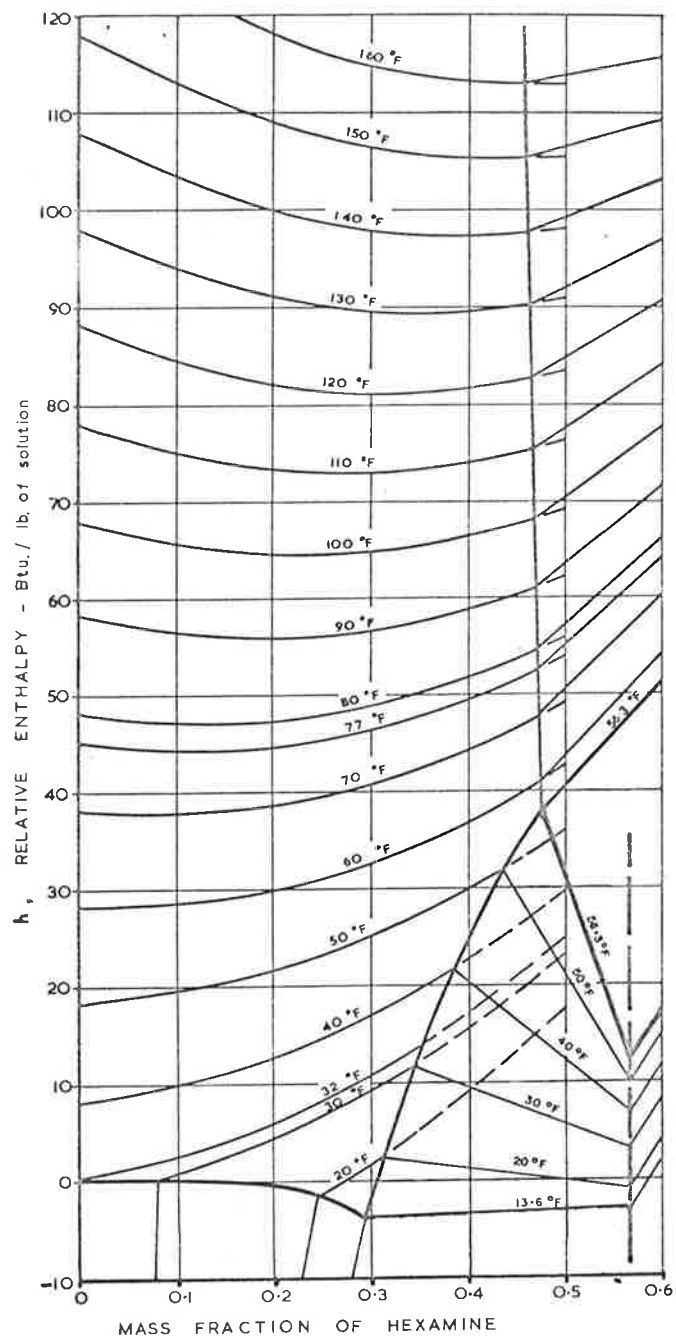


Figure 6. Enthalpy composition diagram for liquid region of hexamine-water system

Enthalpy datum: $h = 0$ for liquid water 32° F.,
 $h = 100$ B.t.u./lb. for solid hexamine at 77° F.

of the anhydrous crystal can be prepared and maintained without difficulty.

The freezing point diagram (Figure 3) demonstrates the presence of a eutectic at $-10.2^\circ \pm 0.5^\circ C.$, corresponding to a mass fraction of hexamine, $x = 0.292 \pm 0.004$. Measured elevations of boiling point (Δt) were correlated within $\pm 0.2^\circ C.$ by the relation

$$\Delta t = 0.08 x^{2.1} (t' + 240) \quad (1)$$

for $10 < t' < 90$, where t' is the boiling point in $^\circ C.$ of pure water at the same pressure. The elevation of boiling point for saturated hexamine solutions over this range varies between 4.2° and $4.9^\circ C.$

Thermal Properties. The heat capacities (c_p) for aqueous hexamine solutions at atmospheric pressure, measured in

