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Isothermal Vapor–Liquid and Liquid–Liquid Equilibria for the Propane–Ammonia and Propylene–Ammonia Systems

Katsuji Noda,* Katsufumi Inoue, Takashi Asai, and Kiyoharu Ishida

Department of Chemical Engineering, Shizuoka University, Hamamatsu 432, Japan

Vapor–liquid equilibrium data are obtained for the propane–ammonia (273.15, 293.15 K) and propylene–ammonia (263.15, 273.15, 293.15 K) systems. These systems have an upper critical solution temperature. Since the liquid mixture changes from two liquid phases to one liquid phase with rising temperature, vapor–liquid–liquid equilibria have to be evaluated. Experimental vapor–liquid equilibrium data are compared with calculated values from the UNIQUAC equation. Agreement of experimental and calculated results is good, although the simultaneous correlation of liquid–liquid equilibria (mutual solubilities) shows slight discrepancies.

Introduction

Vapor–liquid equilibrium (VLE) data are useful not only for the design of separation equipment, but also for understanding the properties of liquid mixtures. It is difficult at present to correlate or to estimate satisfactorily VLE for partially miscible systems which have a large deviation from Raoult's law. Therefore, it is important to obtain accurate data for VLE and liquid–liquid equilibria (LLE) for complex systems.

This paper presents VLE and LLE data for the binary propane–ammonia and propylene–ammonia systems. VLE data for propane–propylene have been reported by many researchers (*1–3*) and correlated by Bae et al. (*4*) and Howat and Swift (*5*). Ishii et al. (*6*) have determined the upper critical solution temperatures (UCST) of propane–ammonia (306.8 K) and of propylene–ammonia (265.1 K) systems.

Experimental Section

Vapor–liquid equilibria were measured by the static method. The experimental apparatus and procedure are similar to those of Noda et al. (*7*), except for the analysis of the liquid composition. Pressure P measurements were made with a Bourdon pressure gauge. The Bourdon pressure gauge was calibrated with a dead-weight gauge; measurements are reproducible to within ±1 kPa. The temperature T of the water bath was determined by a mercury-in-glass thermometer which was calibrated with a standard one in the National Research Laboratory of Metrology, Japan, and maintained within ±0.02 K.

The liquid-phase x_i and vapor-phase y_i mole fractions were determined by means of a gas chromatograph. The column packing was Porapack R, and the column temperature was 368 K. Liquid and vapor compositions were estimated within ±0.001 mole fraction.

Commercially available research-grade propane (Takachiho Chemical, purity >99.9%) and propylene (Takachiho Chemical, purity >99.7%) were used without further purification. Commercially available ammonia was used after simple distillation under pressure, to remove higher- and lower-boiling materials dissolved in it.

Results and Discussion

Experimental VLE data are presented in Tables I and II, and are shown in Figures 1 and 2.

Data for the binary system are correlated by the UNIQUAC equation (*8, 9*) using the maximum-likelihood method (*10*).

Table I. Vapor–Liquid Equilibrium Data for the Propane (2)–Ammonia (1) System: Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Pressure P, and Temperature T

x_1	P/kPa	y_1	x_1	P/kPa	y_1
		T = 273.15 K			
0.0	473	0.0	0.974[a]	892	0.502
0.025	575	0.172	0.981	813	0.557
0.037	619	0.231	0.988	741	0.610
0.047	662	0.270	0.993	647	0.691
0.063	720	0.330	0.994	618	0.720
0.074	747	0.350	0.996	550	0.795
0.083	772	0.375	0.997	519	0.841
0.103	817	0.416	0.998	489	0.890
0.139	867	0.475	1.0	430	1.0
0.157[a]	892	0.502			
		T = 293.15 K			
0.0	836	0.0	0.943[a]	1643	0.540
0.022	974	0.139	0.957	1567	0.577
0.038	1049	0.203	0.968	1455	0.620
0.069	1219	0.293	0.971	1410	0.642
0.098	1332	0.352	0.984	1225	0.735
0.105	1355	0.363	0.987	1167	0.763
0.131	1448	0.402	0.991	1103	0.802
0.185	1544	0.461	0.995	1007	0.852
0.247	1611	0.502	0.998	928	0.914
0.273	1629	0.514	1.0	857	1.0
0.333[a]	1643	0.540			

[a] Liquid–liquid equilibrium.

