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Phase Equilibria for Dimethylethylamine + Water and Trimethylamine + Water Mixtures

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Isothermal vapor-liquid equilibrium data are presented for mixtures of dimethylethylamine + water and trimethylamine + water at temperatures between 10 and 50 °C. The results of tests on these mixtures for liquid-phase immiscibility at elevated temperatures are also presented. A five-parameter NRTL thermodynamic model was fitted to the experimental data and used to calculate enthalpies of mixing for each mixture.

Introduction

Aliphatic amine + water mixtures are known to exhibit partial miscibility, with the liquid-phase solubility decreasing with increasing temperature. Such unusual thermodynamic behavior has been studied by Copp and Everett (*2–4*) who presented equilibrium data for diethylamine + water and diethylmethylamine + water mixtures. Chun et al. (*5, 6*) and Davison et al. (*8, 9*) also presented equilibrium data for a variety of aliphatic tertiary amine + water mixtures.

However, liquid-phase separation has not been reported for the lower molecular weight tertiary amines, namely, dimethylethylamine and trimethylamine in mixtures with water. The sole vapor-liquid equilibrium study of these mixtures by Felsing (*10*) presented solubility data for trimethylamine in water at very low amine concentrations (<4 mol %).

In this study, binary vapor-liquid equilibrium data for dimethylethylamine + water and trimethylamine + water mixtures were obtained in a static equilibrium apparatus at temperatures between 10 and 50 °C over the full range of compositions. The liquid-phase solubility of these mixtures was also investigated at elevated temperatures.

Experimental Section

Liquid-Liquid Equilibrium. Pyrex tubes, constricted near their open end, were charged with various concentration mixtures of water and tertiary amine. The filled ampules were frozen in liquid nitrogen, evacuated, and sealed. Sealed ampules were then placed in a well-stirred water bath and heated until the cloud point was reached.

At the temperatures encountered in these experiments, the pressure inside the ampules exceeded atmospheric pressure. While it was not possible to measure the pressure inside the sealed ampules, the high pressure constitutes a major source of error in the composition analysis as significant loss of the volatile amine to the vapor phase may occur. The ideal gas law was used to estimate the magnitude of the error between the measured amine composition and the composition at equilibrium, assuming the ampule is 75% full and the pressure inside the ampule reaches 4000 kPa at 150 °C for the mixtures of trimethylamine and 3% aqueous salt solution. The measured composition was calculated to be between 6 and 11% greater than the composition inside the ampule at equilibrium conditions. For mixtures of dimethylethylamine and water, the estimated pressure inside the ampule was approximately 1000 kPa. Hence, the measured amine composition may be estimated as between 1.5 and 5.0% greater than that experienced in the ampule at equilibrium conditions.

Table I. Liquid-Liquid Equilibria for Dimethylethylamine (1) + Water (2)

$100x_1$	t/°C	$100x_1$	t/°C	$100x_1$	t/°C
6.0	102.4	20.7	98.8	37.7	100.3
8.1	100.2	26.8	99.1		
13.7	99.6	29.4	99.3		

Table II. Liquid-Liquid Equilibria for Trimethylamine (1) + 3 mass % Aqueous NaCl Solution (2)

$100x_1$	t/°C	$100x_1$	t/°C	$100x_1$	t/°C
11.8	144.3	14.8	136.3	18.6	131.9
13.8	135.6	16.0	130.9	19.6	130.2

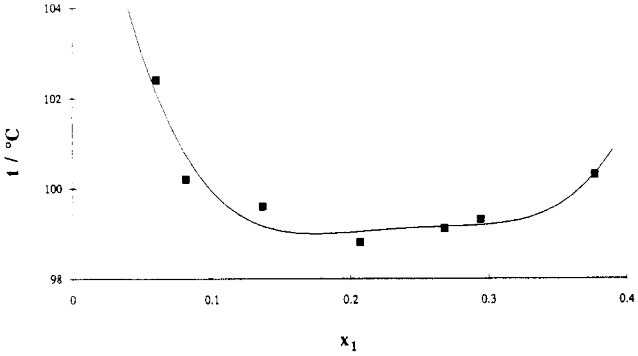

Figure 1. Liquid-phase solubility of dimethylethylamine (1) + water (2): ■, experimentally determined point of phase separation.

