Vapor−Liquid Equilibrium in Methyl Ethyl Ketone + Ketazine and Liquid−Liquid Equilibrium in Water + Ketazine Mixtures

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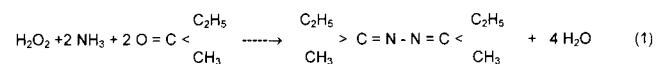
Boiling temperature measurements are reported for methyl ethyl ketone + 2-butanone (ethyl methyl ketazine, referred to as ketazine hereafter) mixtures over the whole composition range at pressures of 95.3, 53.3, 39.9, and 26.7 kPa using a Swietoslawski type ebulliometer. The data are found to be well represented by both Wilson and NRTL models. Liquid−liquid equilibria in the temperature range of 293.15−343.15 K are also measured for water + ketazine binary mixtures.

Introduction

During the development of an ecofriendly process for the production of hydrazine hydrate by the peroxide route, mixtures of methyl ethyl ketone + ketazine and water + ketazine occur. These mixtures have to be separated into pure components for carrying out further reactions or for the treatment of water being discharged as environmentally safe effluent. Vapor−liquid equilibrium data on the methyl ethyl ketone + ketazine system and liquid−liquid equilibrium data in the temperature range of 293.15−343.15 K for ketazine + water would be useful in the design of unit operations for the needed separation processes. No published VLE or LLE data were found for these mixtures.

Experimental Section

Materials. Deionized distilled water, extra pure grade methyl ethyl ketone procured from E. Merck, Mumbai, India, and pure ketazine produced by the following reaction[1] and fractionally distilled are used for the present set of experimental studies.

$$H_2O_2 + 2\,NH_3 + 2\,O=C\underset{CH_3}{\overset{C_2H_5}{<}} \;\xrightarrow{\hspace{1cm}}\; \underset{CH_3}{\overset{C_2H_5}{>}}C=N-N=C\underset{CH_3}{\overset{C_2H_5}{<}} \;+\; 4\,H_2O \qquad (1)$$

Gas chromatographic analysis has show that the purity of the substances is >99%. Some of the characteristic physical properties are compared with the available literature data[2] in Table 1.

Apparatus and Methods. *Vapor−Liquid Equilibria.* A Swietoslawski type ebulliometer very similar to the one described by Hala et al.[3] was used. Connection of the ebulliometer to a good vacuum system, through an in-line mercury manometer, facilitated the measurement and maintenance of the total pressure of the system to within ±0.133 kPa of the chosen value. The equilibrium temperatures are measured using a platinum resistance thermometer, placed in a thermowell (filled with mercury), located at a position in the apparatus where the equilib-

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Table 1. Comparison of the Physical Properties of the Substances Measured in This Work with the Literature Data

substance	density at 293 K/(kg·m⁻³)		normal boiling point/K	
	this work	lit.[1]	this work	lit.[1]
ketazine	840.0		444.65	
methyl ethyl ketone	805.0	804.9	352.70	352.73
water	998.0	998.2	373.15	373.15

rium gas−liquid mixture impinges. The thermometer used in the present set of experiments is calibrated by means of point to point comparison with a standard platinum resistance thermometer, certified by the National Bureau of Standards (now NIST), Gaithersburg, MD. The temperatures measured are accurate to within ±0.1 K. The heating rate is adjusted to yield the desired condensate drop rate of ~30 per minute, following the suggestion of Hala et al.[3] The equilibrium temperature is noted after a steady drop rate and a constant temperature have been maintained for at least 30 min. The liquid mixture samples for the studies are prepared gravimetrically using a Mettler balance accurate to within ±0.0001 g. The compositions reported are expected to be within ±0.1%.

Liquid−Liquid Equilibria. Mixtures of the samples in different proportions of the pure components, prepared by weighing them accurately by means of a Mettler balance accurate to within ±0.0001 g, are placed in a thermostated round-bottom flask with a stirring arrangement, maintained to within ±0.1 K of the chosen temperature and stirred continuously for at least 6 h. The resulting mixed solutions are allowed to settle and separated into the aqueous and organic layers. A small sample from each phase is drawn and analyzed. Equilibrium conditions are expected to have been attained when, even after the samples have been maintained under the same conditions of temperature and continuous stirring for a further period of 6 h, the mixtures show no change in the compositions of the phases. The compositions of both phases are determined by means of a gas chromatograph. On the basis of the extensive testing of the synthetically prepared samples, the compositions reported in the liquid−liquid data are accurate to within ±0.1%.

