J. Chem. Eng. Data **2002,** *47,* 643−647

Vapor−Liquid and Liquid−Liquid Equilibrium for Octane + Maleic Anhydride System

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The octane + maleic anhydride system is partially miscible with very limited mutual miscibility. In this work, the vapor−liquid equilibrium and liquid−liquid equilibrium for this system were measured at atmospheric pressure. Results were correlated with the NRTL equation, and allowance was made for nonideality in the gas phase.

Introduction

The octane (1) + maleic anhydride (2) system is a partially miscible system with very limited mutual miscibility. There do not appear to be any VLE and LLE data in the literature. Experimental measurements of VLE for the binary system are difficult, because of a considerable difference between the properties of the two components (see Table 1) and the unusual properties of maleic anhydride. At room temperature, maleic anhydride is a solid and can sublime readily. In addition, when mixed with water, it can hydrolyze to maleic acid. When heated, it can turn into polymers of maleic anhydride. Effective steps were taken in this work to reduce these additional reactions. The VLE and LLE measurements at a pressure of 101.3 kPa are reported in the paper. This work is part of an ongoing investigation of phase equilibrium for systems of industrial interest sponsored by Project 805 of the Design Institute for Physical Property Data of the American Institute of Chemical Engineers. This paper reports measurements made under Project 805.

Experimental Section

The octane, obtained from Hangzhou Oil Refinery, was of 99.5% purity. The maleic anhydride was obtained from Shanghai Reagent Company with a purity of no less than 99.7%. The chemical components used above were not further purified. Their physical properties are listed in Table 1.

Table 1. Physical Properties of Components

component	boiling point, T/K		density, ρ/(g cm^{-3})		refractive index, n_D	
	lit.[a]	exp	lit.[b]	exp	lit.[b]	exp
octane	398.83	398.51	0.7025 (293.15)	0.7096 (293.15)	1.3974 (293.15)	1.3974 (293.15)
maleic anhydride	473.15	472.78	1.309 (333.15)	1.309 (313.15)		

[a] Daubert (1993). [b] Lide (1993−1994).

Vapor−Liquid Equilibrium. VLE was measured with an equilibrium still with circulation of the both liquid and vapor phase; see Figure 1. The circulation still was similar to that used to measure VLE for the partially miscible system of water + isobutyl aldehyde (Huang and Gu, 1985). Because of the special properties of maleic anhydride, both the still and the measurement method were modified as follow. Magnetic stirrers were added to the reboiler and the vapor condensate receiver to ensure thorough mixing of the liquid phase. The melting point and boiling point of the octane are much lower than those of maleic anhydride. To prevent loss of octane vapor and maleic anhydride vapor solidifying on the condenser wall, a two-step condenser was used. The temperature of the cooling water in condenser 1 was about 55 °C while the temperature of the cooling water in condenser II was room temperature.

The equilibrium chamber was covered with two layers of glass wool casting, as shown. By adjusting the voltage of the electrical resistance heater in the casting, its temperature was maintained close to that of the equilibrium chamber. The outside return tubes were also wound with an electrical heating element to prevent partial solidification of maleic anhydride. When heated, maleic anhydride can readily polymerize, so that the measurement of VLE in the maleic anhydride rich side was difficult. To obtain higher accuracy, repeat VLE measurements were made with short time periods.

The temperature was measured using a standard mercury-in-glass thermometer with 0.1 K graduations. The pressure in the equilibrium still was maintained at (101.3 ± 0.03) kPa with the help of a pressure control system, which consists of a mercury manometer, a water manometer, two solenoid valves, two electromagnetic type relays, two reservoirs, and a vacuum pump.

The experimental apparatus was tested by measuring the vapor−liquid equilibrium for water + butanol at 101.3 kPa. The compositions of the vapor-phase and liquid-phase samples for the water + butanol binary system were analyzed by gas chromatography with a thermal conductivity detector connected to an integrator (C-R1B Chromatopac). The experimental results are listed in Table 2 and plotted in Figure 3. It can be seen that the experimental data of this work agree well with the data in the literature (Gmehling and Onken, 1977).

