Vapor-Liquid Equilibrium at 29.3° C in System 2,6-Lutidine–Water

ZDZISLAW M. KURTYKA[1]
The Ahmadu Bello University, Zaria, Nigeria

Vapor-liquid equilibrium was investigated at 29.3° C in the system 2,6-lutidine–water. Thermodynamic excess functions g^E, h^E, and Ts^E for this system are given.

The system 2,6-lutidine–water exhibits a closed-loop solubility curve (*2*). The vapor-liquid equilibrium in this system was investigated only in the heterogeneous region, relatively far from the lower critical solution temperature, where miscibility of both constituents is complete (*1*). In addition, excess thermodynamic functions g^E, h^E, and Ts^E were computed to show whether they satisfy requirements in the region of lower consolute temperature.

EXPERIMENTAL

The 2,6-lutidine was isolated from the 142–5° fraction of organic bases by fractional crystallization of this hydrochloride. The hydrochloride was recrystallized from the free base, decomposed with sodium hydroxide, and the liberated base was redistilled through a 30-T.P. column. The physicochemical properties of 2,6-lutidine were: bp at 760 mm 144.1° C, refractive index at 25° C, n_D^{25} 1.4957, mp of picrate 166° C, and temperature of hydrochloride crystal disappearance, 239° C. The 2,6-lutidine was dehydrated prior to fractionation with benzene. Carbon dioxide-free double-distilled water was used to make up the mixtures.

The set for measurement of liquid-vapor equilibrium consisted of two Swietoslawski's ebulliometers (connected in series), vacuum pump, electromagnetic valves, U-shape mercury manometer with a mobile contact, and manostatic system of 300-liter capacity (*9*). A simple ebulliometer filled with water served for measurements of pressure, and a modified one was used for determination of the equilibrium parameters (composition of vapor and liquid and of temperature). To prevent any possible contamination of water in the simple ebulliometer with vapor of 2,6-lutidine, a Dewar flask filled with dry ice was placed in between. The total pressure, P, of the mixture at a given temperature was calculated from the boiling temperature of water using the Antoine equation (*7*). The contents of the respective components in the liquid and in the vapor condensate were taken from the standard curve of refractive indices at 25° C. The ebulliometer was filled each time with mixtures containing varying amounts of 2,6-lutidine, the temperature was adjusted to the required value, and, after reaching equilibrium, the samples of vapor and liquid were collected and analyzed.

RESULTS

In Table I are given the results of liquid-vapor equilibrium measurements for the system 2,6-lutidine–water. This table contains the mole fractions of 2,6-lutidine in the liquid, x_1 and in the vapor, y_1, the total pressure, P, the relative volatility, α, as defined by the equation $\alpha = y_1x_2/y_2x_1$, the excess chemical potentials μ_1^E and μ_2^E and the excess free energy of mixing g^E. The μ^E's and g^E's were calculated from the following equations (*8*):

$$\mu_1^E = RT \ln (Py_1/p_1^0x_1) + (B_{11} - V_1^0)(P - p_1^0) \tag{1}$$

$$\mu_2^E = RT \ln (Py_2/p_2^0x_2) + (B_{22} - V_2^0)(P - p_2^0) \tag{2}$$

$$g^E = x_1\mu_1^E + x_2\mu_2^E \tag{3}$$

The corrections for imperfections of the vapor phase were found by computing B for the pure components by Pitzer's

Table I. Vapor-Liquid Equilibrium Data for System 2,6-Lutidine–Water at 29.3° C

x_1	y_1	P, mm Hg	α	μ_1^E	μ_2^E	g^E, cal/mol
0.005	0.077	32.33	16.60	2528.1	−0.4	13
0.013	0.100	32.98	8.43	2130.5	−0.3	28
0.031	0.115	33.06	4.06	1714.6	7.1	59
0.043	0.116	33.09	2.92	1503.9	8.0	69
0.047	0.116	33.15	2.66	1450.5	8.3	75
0.069	0.116	33.19	1.77	1218.9	20.6	104
0.096	0.117	33.23	1.245	1016.8	42.2	136
0.109	0.117	33.27	1.082	957.5	46.7	146
0.115	0.117	33.30	1.009	918.4	53.9	154
0.145	0.117	33.15	0.807	782.9	98.7	176
0.230	0.121	33.11	0.377	526.3	131.5	222
0.319	0.129	32.79	0.313	360.7	204.9	255
0.405	0.135	32.60	0.227	242.1	268.2	258
0.508	0.154	31.65	0.154	152.2	361.0	255
0.624	0.1605	30.34	0.118	65.1	503.0	229
0.701	0.202	28.72	0.108	26.4	585.0	193
0.852	0.340	23.80	0.091	6.8	795.0	123