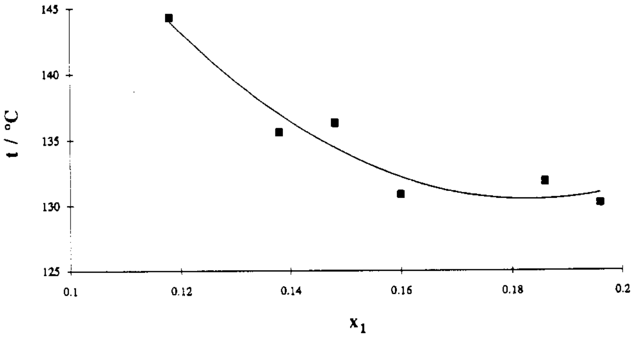

Figure 2. Liquid-phase solubility of trimethylamine + 3% (mass) aqueous salt solution: ■, experimentally determined point of phase separation.

Vapor-Liquid Phase Equilibrium. Vapor-liquid equilibrium data were obtained in a static vapor pressure apparatus similar to that described by Davison et al. (*7*). However, in the current apparatus the mercury manometer

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Table III. Pure Component Vapor Pressure Data for Dimethylethylamine

t/°C	P/kPa	t/°C	P/kPa	t/°C	P/kPa
5.54	30.53	24.51	65.75	38.87	110.12
10.31	37.90	26.44	71.02	41.51	120.55
14.92	45.19	31.36	84.38	44.85	134.14
14.97	45.71	31.90	86.29	48.41	150.22
19.56	54.64	34.69	95.29		

Table IV. Vapor–Liquid Equilibria for Dimethylethylamine (1) + Water (2)

t/°C	x_1	P/kPa	t/°C	x_1	P/kPa
10.0	0.0174	4.27	19.5	0.0174	8.24
	0.0618	11.67		0.0618	20.08
	0.1656	16.45		0.1656	26.74
	0.2533	20.74		0.2533	32.64
	0.3385	24.91		0.3385	37.77
	0.4885	31.10		0.4885	45.01
	0.6077	32.33		0.6077	47.72
	0.7363	34.05		0.7363	49.91
	0.8081	34.69		0.8081	51.25
	0.8719	35.68		0.8719	52.17
29.2	0.0174	15.94	38.9	0.0174	29.21
	0.0618	33.92		0.0618	54.53
	0.1656	41.96		0.1656	65.40
	0.2533	49.80		0.2533	74.77
	0.3385	56.42		0.3385	82.50
	0.4885	64.98		0.4885	93.20
	0.6077	68.72		0.6077	98.01
	0.7363	72.23		0.7363	98.83
	0.8081	74.65		0.8081	104.70
	0.8719	75.22		0.8719	106.38
48.6	0.0174	48.84			
	0.0618	83.94			
	0.1656	98.10			
	0.2533	108.67			
	0.3385	117.47			
	0.4885	129.58			
	0.6077	134.96			
	0.7363	140.48			
	0.8081	144.40			
	0.8719	146.15			

Table V. Vapor–Liquid Equilibria for Trimethylamine (1) + Water (2)

t/°C	x_1	P/kPa	t/°C	x_1	P/kPa
10.7	0.0034	4.27	19.9	0.0034	4.56
	0.0336	10.00		0.0336	17.85
	0.0614	19.09		0.0614	31.50
	0.0803	22.46		0.0803	36.80
	0.1630	51.03		0.1630	74.93
	0.2062	52.83		0.2062	77.00
	0.3127	72.05		0.3127	101.94
	0.5305	98.22		0.5305	137.48
	0.5639	101.48		0.5639	140.25
	0.6358	111.60		0.6358	149.40
	0.6480	108.07		0.6480	149.22
	0.6483	113.97		0.6483	155.95
	0.8320	120.91		0.8320	167.08
	0.8593	118.66		0.8593	164.51
	0.9142	123.07		0.9142	171.90
	0.9733	127.50		0.9733	176.30
24.4	0.6483	183.14	29.6	0.0034	8.12
	0.8320	195.50		0.0336	29.95
39.3	0.0034	13.81		0.0614	50.52
	0.0336	45.72		0.0803	59.23
	0.0614	75.90		0.1630	108.23
	0.0803	90.97		0.2062	112.13
	0.1630	151.34		0.3127	144.05
				0.5305	188.43
				0.5639	191.71
				0.6358	202.87
				0.6480	202.74
			48.9	0.0034	22.42
				0.0336	65.25
				0.0614	109.07
				0.0803	135.04

