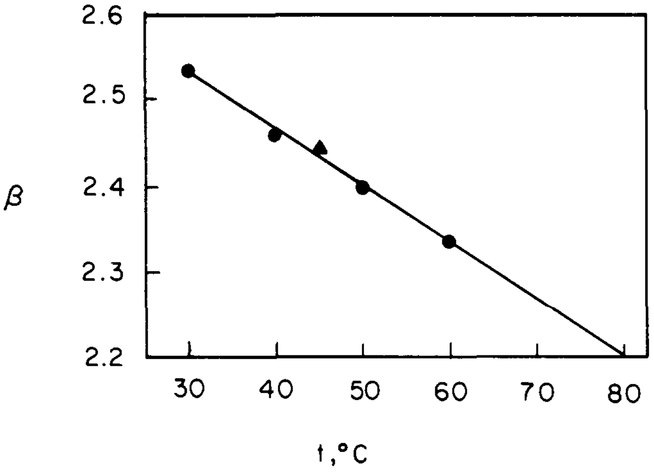

Figure 1. Relative volatility as a function of temperature

● Present data
▲ Brown and Smith (5)
—— Equation 2

$$P = P_1\left[\frac{1 + x_1(\beta - 1)}{\beta}\right] \qquad (3)$$

The vapor pressures of acetone obtained by linear smoothing of the P-x data are correlated very well by the equation:

$$\log_{10}P_1 = 7.1971 - \frac{1247.4}{t + 233} \qquad (4)$$

where P_1 is in mm. of Hg and t is in ° C. Since in Equation 3 both P_1 and β are functions of temperature only, one can determine the P-x relationship at constant t or the t-x relationship at constant P.

Phase equilibrium data for this system at 45° C. are given by Brown and Smith (*5*) and at about 760 mm. of Hg by Pratt (*9*). In both cases these authors found the activity coefficients to be essentially unity. Vapor compositions computed from Equation 1 with β as given by Equation 2 are in substantial agreement with the measured values given in these references.

If this system does obey Raoult's law and yield activity coefficients of unity over a range of temperatures, then the heat of mixing must be zero, or at least very small, within this temperature range. Heat-of-mixing data at 45° C. given by Brown and Fock (*2*) show the system to be endothermic with a value of ΔH equal to about -100 Joules per gram mole at $x_1 = 0.5$. Measurements made in the authors' laboratory conform closely to the literature values, confirming that, while ΔH is small, it is not negligible. Thus the activity coefficients cannot be exactly unity over the temperature range considered, but they can be close to it. Data for the volume change of mixing at 25° C. by Brown and Smith (*6*) show ΔV to be negative with a value of ΔV equal to about -0.13 cm.^{3} per gram mole at $x_1 = 0.5$.

Clearly, the acetone-acetonitrile system exhibits small deviations from ideality. Nevertheless, Raoult's law provides a good practical description of the vapor-liquid equilibria of this system.

ACKNOWLEDGMENT

This work was supported by National Science Foundation Grant GP-2199.

LITERATURE CITED

(1) American Petroleum Institute Research Project 44, "Selected Values of Properties of Hydrocarbons and Related Compounds," College Station, Tex.
(2) Brown, I., Fock, W., *Aust. J. Chem.* **10**, 417 (1957).
(3) Brown, I., Smith, F., *Ibid.*, **7**, 267 (1954).
(4) Ibid., **10**, 423 (1957).
(5) Ibid., **13**, 30 (1960).
(6) Ibid., **15**, 9 (1962).
(7) Dreisbach, R. D., *Advan. Chem. Ser.* **29**, (1961).
(8) Kochar, N. K., Ph.D. thesis, Rensselaer Polytechnic Institute, Troy, N.Y., 1965.
(9) Pratt, H. R. C., *Trans. Inst. Chem. Engrs.* **25**, 43 (1947).

RECEIVED for review August 10, 1966. Accepted October 31, 1966.

Hydrazine–1,1-Dimethylhydrazine Solid-Liquid Phase Diagram

J. A. McMILLAN
Solid State Science Division, Argonne National Laboratory, Argonne, Ill.

Hydrazine and 1,1-dimethylhydrazine form a binary eutectic system. The first addition of either component causes a lowering of the melting point. The liquidus curve exhibits a minimum at 214° K. and 94 mole % of 1,1-dimethylhydrazine, where it joins the eutectic solidus, which extends toward the pure components. No solid solutions are detected.

