# Vapor-Liquid Equilibrium of Ethyl Isopropylamine–Water and Dimethyl Isopropylamine–Water

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**Vapor-liquid equilibria of water with ethyl isopropylamine and dimethyl isopropylamine are reported at 10°, 20°, 30°, and 40°C.**

This work is part of a continuing study of phase relations in highly nonideal hydrogen bonding-type solutions. Amines and water are among the examples in this category, with large values for all the excess functions, having lower critical solution points and solubility curves that are temperature-sensitive and exhibiting excess free energies that are extremely difficult to represent by the usual thermodynamically consistent polynomials.

## EXPERIMENTAL

The apparatus and the experimental methods used in this work have been described (*2*, *4*). In brief, the apparatus is a static vapor pressure device in which a mixture can be degassed without change in composition. The entire apparatus, consisting of sample flasks, mercury manometers, and glass manifold, is submerged in a constant-temperature bath and suspended so that it can be agitated to hasten equilibrium.

The manometers are read within the bath by means of a cathetometer to 0.05 mm of Hg. The apparatus contains two sample flasks and two manometers so that two samples can be run at once. A common reference pressure is applied to the outside arm of each manometer. If the total pressure is less than the manometer length (about 130 mm), a high vacuum is maintained on the outer legs. Otherwise a third flask containing a pure liquid of known vapor pressure is installed and serves as a reference pressure. In this work either water or chloroform (*1*) was used as a reference depending on the pressure. All manometer readings were corrected for gravity and temperature. The correction for vapor density is insignificant.

The temperature was controlled to within 0.01°C by a thermistor-operated Sargent temperature controller. An external circulating pump maintained a uniform temperature within the bath. The temperature was measured with an accuracy of about 0.03°C with a glass thermometer graduated in tenths of a degree that had been calibrated with a platinum resistance thermometer. This temperature error would result in a maximum pressure error of less than 0.4 mm of Hg at the highest pressures. The overall pressure accuracy is probably within 0.5 mm of Hg.

Chemical analysis of the liquid phase was by acid titration of the amine except at water concentrations below about 10 wt %. At low water content, analysis was by gas chromatography, using a 20-ft by 1/4-in. column packed with Fluoropac (Aerograph) with a silicone coating. These methods gave amine concentration reproducibilities of one part in 250 to 500, and water concentrations having a maximum deviation of ±1 mol % at the higher amine concentrations. At high amine concentrations, an error of 1 part in 500 in the amine content would result in an error of about 0.2% in the weight percent amine or nearly 1% in the mole percent.

Water vapor pressures were taken from Lange's Handbook (*5*). These data are in excellent agreement with more recent tabulations, such as the 1967 ASME steam tables, over the temperature range in question.

The pure amines were synthesized for this research. Each was distilled on a Stedman column, and a fraction having a boiling range of less than 0.1°C was used. These fractions show a single peak on the gas chromatograph. The conductivity detector used is very sensitive to water and none was detected in the purified amine samples.

## CALCULATION OF PHASE EQUILIBRIUM

The results of the total pressure measurements are shown in Tables I and II and Figures 1 and 2. Dimethyl isopropylamine has an azeotrope between amine mole fraction of 0.9–0.95 at all temperatures, while ethyl isopropylamine exhibits an azeotrope only at 30° and 40°C at about $x_a = 0.975$ and 0.95, respectively. At 10° and 20°C, and perhaps even at 30°C, the system exhibits near tangent azeotropes.

The vapor composition and activity coefficients were calculated by the total pressure method in which the Gibbs-Duhem equation is integrated numerically with the total pressure liquid composition data. The Gibbs-Duhem equation was expressed in the form

$$\ln \gamma_2 = -\frac{x_1}{x_2} \ln \gamma_1 + \int_0^{x_1} \frac{\ln \gamma_1}{x_2^2}\, dx_1 \qquad (1)$$

which involves the assumption that the activity coefficients are independent of pressure.