---

[1] Present address, 575 Jamestown St., Philadelphia, Pa. 19128

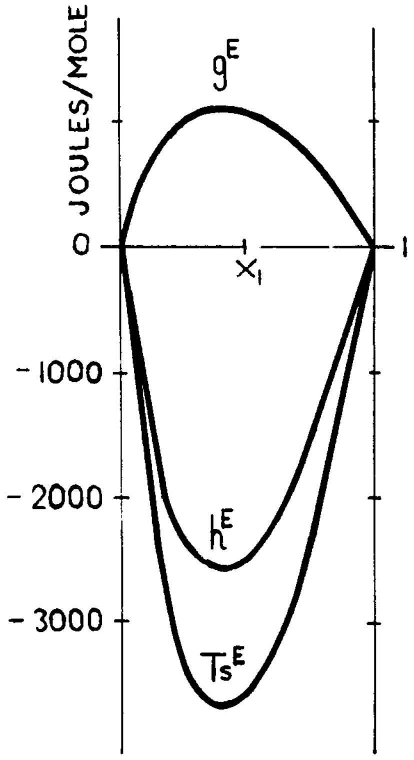

Figure 1. Thermodynamic excess functions for the system 2,6-lutidine–water at 25° C

method (*5*). The unlike interactions in the vapor phase, δ_{12}, were assumed to be zero.

The critical constants T^c and P^c were estimated by means of the Lydersen and Riedel rules (*6*), respectively. The reduced pressure at 0.7 T^c was computed using the Antoine constants to find the values of acentric factor ω. The values of Antoine's constants used in these calculations were taken for 2,6-lutidine from Herington's paper (*3*) and for water from Rossini's data (*7*). The vapor pressures of pure 2,6-lutidine p_1^0 and of water p_2^0 and the second virial coefficients B_{11} and B_{22} (all at 29.3° C) were found to be: p_1^0 7.25 mm, p_2^0 30.34 mm Hg, B_{11} −3460 cm^3/mol and B_{22} −770 cm^3/mol. The acentric factors ω are 0.342 for water and 0.363 for 2,6-lutidine. However, for water at 29° C, McCullough's value of B_{22} is in the neighborhood of −1100 cm^3/mol (*4*). Since the corrections for deviation of vapor from ideal behavior are very small at this temperature and do not affect significantly the values of μ^E and g^E, it is therefore immaterial which value of B_{22} is used for their calculation.

The data were tested for thermodynamic consistency by the equal area method. From reasonable estimates in T ($\pm0.05°$), x and y ($\pm0.1\%$), and B (±50 cm^3), the g^E values are reliable to $\sim2.5\%$ (~7.5 cal for the peak values). The values of g^E at various compositions were graphically smoothed to find the constants for g^E as the function of composition under isothermal conditions.

Table II. Heat of Mixing $h^{M(E)}$ in System 2,6-Lutidine–Water at 25° C

x_1	$-h^M$, cal/mol	$-h^M$, J/mol
0.099	279	1168
0.220	497	2080
0.301	580	2426
0.402	619	2592
0.502	600	2514
0.588	546	2287
0.704	428	1792
0.802	301	1258

The function into which the constants A_0, A_1, and A_2 are to be substituted is:

$$g^E = x_1x_2[A_0 + A_1(x_2 - x_1) + A_2(x_2 - x_1)^2] \quad (4)$$

The constants are: A_0 = 1016, A_1 = 350, and A_2 = 475.

In Table II are listed the values of heat of mixing, h^M at 25° C for the system 2,6-lutidine-water (*10*).

Figure 1 shows the thermodynamic excess functions g^E, h^E, and Ts^E at 25° C for the system 2,6-lutidine-water. From the course of the curves h^E and Ts^E against composition, it is evident that they satisfy the requirement for the region of lower consolute temperature.

ACKNOWLEDGMENT

The author thanks Wladyslaw Woycicki, Institute of Physical Chemistry PAN, Warsaw, Poland, for his permission to use in this system the unpublished data of heat of mixing, $h^{E(M)}$.

LITERATURE CITED

(1) Andon, R. J. L., Cox, J. D., Herington, E. F. G., *Trans. Faraday Soc.*, **53**, 410 (1957).
(2) Cox, J. D., Andon, R. J. L., *J. Chem. Soc.*, **1952**, p 4601.
(3) Herington, E. F. G., Martin, J. F., *Trans. Faraday Soc.*, **49**, 154 (1953).
(4) McCullough, A. P., *J. Amer. Chem. Soc.*, **74**, 4439 (1952).
(5) Pitzer, K. S., Curl, R. F., Jr., *ibid.*, **71**, 2369 (1957).
(6) Reid, R. C., Sherwood, T. K., "The Properties of Gases and Liquids," McGraw-Hill, 1958.
(7) Rossini, F. D., "Selected Values of Properties of Chemical Compounds," Manu. Chem. Assn. Research Project, 1959.
(8) Scatchard, G., Raymond, C. L., *J. Amer. Chem. Soc.*, **60**, 1278 (1938).
(9) Swietoslawski, W., Zieborak, K., Brzostowski, W., *Bull. Acad. Polon. Sci.*, **III**, 5, 305 (1957).
(10) Woycicki, W., Inst. Phys. Chem., Warsaw, private communication, 1968.

RECEIVED for review November 10, 1969. Accepted January 1, 1971.