THE hydrazine–1,1-dimethylhydrazine binary system is of some interest for it is used as a rocket propellant. The liquid-vapor phase diagram has been studied by Pannetier and Mignotte (*4*). These authors have also studied the refractivity (*5*), the enthalpy of mixing (*7*), and the molar volume (*6*). In this latter case, they found a negative excess function with an absolute maximum at the molar ratio 1 to 1. The excess function increases in absolute value with increasing temperature; the existence of a chemical compound may not be inferred therefore. The present paper reports results on the solid-liquid equilibrium diagram. The diagram, shown in Figure 1, indicates formation of a eutectic of 94 mole % of 1,1-dimethylhydrazine melting at 214° K., and no evidence of compound formation. The very narrow solid-solution ranges of the pure components are undetectable and appear in the phase-equilibria diagram of Figure 1 as single vertical lines overlapping the temperature axes. Unlike the systems of the components with water (*3*), the mixture hydrazine–1,1-dimethylhydrazine does not supercool, thermal analysis being therefore

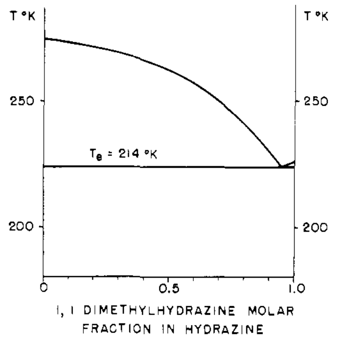

Figure 1. Solid-liquid phase diagram of the system hydrazine–1,1-dimethylhydrazine

Table I. Solidus and Liquidus Temperatures of the System Hydrazine–1,1-Dimethylhydrazine

Molar Fraction of 1,1-Dimethylhydrazine	Solidus Temp., ° K.	Liquidus Temp., ° K.
0.00	...	275
0.01	214	275
0.05	214	274
0.20	214	271
0.35	214	269
0.50	214	262
0.55	214	260
0.59	214	257
0.72	214	250
0.83	214	225
0.90	214	220
0.95	214	215
0.99	...	216
1.00	...	216

straightforward. The components were purified by distillation in nitrogen atmosphere in the presence of sodium hydroxide in the case of hydrazine, and at reduced pressure in the presence of calcium hydride in the case of 1,1-dimethylhydrazine (*1*), collecting the middle fraction and discarding the first and last 25% of the distillate. Chromatographic runs did not show any appreciable peak owing to impurities in the case of hydrazine. A faint, unidentified peak was always present in the case of 1,1-dimethylhydrazine. The samples were prepared by weighing the pure components. The molar fractions are therefore certain to within ±0.005. The samples were sealed in borosilicate glass cells (*2*) in a nitrogen atmosphere and kept in the dark. Thermal analysis of these samples was repeated at intervals over a period of six months with very good reproducibility of results. Samples that were not kept in the dark showed visible signs of decomposition with development of a yellow color and exhibited, in general, depression of the liquidus and solidus points. Thermal analysis was performed following a procedure described elsewhere (*2*). The temperatures were measured with copper-constanant thermocouples and a recorder with a resolution of 0.2° K. Since the rates of cooling and warming were always kept well below one degree per minute, the thermal homogeneity of the sample was better than 0.2° K., which leads to a maximum uncertainty in the temperature of 0.2° K. Table I displays the solidus and liquidus temperatures for various compositions.

LITERATURE CITED

(1) Lucien, H. W., J. CHEM. ENG. DATA **7**, 541 (1962).
(2) McMillan, J. A., Los, S. C., *J. Chem. Phys.* **42**, 160 (1965).
(3) *Ibid.*, p. 829.
(4) Pannetier, G., Mignotte, P., *Bull. Soc. Chim. France* **1961**, pp. 694, 985.
(5) *Ibid.*, p. 982.
(6) *Ibid.*, **1963**, p. 699.
(7) *Ibid.*, p. 701.

RECEIVED for review August 17, 1966. Accepted November 2, 1966. Based on work performed under the auspices of the U. S. Atomic Energy Commission.

Refractive Indices of Some Ternary Systems Containing Naphthalene

Binary Solvent Mixtures Containing Hexane or Cyclohexane

E. L. HERIC and CECIL D. POSEY[1]
Department of Chemistry, University of Georgia, Athens, Ga.

IN PREVIOUS publications, refractive indices of some ternary systems containing naphthalene have been reported (*4*, *5*). Those studies were concerned with the six solvent pairs from among benzene, toluene, ethylbenzene, and carbon tetrachloride (*4*) and the six solvent pairs of hexadecane with each of benzene, toluene, ethylbenzene, carbon tetrachloride, hexane, and cyclohexane (*5*). Also included were the pertinent binary subsystems. The first set of ternary systems is characterized by a small energy of interaction between the components (*1*, *2*), and relatively small differences in component molar volumes. The second set involved systems containing components of greater dissimilarity.

The present work concludes the study of the set of naphthalene-mixed solvent systems, adding the remaining nine ternaries of the total of 21 possible for naphthalene with these solvent components. All of the present systems contain hexane or cyclohexane as one of the mixed solvent components. As in the previous two works, the question of the suitability of equations used in representing the experimental data is considered.

---

[1] Present address: Radiological Health Section, Georgia Department of Public Health, Atlanta, Ga.