Vapor-Liquid Equilibria: Acetone-Acetonitrile

H. C. VAN NESS and N. K. KOCHAR[1]
Chemical Engineering Department, Rensselaer Polytechnic Institute, Troy, N. Y.

Vapor liquid equilibrium data reported for the temperature range 30° to 60° C. show that the acetone-acetonitrile system conforms closely to Raoult's law. Heat-of-mixing and volume-change-of-mixing data confirm that this system exhibits only very small departures from ideal-solution behavior.

MEASUREMENTS have been made of the saturation pressures exerted by solutions of acetone and acetonitrile in vapor-liquid equilibrium at 30°, 40°, 50°, and 60° C. Data were taken with a static cell for eight different liquid concentrations, including the pure components. At each temperature the results are well correlated by a linear relation between pressure and liquid mole fraction, demonstrating that this system closely obeys Raoult's law.

The equilibrium cell was a 140-cm.^{3} glass vessel equipped with a magnetically driven stirrer. Thoroughly degassed pure materials were distilled into the evacuated cell until it was very nearly full of liquid. Since the cell was light and portable, successive weighings of the cell on an analytical balance allowed determination of the composition of its contents. The small vapor space contained less than one ten thousandth of the mass of solution in the cell. Thus the measured composition was taken as that of the liquid phase. Pressure measurements were made with a miniature pressure transducer. Considerable experience with this device has led to the conclusion that the uncertainty of any single pressure determination is well within ±0.5 mm. of Hg. The cell was submerged in a water bath controlled to the set temperature to within ±0.001° C. Details of the apparatus and procedure are given elsewhere (*8*).

"Chromatoquality" reagents were supplied by Matheson, Coleman, and Bell with indicated purities of 99.8 mole %. Vapor pressures for the pure materials are compared with literature values in Table I. The values designated as smoothed were obtained from a least squares fit of all data at a given temperature to a linear equation in liquid mole fraction. All such smoothed pure-component vapor pressures are slightly higher than the experimental, indicating that the *P-x* relation actually may show very small positive deviations from Raoult's law. Nevertheless, the linear equations in every case correlate the data with a root mean-square deviation of less than 0.2%. No significant improvement is obtained by use of a quadratic expression.

The literature values reported for the vapor pressures of the pure components are not in complete agreement, and the present values are generally higher than the literature values. However, these discrepancies are not serious enough to impair the primary conclusion that, for practical purposes, the acetone-acetonitrile binary system follows Raoult's law.

Vapor-liquid phase-equilibrium data for this system at 45° C. are reported by Brown and Smith (*5*). Their *P-x* data also are correlated by a linear equation, and results are included in Table I. The root mean square deviation in this case is 0.27% and no improvement is effected by use of a quadratic equation.

For a system obeying Raoult's law, the vapor-phase composition is given by

$$y_1 = \frac{x_1\beta}{1 + x_1(\beta - 1)} \qquad (1)$$

where β is the relative volatility, equal to P_1/P_2. Usually, β is a weak function of temperature. A value of $\beta = P_1/P_2$ was computed for each of the five temperatures listed in Table I from the vapor pressures obtained by linear smoothing of the *P-x* data. Results are shown in Figure 1. Although the β-*t* relationship cannot be exactly linear if the vapor pressures conform to the Antoine equation, a linear equation will represent the results to a very good approximation. The following equation correlates the data with a root mean-square deviation of 0.24%:

$$\beta = 2.729 - 0.00655t \qquad (2)$$

where t = °C.

By Raoult's law, $P = x_1P_1/y_1$. Thus

Table I. Vapor Pressures, Mm. of Hg

	Acetone (1)				Acetonitrile (2)			
	Experimental value	Smoothed by linear *P-x* equation	Literature		Experimental Value	Smoothed by linear *P-x* equation	Literature	
t, ° C.			(*1*)	(*4*)[a]			(*7*)	(*3*)[a]
30	284.37	284.58	285.18	285.06	112.10	112.29	108.97	110.74
40	424.10	424.42	424.16	424.69	172.09	172.59	169.08	170.05
45	512.72[b]	512.74[b]	511.87	512.78	208.35[b]	209.78[b]	208.04	208.36
50	615.05	615.90	613.70	614.95	255.88	256.75	254.06	253.54
60	...[c]	870.46	866.16	868.00	371.44	372.61	370.96	368.06

[a] The vapor pressure data of Brown and Smith (*3, 4*) were used to determine new constants for the Antoine equation by machine computation, and the values listed are calculated with this equation.
[b] Data of Brown and Smith (*5*).
[c] The static cell is not designed for pressures above atmospheric.

---

[1] Present address: The Lummus Co., Newark, N. J.

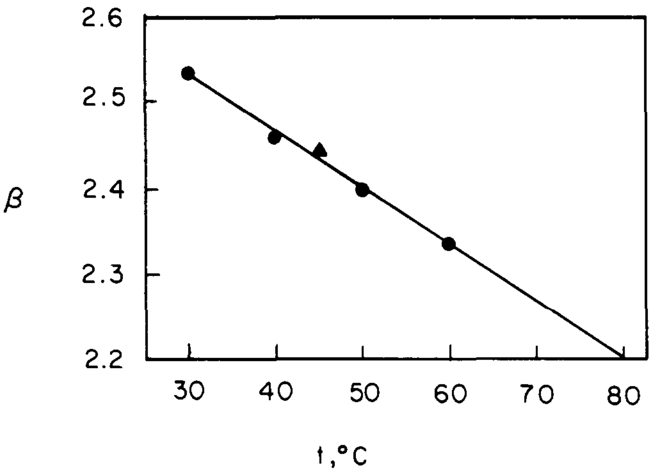

Figure 1. Relative volatility as a function of temperature

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

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

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

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

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