Liquid−Liquid Equilibrium. The sketch of the apparatus used for LLE measurement is shown in Figure 2. The top of the equilibrium cell is connected with a condensation tube and a desiccator vessel filled with silica gel. At the lower temperatures, water is used as the medium of the constant-temperature bath, but for mea-

10.1021/je000383g CCC: $22.00

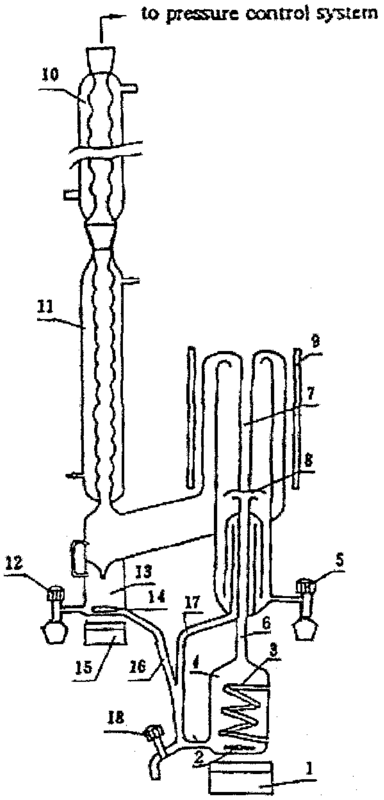

Figure 1. Vapor–liquid equilibrium still: 1, magnetic stirrer; 2, stirring bar; 3, heater; 4, reboiler; 5, sample cock; 6, cottrall tube; 7, thermometer well; 8, equilibrium chamber; 9, two-layer glass casing; 10, condenser II; 11, condenser I; 12, sample cock; 13, receiver of vapor condensate; 14, stirring bar; 15, magnetic stirrer; 16, vapor-phase circulation tube; 17, liquid-phase circulation tube; 18, stopcock.

Table 2. Experimental VLE Data for the Water (1) + Butanol (2) System at 101.3 kPa

T/K	x_1	y_1	T/K	x_1	y_1
379.25	0.1050	0.4240	366.25	0.9670	0.7299
372.75	0.1864	0.5752	368.25	0.9879	0.7902
367.05	0.4527	0.7284	368.65	0.9922	0.8335
366.75	0.5015	0.7419	369.15	0.9910	0.8442
366.55	0.5026	0.7405	370.80	0.9952	0.9353

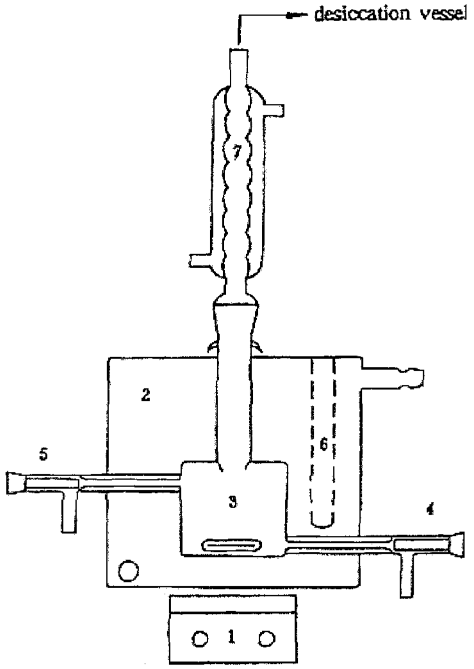

Figure 2. Liquid–liquid equilibrium apparatus: 1, magnetic stirrer; 2, constant-temperature bath; 3, glass equilibrium cell; 4, lower liquid-phase sample cock; 5, upper liquid-phase sample cock; 6, thermometer well; 7, condenser.

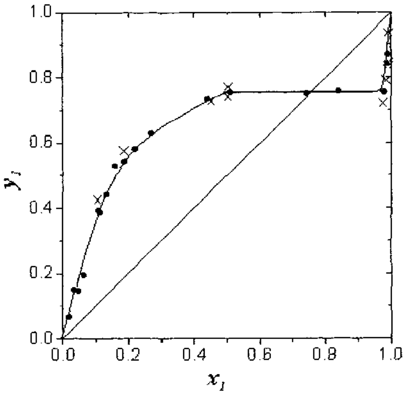

Figure 3. VLE for the water (1) + butanol (2) system at 101.3 kPa: ×, experimental values; ●, literature values.

Table 3. Effect of Stratification Time on Liquid–Liquid Equilibrium (Stirring Time 0.5 h, t = 101 °C)

stratification time/h	mole fraction of maleic anhydride in lower phase	mole fraction of maleic anhydride in upper phase
2	0.9826	0.0280
3	0.9861	0.0274
3.5	0.9860	0.0273

Table 4. Check on Validity of Titration Method

	known mole fraction of maleic anhydride, x	measured mole fraction of maleic anhydride, x_{exp}	$100(x - x_{exp})/x$
1	0.0312	0.0313	0.32
2	0.0615	0.0617	0.32
3	0.8726	0.8708	0.21

surements higher than 80 °C, glycerine was used as the medium. Temperatures were measured using a standard mercury-in-glass thermometer with 0.1 K graduations. To determine LLE, the two liquid phases were thoroughly mixed for 0.5 h at the constant temperature and then the mixture was left to settle for more than 3 h at the same temperature. Samples of each phase were then analyzed.