The activity coefficients γ_i are expressed in the form

$$\ln \gamma_i = \ln (\phi_i/x_i) + (z/2)q_i \ln (\theta_i/\phi_i) + l_i(\phi_i/x_i)\sum_j (x_j l_j) - q_i\{\ln (\sum_j \theta_j \tau_{ji}) - 1 + \sum_j (\theta_j \tau_{ij}/\sum_k (\theta_k \tau_{kj}))\} \quad (1)$$

where

$$\phi_i = x_i r_i/\sum_i (x_i r_i) \qquad \theta_i = x_i q_i/\sum_i (x_i q_i) \quad (2)$$

$$l_i = (z/2)(r_i - q_i) - (r_i - 1) \quad (3)$$

$$\tau_{ji} = \exp(-a_{ji}/T) \quad (4)$$

and z is the coordination number (z = 10). r and q are structural size parameters and structural area parameters, and are cited from Prausnitz et al. (*11*). a_{ij} are the adjustable parameters.

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Table II. Vapor–Liquid Equilibrium Data for the Propylene (2)–Ammonia (1) System: Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Pressure P, and Temperature T

x_1	P/kPa	y_1	x_1	P/kPa	y_1
		T = 263.15 K			
0.0	427	0.0	0.921	647	0.454
0.030	532	0.182	0.955	621	0.485
0.046	564	0.244	0.959	603	0.499
0.083	600	0.313	0.972	564	0.533
0.121	630	0.355	0.988	452	0.657
0.193	645	0.391	0.989	413	0.715
0.277	653	0.407	0.990	401	0.737
0.338	655	0.427	0.991	392	0.748
0.426[a]	657	0.432	0.994	369	0.793
0.857[a]	657	0.432	1.0	291	1.0
0.896	651	0.440			
		T = 273.15 K			
0.0	584	0.0	0.621	891	0.483
0.016	620	0.062	0.687	889	0.487
0.078	741	0.239	0.771	888	0.489
0.099	765	0.271	0.773	888	0.489
0.105	774	0.290	0.848	880	0.494
0.110	777	0.291	0.860	875	0.505
0.147	811	0.322	0.872	868	0.511
0.297	881	0.418	0.901	849	0.523
0.317	883	0.419	0.914	836	0.540
0.339	887	0.428	0.962	721	0.621
0.464	892	0.462	0.978	658	0.669
0.472	891	0.463	0.991	562	0.781
0.590	891	0.471	0.993	505	0.859
		T = 293.15 K			
0.0	1017	0.0	0.741	1566	0.526
0.022	1142	0.108	0.844	1530	0.546
0.046	1213	0.162	0.876	1505	0.558
0.076	1305	0.236	0.922	1443	0.585
0.131	1416	0.311	0.931	1422	0.605
0.192	1496	0.367	0.966	1305	0.662
0.226	1523	0.388	0.973	1225	0.700
0.292	1552	0.421	0.989	1081	0.839
0.378	1557	0.462	0.985	1030	0.794
0.494	1586	0.494	0.993	938	0.917
0.600	1579	0.511			

[a] Liquid–liquid equilibrium.

The computer programs used in this work are similar to those described by Prausnitz et al. (*11*), and the pure component parameters (r, q) are obtained from Prausnitz et al. (*11*). For binary VLE, the parameters sought are those that minimize the objective function

$$S=\sum_{n=1}^{M}\left\{\frac{(P_{\mathrm{calcd},n}-P_{\mathrm{exptl},n})^2}{\sigma^2(P)}+\frac{(T_{\mathrm{calcd},n}-T_{\mathrm{exptl},n})^2}{\sigma^2(T)}+\frac{(x_{1,\mathrm{calcd},n}-x_{1,\mathrm{exptl},n})^2}{\sigma^2(x_1)}+\frac{(y_{1,\mathrm{calcd},n}-y_{1,\mathrm{exptl},n})^2}{\sigma^2(y_1)}\right\} \qquad (5)$$

where σ^2 is the estimated variance of each of the measured variances and $\sigma(P)$ = 1 kPa, $\sigma(T)$ = 0.02 K, and $\sigma(x)$ = $\sigma(y)$ = 0.001.

Pure-component vapor pressures are calculated by using the Frost–Kalkwarf equation whose parameters are available or can be determined from the literature (*12–14*). The pure vapor pressures of propane and propylene are measured in this apparatus and listed in Tables I and II. The observed values are in agreement with calculated values within the standard deviation (±1 kPa).

Figure 1 shows a comparison of the calculated results with experimental data for the propane–ammonia system at 273.15 and 298.15 K. Figure 2 shows a comparison of the calculated results with experimental data for the propylene–ammonia system at 263.15, 273.15, and 298.15 K.