Equation 1 was integrated over mole fraction increments of

Table I. Measured Total Pressure-Composition Data for Dimethyl Isopropylamine–Water

| Mol % amine | Temperature, °C | | | |
|---|---|---|---|---|
| | 10 | 20 | 30 | 40 |
| | Pressures in Mm of Hg | | | |
| 0.29 | 11.4 | 23.7 | 46.15 | 85.15 |
| 0.65 | 15.1 | 30.3 | 61.5 | 116.45 |
| 1.18 | 17.6 | 39.2 | 81.25 | |
| 2.42 | 26.3 | 56.65 | 112.15 | |
| 4.64 | 33.9 | 67.7 | 125.45 | 221.1 |
| 9.25 | 40.0 | 75.2 | 134.9 | 231.05 |
| 17.48 | 47.85 | 85.9 | 147.25 | 244.65 |
| 28.48 | 58.4 | 99.85 | 165.3 | 264.5 |
| 34.83 | 62.25 | 105.65 | 172.9 | 272.6 |
| 48.65 | 70.05 | 115.65 | 185.2 | 287.75 |
| 57.92 | 74.05 | | 192.9 | 296.5 |
| 67.76 | 77.0 | 125.2 | 197.7 | 302.7 |
| 77.58 | 80.45 | 129.7 | 202.35 | 308.5 |
| 84.96 | 82.25 | 132.2 | 206.35 | 312.6 |
| 86.74 | 82.85 | 133.2 | 207.15 | 313.55 |
| 90.79 | 84.45 | 134.25 | 208.25 | 313.3 |
| 94.50 | 82.8 | 133.7 | 208.7 | 312.5 |
| 100.00 | 83.6 | 133.9 | 205.3 | 304.1 |

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0.025 and solved simultaneously at each increment with the equation

$$P = P_1^0\Phi_1\gamma_1x_1 + P_2^0\Phi_2\gamma_2x_2 \qquad (2)$$

in which $\Phi$ is the ratio of the fugacity coefficient of the pure component vapor to the fugacity coefficient of the component in the vapor mixture. Computer input included total pressures at increments of 0.025 mole fractions including pure component vapor pressures. These were determined by plotting the experimental data in Tables I and II on large graph paper and interpolating the evenly spaced values. Activity coefficients at infinite dilution were estimated graphically. These were included in the input to initiate the numerical integration. The activity coefficients at the first increment were determined by the trapezoidal rule and beyond this Simpson's rule was used. Integration started at the pure component of lowest vapor pressure. If an azeotrope was encountered, the integration was reinitiated at the other pure component and continued until the azeotrope was reached from the other side. The fugacity coefficients were calculated as proposed by Prausnitz et al. (*6*) for polar compounds. Details of the numerical procedures have been given elsewhere (*3*).

A sample result is shown in Table III for ethyl isopropylamine at 30°C. The pressures in this table are interpolated values used in the numerical integration. The last digit in the pressure is not significant but is included to reduce round-off error in the numerical integrations. The complete tables of results have been deposited with the ACS Microfilm Depository Service. The vapor compositions are shown in Figures 1 and 2. For amine mole fractions below 0.025, the vapor composition can be calculated closely assuming the water to obey Raoult's law, since