Table VI. NRTL Parameters for Amine + Water

mixture	a_1	a_2	b_1	b_2	α
dimethylethylamine + water	4620.0	−2413.5	−12.42	9.90	0.6146
trimethylamine + water	3842.4	−4599.5	−9.88	16.58	0.6107

length exceeded 0.76 m (i.e., 101.3 kPa), allowing the vapor pressure to be measured directly. The use of a second, pressure-balancing fluid exerting its vapor pressure on the opposite leg of the manometer was avoided.

A mixture of tertiary amine and water was charged to the equilibrium cell and refluxed at atmospheric pressure for 10 min, and the filled cell was frozen in liquid nitrogen, evacuated, and sealed. The sealed cell was connected to the evacuated manometer and the entire apparatus immersed in a well-stirred water bath. A water bath heater was employed to control the water bath temperature to within ±0.2 K. The charge was assumed to be in equilibrium when no further change in vapor pressure was observed (approximately 2 h).

Compositions were not corrected for increasing vapor pressure in the apparatus as this correction is a function of both the cell and charge volumes, and the sampling temperature. At amine concentrations greater than 5%, the measured composition was estimated to be 1.5–6.5% greater than that at equilibrium conditions. However, at low amine concentrations, this error increased to a maximum of approximately +12.5%. The magnitude to this error results in part from the necessity of sampling at temperatures below 0 °C to prevent flashing of the mixture.

In both experiments, the water bath temperature was measured with a platinum resistance probe attached to a high-precision bridge. Ambient pressure was measured with an aneroid barometer with bimetallic strip temperature compensation, accurate to ±13.3 Pa. Vapor pressure readings were determined from the mercury manometer using a cathetometer accurate to better than ±0.1 mm. These values were adjusted for ambient pressure and bath temperature. Amine compositions were determined by back-titration of an acidified sample of the mixture using a methyl red indicator. Compositions were not corrected for increasing vapor pressure in the apparatus as the cell volume was not determined. Tests with mixtures of ammonia and water indicate that inadequate outgassing elevated the experimentally determined vapor pressure by a maximum of 800 Pa.

Results

Liquid–Liquid Equilibrium. Filled ampules were not evacuated prior to sealing in some initial experiments with dimethylethylamine + water mixtures. In these experiments, the cloud point temperature appeared to decrease with time and a yellow color change was observed. Fourier transform NMR spectra were obtained from samples of the discolored mixture to identify and quantify the source of discoloration. The discoloration appears as a consequence of amine decomposition with approximately 2% decomposition measured in one sample. Clearly, industrial applications employing these amines as solvents would be severly constrained by the poor stability of the amine. Some hysteresis was observed between measurements of the cloud point with increasing and decreasing water bath temperature.

Liquid–liquid phase separation was not observed for trimethylamine + water mixtures at temperatures up to 160 °C. However, phase separation was observed when sodium chloride was added to mixtures of trimethylamine and water. For mixtures of trimethylamine in 3 mass % sodium chloride solution, phase separation was observed at temperatures above

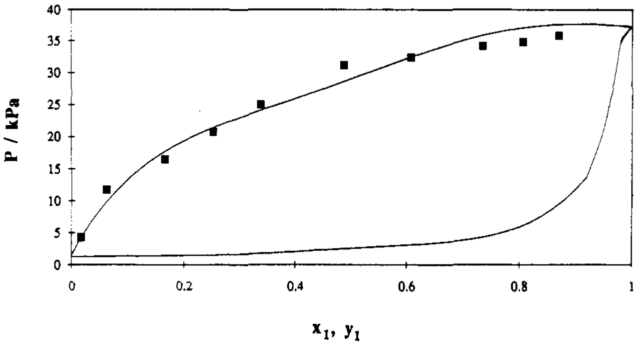

Figure 3. Calculated dew point and bubble point curves for dimethylethylamine + water at 10.0 °C: ■, experimental x_1; —, NRTL prediction.