Table 2. ($T - x_1$) Measurements for Methyl Ethyl Ketone (1) + Ketazine (2) System

26.7 kPa		39.9 kPa		53.2 kPa		95.3 kPa	
T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1
396.65	0.0000	409.85	0.0000	420.05	0.0000	442.05	0.0000
355.55	0.1560	368.35	0.1560	388.15	0.1000	409.95	0.1000
339.95	0.3057	352.05	0.3057	371.75	0.2000	392.65	0.2000
328.55	0.4450	342.95	0.4450	361.44	0.3000	381.55	0.3000
325.45	0.5950	336.65	0.5950	354.35	0.4000	373.75	0.4000
320.35	0.7784	331.25	0.7784	348.95	0.5000	367.85	0.5000
318.15	0.8743	328.75	0.8743	344.75	0.6000	363.25	0.6000
316.15	0.9690	326.55	0.9690	341.45	0.7000	359.55	0.7000
315.35	1.0000	325.85	1.0000	338.75	0.8000	356.45	0.8000
				336.15	0.9000	353.65	0.9000
				333.65	1.0000	350.95	1.0000

Table 3. Liquid−Liquid Equilibria for Water + Ketazine System

	equilibrium mole fraction of water	
T/K	aqueous phase	organic phase
293.15		0.1356
303.15	0.9629	0.2894
313.15	0.9396	0.2434
323.15	0.9519	0.2434
333.15	0.9519	0.2385
343.15	0.8808	0.1929

Table 4. Antoine Constants for the Equation $\log(P/\text{kPa}) = A - [B/(T + C)]$

substance	A	B	C
methyl ethyl ketone	6.3323	1367. 96	−36.65
ketazine	5.9817	1501.50	−67.05

Table 5. Representation of the ($T - x$) Measurements by Wilson and NRTL Models

model parameters/K	standard deviation in T/K
Wilson	
$[(\lambda_{12} - \lambda_{11})/R] = -134.9$	0. 06
$[(\lambda_{12} - \lambda_{22})/R] = -372.4$	
NRTL	
$\Delta g_{12} = 894.0$	0. 12
$\Delta g_{21} = -575.9$	
$\alpha_{12} = 0.12$	

Results and Discussion

The experimental $T - x$ measurements on the methyl ethyl ketone (1) + ketazine (2) system are presented in Table 2, and the liquid−liquid equilibrium data are presented in Table 3. The $T - x$ measurements are fitted to the Wilson[4] model in the form

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right] \quad (2)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) + x_1 \left[\frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_1} \right] \quad (3)$$

where

$$\Lambda_{12} = (V_2/V_1) \exp[-(\lambda_{12} - \lambda_{11})/RT] \quad (4)$$

$$\Lambda_{21} = (V_1/V_2) \exp[-(\lambda_{12} - \lambda_{22})/RT] \quad (5)$$

V_1 and V_2 are the liquid molar volumes and λ_{ij} values are the energies of interaction between the molecules designated by the subscripts and the NRTL[5] model in the form

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left\{ \frac{G_{21}}{x_1 + x_2 G_{21}} \right\}^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \quad (6)$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left\{ \frac{G_{12}}{x_2 + x_1 G_{12}} \right\}^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \quad (7)$$

where

$$\ln G_{12} = -\alpha_{12} \tau_{12} \quad (8)$$

$$\ln G_{21} = \alpha_{12} \tau_{21} \quad (9)$$

$$\tau_{12} = \Delta g_{12}/RT \quad (10)$$

$$\tau_{21} = \Delta g_{21}/RT \quad (11)$$

$$\Delta g_{12} = g_{12} g_{11} \quad (12)$$

$$\Delta g_{21} = g_{21} - g_{11} \quad (13)$$

and

$$\alpha_{12} = -0.12 \quad (14)$$

The optimum model parameters are determined by minimizing the objective function defined as

$$\varphi = [(P_{\text{calcd}}/P_{\text{exptl}}) - 1]^2 \quad (15)$$

The Nelder−Mead optimization technique described in detail in Kuester and Mize[6] is used to optimize φ. Vapor pressures, required in the computations, are determined from the Antoine equation with the set of constants noted in Table 4, which represent all of the vapor pressure data on the substances with an average absolute deviation of 0.3%. The constants for methyl ethyl ketone from Reid et al.[7] are converted to the proper units, whereas those for ketazine are the ones determined from the vapor pressure measurements of the present study. The results of the representation by the two models are summarized in Table 5. The data and the representation presented are expected to be useful for design purposes.

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