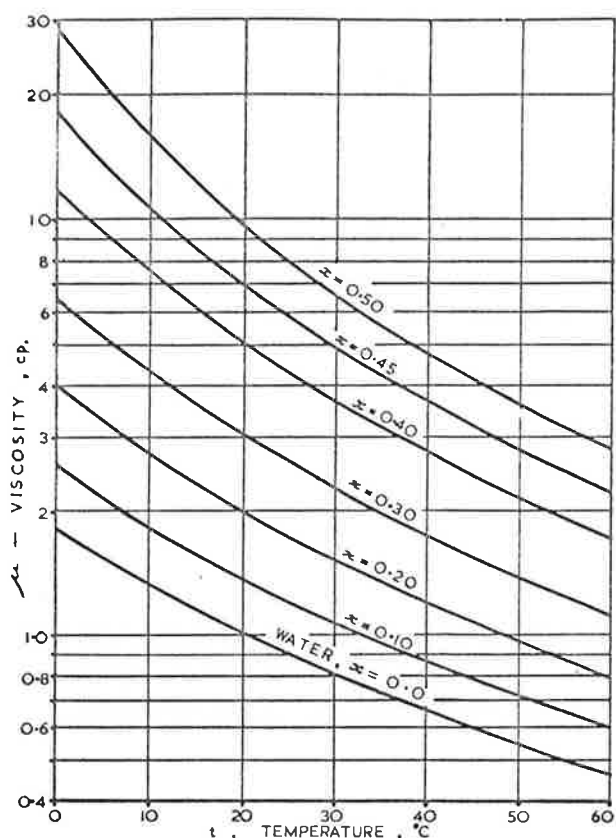


Figure 7. Viscosities of aqueous hexamine solutions—smoothed data

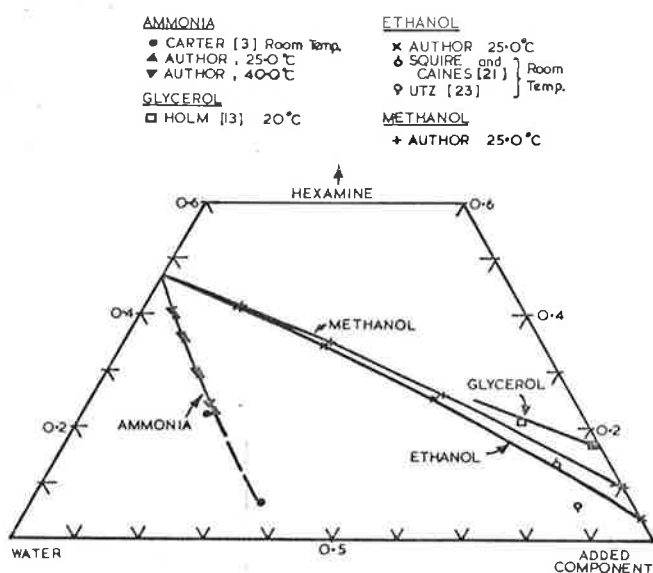


Figure 8. Effect of third component on solubility of hexamine in aqueous solution

All compositions as mass fractions.

an electrically heated calorimeter, could be correlated within ± 0.015 cal. per gram $^{\circ}\text{C}.$ over the full concentration range by the relation

$$c_p = 1.00 - (0.77 - 0.004t)x \quad (2)$$

for t between 10° and $70^{\circ}\text{C}.$

The integral heats of solution (Figure 4) were evaluated from measurements of the adiabatic temperature rise on mixing the pure components at $25.0^{\circ}\text{C}.$ The values are in reasonable agreement with published data at infinite dilution (5, 11).

Enthalpy Composition Diagram. The enthalpy composition diagram (Figure 5) was constructed from the above data. The aqueous solution region is shown to larger scale in Figure 6. These charts are for technical use and are given in engineering units. Enthalpies are given relative to a datum of zero enthalpy for liquid water under its own vapor pressure at $32^{\circ}\text{F}.$ (the steam table datum), and $h = 100$ B.t.u. per pound for solid hexamine at $77^{\circ}\text{F}.$ Enthalpy values are probably accurate to within ± 2 B.t.u. per pound.