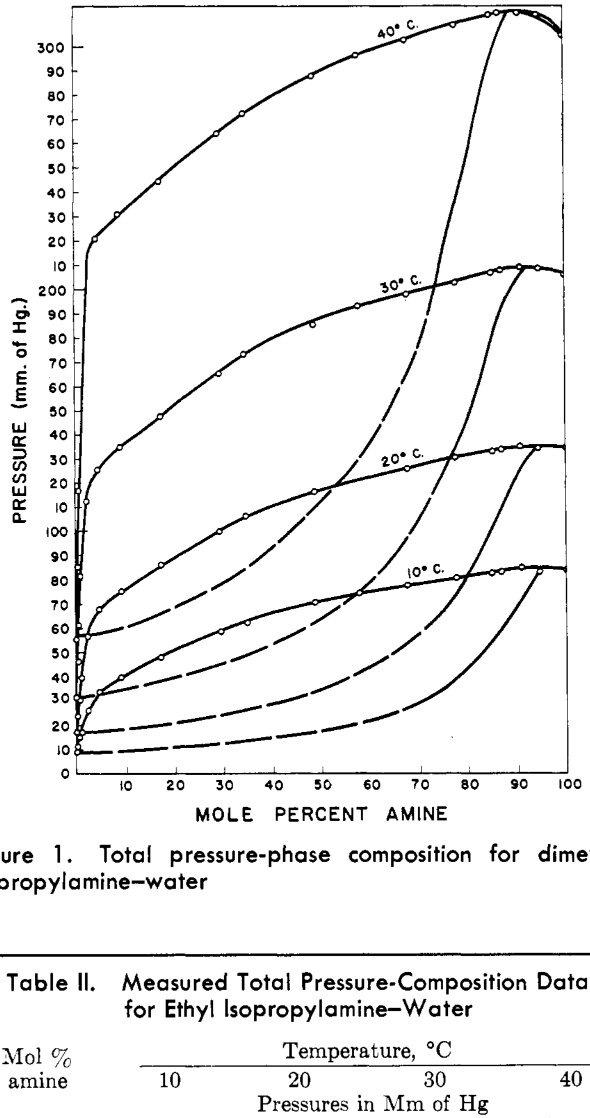

Figure 1. Total pressure-phase composition for dimethyl isopropylamine–water

Table II. Measured Total Pressure-Composition Data for Ethyl Isopropylamine–Water

| Mol % amine | Temperature, °C<br>10 | 20 | 30 | 40 |
|---|---|---|---|---|
| | | Pressures in Mm of Hg | | |
| 0.29 | 10.35 | 20.4 | 39.6 | 72.85 |
| 0.61 | 11.3 | 23.9 | 46.8 | 89.95 |
| 1.26 | 13.6 | 29.95 | 61.55 | 119.0 |
| 2.42 | 18.35 | 41.6 | 82.35 | 154.5 |
| 4.74 | 25.45 | 50.35 | 95.5 | 169.35 |
| 9.61 | 29.05 | 55.7 | 102.15 | 176.05 |
| 17.75 | 32.3 | 61.05 | 108.8 | 182.0 |
| 30.15 | 38.0 | 69.15 | 119.7 | 195.0 |
| 39.97 | 42.95 | 96.55 | 128.45 | 215.75 |
| 48.27 | 46.35 | 80.9 | 135.7 | 219.2 |
| 59.26 | 51.1 | 87.7 | 144.8 | 231.15 |
| 70.33 | 55.3 | 93.45 | 152.8 | 241.6 |
| 79.12 | 58.4 | 97.95 | 159.2 | 248.9 |
| 85.27 | 60.5 | 100.8 | 163.4 | 253.3 |
| 89.32 | 61.2 | 101.85 | 163.15 | 253.15 |
| 90.76 | 62.8 | 103.55 | 165.15 | 255.2 |
| 98.36 | 64.2 | 105.25 | 166.55 | 255.1 |
| 100.00 | 64.25 | 105.3 | 166.5 | 254.45 |

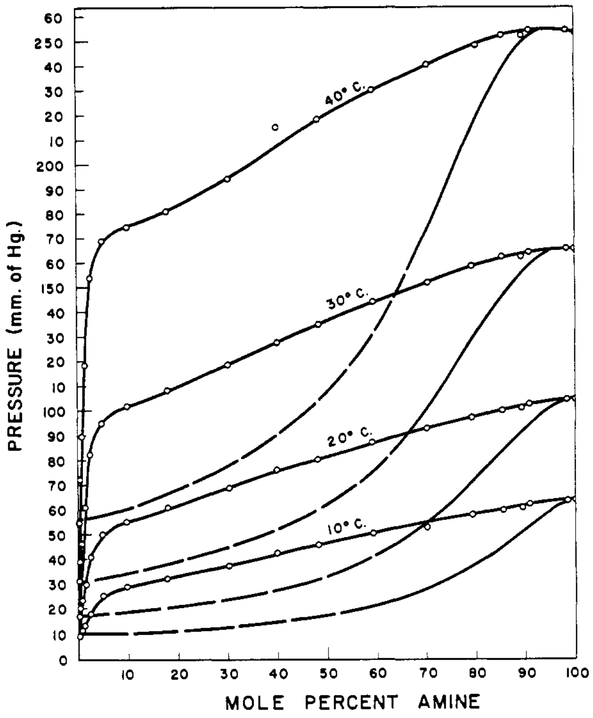

Figure 2. Total pressure-phase composition for ethyl isopropylamine–water

Table III. Calculated Vapor-Liquid Equilibria for Ethyl Isopropylamine–Water at 30°C