Table III. Parameters a_{ij} and Root Mean Square Deviations (RMS)[a] in Temperature T, Liquid Mole Fraction x, Vapor Mole Fraction y, and Pressure P for the Propane (2)–Ammonia (1) and Propylene (2)–Ammonia (1) Systems

T/K	a_{21}/K	a_{12}/K	RMS(T)/K	RMS(x_1)	RMS(P)/kPa	RMS(y_1)
			Propane–Ammonia			
273.15	376.2	587.6	0.01	0.0006	5.5	0.0061
298.15	279.6	543.9	0.03	0.0022	8.3	0.0088
			Propylene–Ammonia			
263.15	235.0	549.1	0.02	0.0074	10.5	0.0043
273.15	231.2	433.1	0.02	0.0031	7.8	0.0100
293.15	210.7	414.4	0.04	0.0075	8.8	0.0050

[a] $\mathrm{RMS}(Q) = \{\sum_{i=1}^{M}(Q_{\mathrm{calcd}} - Q_{\mathrm{exptl}})_i^2/M\}^{0.5}$. ($M$ = number of data).

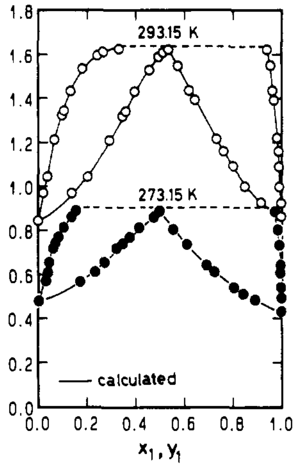

Figure 1. Vapor–liquid equilibria for the ammonia (1)–propane (2) system: pressure P as a function of the mole fraction of ammonia, x_1, y_1.

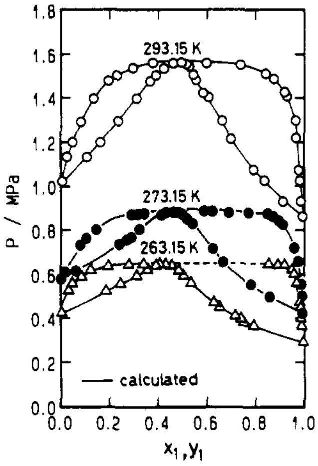

Figure 2. Vapor–liquid equilibria for the ammonia (1)–propylene (2) system: pressure P as a function of the mole fraction of ammonia, x_1, y_1.

Table III lists the parameters and the root mean square deviations (RMS) in total pressure, temperature, and liquid and vapor compositions. Table IV lists the calculated and experimental x, P, and y at liquid–liquid equilibrium. Table IV also lists the experimental and calculated P and y_1 (=x_1) of an azeotropic mixture.

Tables III and IV and Figures 1 and 2 show that the calculated values represent the experimental ones fairly well, although further development is needed for more precise agreement in the three-phase region.

Table IV. Calculated and Experimental Heterogeneous (LLE) or Homogeneous Azeotropic Pressure P and Mole Fractions (x', x'', y) for the Propane (2)–Ammonia (1) and Propylene (2)–Ammonia (1) Systems at Temperature T

T/K	$x'_{1,\mathrm{exptl}}$	$x'_{1,\mathrm{calcd}}$	$x''_{1,\mathrm{exptl}}$	$x''_{1,\mathrm{calcd}}$	P_{exptl}/MPa	P_{calcd}/MPa	$y_{1,\mathrm{exptl}}$[a]	$y_{1,\mathrm{calcd}}$[a]
				Propane–Ammonia				
273.15[b]	0.157	0.179	0.974	0.986	0.892	0.904	0.502	0.493
298.15[b]	0.333	0.348	0.943	0.939	1.643	1.667	0.540	0.532
				Propylene–Ammonia				
263.15[b]	0.426	0.340	0.857	0.886	0.657	0.669	0.432	0.429
273.15[c]					0.892	0.885	0.462	0.465
298.15[c]					1.586	1.599	0.494	0.497

[a] Azeotropic composition ($x_1 = y_1$). [b] Heterogeneous azeotrope. [c] Homogeneous azeotrope.

Glossary

a	binary interaction parameter, K^{-1}
l	defined by eq 3
P	pressure, kPa
q	pure-component area parameter
r	pure-component volume parameter
S	objective function defined by eq 5
T	absolute temperature, K
x	liquid-phase mole fraction
y	vapor-phase mole fraction
z	coordination number

Greek Letters

γ	activity coefficient
θ	area fraction
σ	standard deviation
τ	binary interaction parameter defined by eq 4
ϕ	segment fraction

Subscripts

calcd	calculated
exptl	experimental
i,j,k	components

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