OTHER PROPERTIES OF AQUEOUS SOLUTIONS

Density. Densities of aqueous solutions measured at $25.0^{\circ}\text{C}.$ are correlated to within ± 0.00015 gram per ml. by the relation

$$\rho = 0.99707 + 0.2135x + 0.064x^2 \quad (3)$$

Data at other temperatures are available (14, 18, 27).

Refractive Index. The refractive index (n_D) of an aqueous hexamine solution at $25.0^{\circ}\text{C}.$ (7, 18, 27) is given to within ± 0.0002 unit by the relation

$$n_D = 1.33250 + 0.169x + 0.048x^2 \quad (4)$$

Values at $20^{\circ}\text{C}.$ have also been published (9, 19).

Viscosity. Smoothed viscosity data are presented as Figure 7. The data are probably accurate to within 2%.

Surface Tension. The surface tensions of hexamine solutions are only slightly lower than that of water (14, 27). For saturated solutions at room temperature the reduction is about 6%.

EFFECT OF A THIRD COMPONENT ON SOLUBILITY

The effects of methanol and ethanol on the solubility of hexamine in aqueous solution at $25^{\circ}\text{C}.$ are shown in Figure 8. The effects of glycerol at $20^{\circ}\text{C}.$ (13) and ammonia at 25° and $40^{\circ}\text{C}.$ are also shown. Of these materials, only ammonia causes the salting out of hexamine.

NOMENCLATURE

- c_p = heat capacity, cal. per gram $^{\circ}\text{C}.$
- n_D = refractive index
- t = temperature, $^{\circ}\text{C}.$
- t' = boiling point of pure water at same pressure, $^{\circ}\text{C}.$
- Δt = elevation of boiling point, $^{\circ}\text{C}.$
- x = mass fraction of hexamine in mixture
- ρ = density, grams per ml.

LITERATURE CITED

- (1) Becka, L.N., Cruickshank, D.W.J., *Proc. Roy. Soc. (London)* A273, 435 (1963).
- (2) Beilstein, F., "Handbuch der Organischer Chemie," 4th ed., XXVI, E1126-200, Springer, Berlin, 1954.
- (3) Carter, C.B., U.S. Patent 1,566,820 (1935).
- (4) Chang, S.S., Westrum, E.F., *J. Phys. Chem.* 64, 1547 (1960).
- (5) Delépine, M., *Bull. soc. chim. France* 13 (3), 353 (1895); *Ibid.*, 17 (3), 110 (1897).
- (6) Dodge, B.F., "Chemical Engineering Thermodynamics," McGraw-Hill, New York, 1944.
- (7) Evrard, V., *Natuurw. Tijdschr. (Ghent)* 11, 99 (1929); *CA* 23, 4875 (1929).
- (8) Faith, W.L., Keyes, D.B., Clark, R.L., "Industrial Chemicals," 2nd ed., Wiley, New York, 1957.
- (9) Fialkov, Y.A., Egerskaya, V.A., *Farmatsiya (Sofia)* 6, No. 2, 14 (1943).
- (10) Hammarlund, E.R., Larsen, J., Pedersen-Bjergaard, K., *Pharm. Acta Helv.* 35, 593 (1960).
- (11) Harvey, M., Baekeland, L.H., *Ind. Eng. Chem.* 13, 135 (1921).
- (12) Hendricks, S.B., Jefferson, M.E., *J. Opt. Soc. Am.* 23, 299 (1933).
- (13) Holm, K., *Am. J. Pharm.* 94, 138 (1922); *Pharm. J.* 107, 538 (1921).