| $x_a$ | $y_a$ | $\gamma_a$ | $\gamma_w$ | $g^E$ | $P$ |
|---|---|---|---|---|---|
| 0 | 0 | 17.88 | 1.000 | 0 | 31.82 |
| 0.025 | 0.624 | 12.50 | 1.005 | 40.7 | 82.89 |
| 0.05 | 0.679 | 7.901 | 1.023 | 75.4 | 96.37 |
| 0.1 | 0.700 | 4.331 | 1.073 | 126.3 | 102.48 |
| 0.2 | 0.729 | 2.435 | 1.182 | 187.7 | 110.82 |
| 0.3 | 0.758 | 1.821 | 1.300 | 218.7 | 119.57 |
| 0.4 | 0.788 | 1.525 | 1.429 | 230.6 | 128.55 |
| 0.5 | 0.817 | 1.347 | 1.581 | 227.6 | 137.00 |
| 0.6 | 0.846 | 1.233 | 1.760 | 212.0 | 145.38 |
| 0.7 | 0.874 | 1.146 | 2.019 | 184.4 | 152.66 |
| 0.8 | 0.907 | 1.089 | 2.353 | 144.1 | 159.90 |
| 0.9 | 0.937 | 1.032 | 3.277 | 88.3 | 164.96 |
| 0.975 | 0.976 | 1.001 | 5.115 | 25.0 | 166.51 |
| 1.000 | 1.000 | 1.000 | 5.410 | 0 | 166.50 |

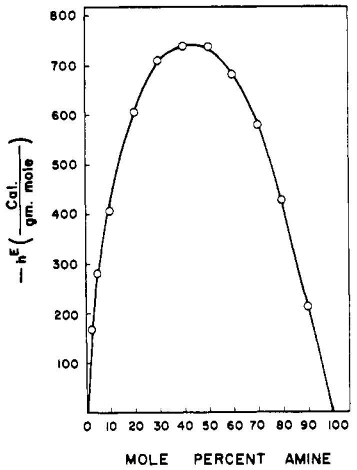

Figure 3. Calculated excess enthalpies for ethyl isopropylamine–water

at this concentration $\gamma_w$ is always below 1.006. Then the mole fraction amine is given approximately by

$$y_a = \frac{P - P_w^0 x_w}{P} \qquad (3)$$

The dotted line in Figures 1 and 2 were calculated by this equation. Figure 3 shows average excess enthalpies for ethyl isopropylamine–water calculated from the slopes of plots of $g^E/T$ vs. $1/T$ at various mole fractions over the range of 10–40°C.

An attempt was made to represent the excess free energy of these systems by a thermodynamically consistent polynomial. As with other amine–water systems, this could not be done satisfactorily even with seven arbitrary constants.

## NOMENCLATURE

$f$ = fugacity
$g^E$ = excess Gibbs free energy in cal/g-mol
$h^E$ = excess enthalpy in cal/g-mol
$P$ = pressure in mm of Hg
$x$ = mole fraction in the liquid
$y$ = mole fraction in the vapor

GREEK

$\gamma$ = activity coefficient, $f/f^0x$
$\Phi$ = the ratio of the fugacity coefficient of a pure component vapor to that in the vapor mixture

SUBSCRIPTS

1 = component 1
2 = component 2
$a$ = amine
$w$ = water

SUPERSCRIPTS

0 = pure component

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RECEIVED for review May 17, 1971. Accepted December 12, 1971. Two tables of complete data on the calculated vapor-liquid equilibria of dimethyl isopropylamine–water and of ethyl isopropylamine–water will appear following these pages in the microfilm edition of this volume of the Journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D.C. 20036, by referring to author, title of article, volume, and page number. Remit by check or money order $3.00 for photocopy or $2.00 for microfiche.

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# Self-Ionization of Water in Dilute Sodium Chloride Solutions from 5–35°C and 1–2000 Bars

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**An improved form of glass electrode cell was used to estimate the degree of self-ionization of water over the oceanographically interesting temperature and pressure range. The results indicate that the estimates of Owen and Brinkley may be in serious error at temperatures below 25°C. This conclusion is supported by the compressibility data of Kearns and by recent studies of the self-ionization of water over a broad temperature and pressure range (to 1000°C and 133K bars).**

Because of its pivotal importance in aqueous solution chemistry, the self-ionization of water has been intensively studied over a wide temperature range at atmospheric pressure (*6,13,22*) and at very high temperatures and pressures in the supercritical region (*5, 9, 16, 20, 21, 25, 26, 38*). However, little attention has been paid to the more moderate temperature and pressure range of interest to biologists and marine scientists, mainly because of the lack of a suitable experimental method.

The potentiometric method was used by Hamann (*19*) in the first experimental study of water ionization in this region, and recent improvements in techniques for using glass electrodes at high pressures (*41–43*) now make it possible to ex-

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