If the stirring time is longer than 0.5 h, the maleic anhydride in the lower phase tends to polymerize, especially at high temperature. Experiments were done to determine the optimum stratification time; see Table 3.

Analytical Methods. For the liquid–liquid equilibrium, samples were analyzed by titration. For vapor–liquid equilibrium, both titration and gas chromatography were used. The results presented are based primarily on the titration.

The titration method was based on the quantitative analysis of acid anhydrides (Zhang and Zhang, 1990). The uncertainty of the analysis was checked by making several synthetic mixtures of known compositions. The results of this analysis are given in Table 4. They show that the average relative error of the titration is about 0.3%. The gas chromatography column was packed with a support coated with a mixture of dibutyl phthalate and silicone fluid DC-200.

The VLE results are presented in Table 6 and plotted in Figures 4 and 5. The LLE results at various temperature are presented in Table 7.

Table 5. Constants and Values Used in the Data Reduction[a]

component	M	P_c/kPa	T_c/K	Z_c	acentric factor, ω	dipole moment, μ/D
octane	114.23	2.4863×10^3	568.83	0.259	0.3941	0.0
maleic anhydride	98.058	7.28×10^3	721	0.266	0.5463	4.0

Coefficients for the Saturation Vapor Pressure Equation[a]

	A	B	C	D	E
octane	71.886	−6933.9	−7.2653	3.3802×10^{-6}	2.00
maleic anhydride	68.88	−7722.6	−7.2087	7.0169×10^{-3}	1.00

Coefficients of Liquid Density Equation[a]

	A	B	C	D
octane	0.47451	0.2467	568.83	0.2576
maleic anhydride	1.0672	0.2515	710.0	0.2857

[a] Daubert et al. (1993).

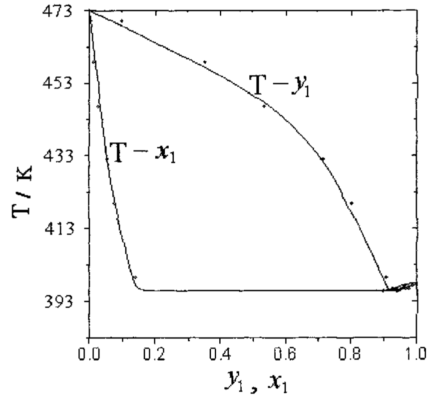

Figure 4. $T-x-y$ for the octane (1) + maleic anhydride (2) at 101.3 kPa: ○, experimental values of x_1; ●, experimental values of y_1; —, calculated values from the NRTL equation.

Table 6. Experimental VLE Results for the Octane (1) + Maleic Anhydride (2) System

experimental data			calculated results	
T/K	x_1	y_1	$(t_{calc} - t)$/°C	$y_{calc} - y$
398.51	1.0000	1.0000	0.00	0.00
397.35	0.9887	0.9664	−1.35	0.0121
396.65	0.9789	0.9385	−1.47	0.0055
396.45	0.9698	0.9276	−1.35	0.0078
396.15	0.9629	0.9170	−1.49	0.0047
395.75	0.9537	0.9292	−1.75	0.0244
395.75	0.9022	0.9441	−1.56	0.0536
399.55	0.1815	0.9086	−3.43	0.0161
420.15	0.0785	0.8142	1.31	0.0164
432.05	0.0566	0.7125	4.74	−0.0175
446.65	0.0289	0.5328	1.89	−0.0048
458.95	0.0135	0.3727	0.25	0.0540
470.25	0.0044	0.1024	1.68	−0.0190
472.78	0.0000	0.0000	0.00	0.00
mean deviation			1.59	0.0168
max. deviation			4.74	0.0540

NRTL Equation Parameters

α	C_1	D_1	C_2	D_2
0.20	−19 934.66	53.875	−2350.86	5.820

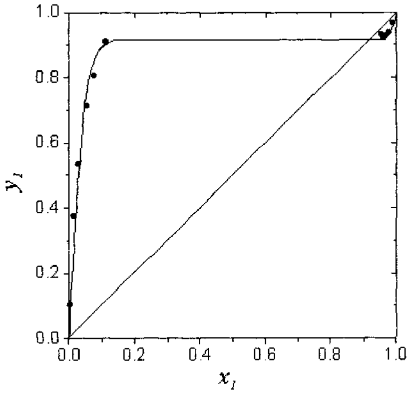

Figure 5. VLE for the octane (1) + maleic anhydride (2) at 101.3 kPa: —, calculated values from the NRTL equation; ●, experimental values.