- (14) Huang, T.C., Peng, M.Y., Hu, K.S., Soh, P.P.T., *J. Am. Chem. Soc.* **60**, 489 (1938).
- (15) Husa, W.J., Rossi, D.A., *J. Am. Pharm. Assoc.* **31**, 270 (1942).
- (16) Jeffrey, G.A., Mak, T.C.W., *Science* **149**, 178 (1965).
- (17) Keenan, J.H., Keyes, F.G., "Thermodynamic Properties of Steam," Wiley, New York, 1936.
- (18) Le Fèvre, R.J.W., Rayner, G.J., *J. Chem. Soc.* 1938, p. 1921.
- (19) Mosebach, R., *Z. Naturforsch.* **16B**, 614 (1961).
- (20) Pummerer, R., Hofmann, J., *Ber.* **56B**, 1255 (1923); *CA* **17**, 3159 (1923).
- (21) Squire, P.W., Caines, C.M., *Pharm. J.* **74**, 720, 784 (1905).
- (22) Stranski, I.N., Klipping, G., Bogenschultz, A.F., Heinrich, H.J., Maennig, H., *Advan. Catalysis* **9**, 406 (1957).
- (23) Utz, F., *Süddeut Apoth.-Ztg.* **59**, 832 (1919); *CA* **14**, 3345 (1920).
- (24) Walker, J.F., "Formaldehyde," 3rd ed., Chap. 19, ACS Monograph 159, Reinhold, New York, 1964.
- (25) Wells, A.F., "Structural Inorganic Chemistry," 3rd ed., p. 609, Clarendon Press, Oxford, 1962.
- (26) Weissberger, A., Ed., "Techniques of Organic Chemistry," 3rd ed., Wiley, New York, 1959.
- (27) White, E.T., Ph.D. thesis, University of London, 1964.

RECEIVED for review August 23, 1965. Accepted March 9, 1967.

Partial Miscibility Phenomena in the Ternary System Ethane-*n*-Nonadecane-*n*-Eicosane

YANG JOO KIM, JAMES A. CARFAGNO, DAVID S. McCAFFREY, Jr., and JAMES P. KOHN

Department of Chemical Engineering, University of Notre Dame, Notre Dame, Ind.

Pressure, composition, and molar volumes of the two liquid phases which coexist for constant molar ratio mixtures of *n*-nonadecane and *n*-eicosane in solution with ethane are presented at representative temperatures along the three phase (L_1 - L_2 - V) border curves. The lower critical solution temperature (LCST) points and the type-K singular points for the ternary mixtures represent nearly linear interpolations of the behavior of the ethane-*n*-nonadecane and ethane-*n*-eicosane binary systems. Both coexisting liquid phases were sampled at several temperatures and at over-all mole fractions of *n*-eicosane of approximately 0.25, 0.50, and 0.75 on an ethane-free basis. The analysis of these samples indicated that the distribution coefficients of the *n*-nonadecane and *n*-eicosane were independent of over-all composition but depended only on the temperature.

IN THE binary system study on partial miscibility of ethane with high molecular weight paraffinic hydrocarbons reported by Kohn (3), *n*-nonadecane was shown to be the lowest molecular weight normal paraffin hydrocarbon which is partially immiscible with ethane. The extension of the partial miscibility work to ternary systems seems necessary if further understanding of the immiscibility phenomenon is to be attained. This paper reports the immiscibility behavior of one ternary system in which the two high molecular weight paraffin hydrocarbons both form partially miscible liquid phases with ethane. Further work will report the immiscibility behavior of a ternary system in which only one of the high molecular weight components is partially immiscible with ethane.

EXPERIMENTAL

The apparatus, techniques, and experimental materials were identical to those reported previously (1-5). The con-

stant molar ratio mixtures of *n*-nonadecane and *n*-eicosane were prepared from the pure components by weighing techniques. The mixtures were kept in closed bottles. Each sample bottle was heated prior to use so that the entire sample material was in the completely melted condition. The liquid sample was withdrawn from the sample bottle by means of a pipet having a hypodermic needle extension, which permitted the liquid to be introduced into the equilibrium cell through its long capillary neck. The mass added to the cell was determined by accurately weighing the cell on an analytical balance.

During the experimental runs, accurate amounts of pure ethane gas were added to the glass equilibrium cell from a high pressure bomb, through use of a positive displacement mercury pump. As the pressure rose in the thermostated cell and ethane dissolved into the liquid phase, a pressure was reached at which a trace of the second liquid (L_2) phase appeared on top of the original liquid (L_1) phase. At this point, the over-all mixture was essentially at the (L_1 - L_2 - V) phase border curve. The molar ratio of *n*-non-