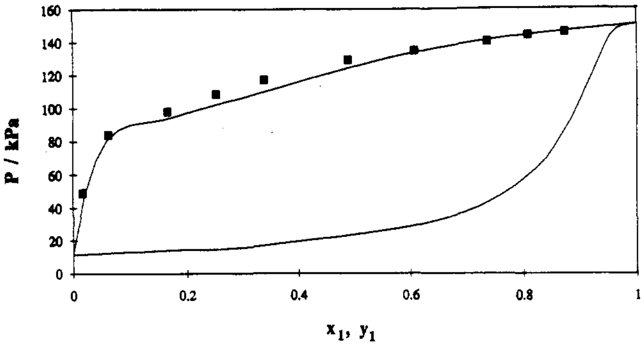

Figure 4. Calculated dew point and bubble point curves for dimethylethylamine (1) + water (2) at 48.6 °C: ■, experimental x_1; —, NRTL prediction.

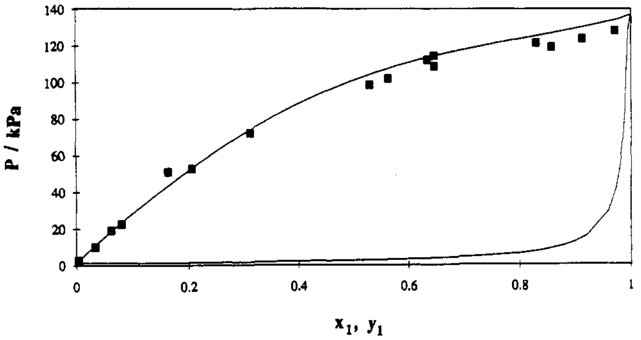

Figure 5. Calculated dew point and bubble point curves for trimethylamine (1) + water (2) at 10.7 °C: ■, experimental x_1; —, NRTL prediction.

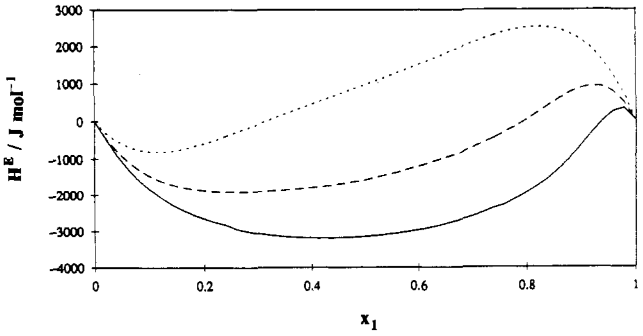

Figure 6. Calculated enthalpy of mixing for dimethylethylamine (1) + water (2) as a function of temperature: - - -, 50 °C; – – –, 30 °C; —, 10 °C.

130 °C. For mixtures of dimethylethylamine and water, phase separation was observed at temperatures above 98.8 °C.

The experimental liquid-phase solubility data for dimethylethylamine + water and trimethylamine + 3 mass % sodium chloride solution are presented in Tables I and II, respectively. The data are also summarized graphically in Figures 1 and 2. The achievable liquid-phase separation declines considerably as the boiling point of the amine increases.

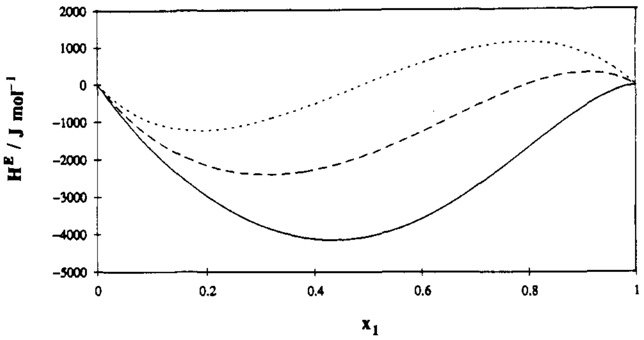

Figure 7. Calculated enthalpies of mixing for trimethylamine (1) + water (2) as a function of temperature: - - -, 50 °C; – – –, 30 °C; —, 10 °C.

Pure Component Vapor Pressure. The vapor pressures of trimethylamine can be calculated using Antoine constants fitted to the experimental data presented by Stull (*14*) (eq 1). As no data exist for the vapor pressure of dimethylethylamine, the static vapor–liquid equilibrium apparatus was used to measure the vapor pressure of pure dimethylethylamine over a range of temperatures. The observed vapor pressure data (Table III) were correlated by eq 2 with an accuracy of ±350 Pa.

trimethylamine

$$\log (P/\mathrm{kPa}) = 5.9411 - \frac{937.49}{T/\mathrm{K} - 37.79} \qquad (1)$$

dimethylethylamine

$$\log (P/\mathrm{kPa}) = 6.19185 - \frac{1171.74}{T/\mathrm{K} - 29.71} \qquad (2)$$

Vapor–Liquid Equilibrium. The vapor pressures of various dimethylethylamine + water and trimethylamine + water mixtures were determined at temperatures between 10 and 50 °C over a range of compositions. Results of these experiments are presented in Tables IV and V. The data are correlated with a five-parameter NRTL (*12*) model (eq 3), where the adjustable parameters $g_{12} - g_{22}$ and $g_{21} - g_{11}$ are functions of temperature. As the measured vapor pressures were low, the vapor and liquid fugacity coefficients and the Poynting corrections were neglected. Values for the five parameters were obtained by nonlinear, least-squares regression. These parameters are presented in Table VI. Using these parameters, the experimental vapor pressures could be predicted with average accuracies of ±4.9% and ±5.9% for dimethylethylamine + water and trimethylamine + water mixtures, respectively. Figures 3 and 4 present a comparison between the calculated and experimental vapor pressures of dimethylethylamine + water mixtures at 10.0 and 48.6 °C, respectively. A similar comparison between calculated and experimental vapor pressures for mixtures for trimethylamine and water at 10.7 °C is presented in Figure 5.

Enthalpy of Mixing. Unfortunately, experimental enthalpy of mixing data are not available for these mixtures. However, a knowledge of the temperature dependence of the excess Gibbs free energy function allows these excess enthalpies to be calculated using eq 4. Several researchers (*1, 11,*

$$\frac{G^E}{RT} = x_1x_2\left[\frac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1G_{12}}\right] \quad (3)$$

$$G_{12} = \exp(-\alpha\tau_{12}) \quad (3a)$$

$$G_{21} = \exp(-\alpha\tau_{21}) \quad (3b)$$

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} \quad (3c)$$

$$\tau_{21} = \frac{g_{21} - g_{11}}{RT} \quad (3d)$$

$$g_{12} - g_{22} = a_1 + b_1(T/\mathrm{K}) \quad (3e)$$

$$g_{21} - g_{11} = a_2 + b_2(T/\mathrm{K}) \quad (3f)$$

$$H^E = -RT^2[\partial[G^E/RT]/\partial T]_P \quad (4)$$

13) have introduced temperature-dependent interaction parameters into local composition models in order to correctly represent the functional dependence with temperature of the excess Gibbs free energy function. The five-parameter NRTL model employed in this study is one such model. Calculated enthalpy of mixing data are plotted in Figures 6 and 7 for dimethylethylamine + water and trimethylamine + water, respectively.

List of Symbols

a_i,b_i,α	NRTL adjustable parameters
g_{ij}	energy of interaction between an *i–j* pair of molecules
G^E	excess Gibbs energy
G_{ij}	coefficient defined by eqs 3a and 3b
H^E	enthalpy of mixing
P	vapor pressure
R	gas constant
T	temperature
x_i	mole fraction of component *i*

Greek Letters

τ_{ij}	coefficient defined by eqs 3c and 3d

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