Table 7. Experimental LLE Results for the Octane (1) + Maleic Anhydride (2) System

	x_2 (maleic anhydride phase)		x_2 (octane phase)	
t/°C	x^α	$x^\alpha_{calc} - x^\alpha$	x^β	$x^\beta_{calc} - x^\beta$
62.20	0.9865	−0.0068	0.0108	0.0010
64.50	0.9890	0.0000	0.0124	0.0000
70.50	0.9936	−0.0067	0.0140	0.0000
73.00	0.9914	−0.0054	0.0145	0.0003
75.80	0.9912	−0.0064	0.0158	−0.0002
93.10	0.9922	−0.0107	0.0183	−0.0001
90.20	0.9898	−0.0122	0.0217	−0.0006
94.80	0.9875	−0.0129	0.0243	−0.0011
101.00	0.9865	−0.0164	0.0273	−0.0010
110.60	0.9717	−0.0100	0.0327	−0.0005
115.20	0.9569	0.0000	0.0355	0.0000
mean deviation[a]		0.0079		0.0004
max. deviation		0.0164		0.0011

NRTL Equation Parameters

α	C_1	D_1	C_2	D_2
0.20	2650.84	−4.831	1571.44	−1.778

[a] Mean deviation $\Delta x = \sum_{j=1}^{n} |(x - x_{calc})|/n$.

Results and Data Correlation

Vapor−Liquid Equilibrium. The basic thermodynamic equation of vapor−liquid equilibrium is

$$p y_i \hat{\phi}_i = \gamma_i x_i f_i^\circ \tag{1}$$

where p is the pressure, y_i and x_i are the mole fractions of component i in the vapor and liquid phases, respectively, γ_i is the activity coefficient of component i in the liquid phase, $\hat{\phi}_i$ is the fugucity coefficient of component i in the vapor phase, and f_i° is the standard state fugacity

$$f_i^\circ = p_i^s \phi_i^s \exp \int_{p_i^s}^{p} \frac{V_i^L}{RT}\, dp \tag{2}$$

For a system at low pressure,

$$f_i^\circ = p_i^s \phi_i^s \exp \frac{V_i^L}{RT}(p - p_i^s) \tag{3}$$

where p_i^{s} and ϕ_i^{s} are the saturated vapor pressure and fugacity coefficient of pure component i, respectively, and V_i^{L} is the molar volume of pure liquid i.

Combining eqs 1, 2, and 3, the liquid-phase activity coefficient γ_i is given by

$$\gamma_i = \frac{\hat{\phi}_i y_i p}{p_i^{\mathrm{s}} \phi_i^{\mathrm{s}} x_i} \exp\{V_i^{\mathrm{L}}(p_i^{\mathrm{s}} - p)/RT\} \tag{4}$$

In the present study the activity coefficients were correlated with the NRTL equation of Renon and Prausnitz (1968).

$$\ln \gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right] \tag{5a}$$

$$\ln \gamma_2 = x_1^2\left[\tau_{21}\left(\frac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2}\right] \tag{5b}$$

and

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

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

$$\tau_{12} = (g_{12} - g_{22})/RT$$

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

where α, $(g_{12} - g_{22})$, and $(g_{21} - g_{11})$ are constants obtained by fitting to the data.

The vapor-phase fugacity coefficient $\hat{\phi}_i$ and pure component fugacity coefficient φ_i^{s} were calculated using the virial equation of state truncated after the second term. The second virial coefficients for the pure components were calculated with the correlation of Tsonopoulos (1974) and Prausnitz et al. (1986).

The cross second virial coefficients B_{ij} ($i \neq j$) were estimated from the correlating equations for the pure components with the following mixing rules.

$$\mu_{ri} = \frac{10^5\mu^2P_{\mathrm{c},ij}}{T_{\mathrm{c},ij}^2} \tag{6}$$

$$\mu = \frac{1}{2}(\mu_i + \mu_j) \tag{7}$$

where $P_{\mathrm{c},ij}$ and $T_{\mathrm{c},ij}$ values were calculated by the mixing rule recommended by Prausnitz et al. (1986).

The critical properties and other parameters required for estimating the second virial coefficient are listed in Table 5. The pure component saturated vapor pressure p_i^{s} and liquid molar volume V_i^{L} were calculated from the equations reported by Daubert and Danner (1993). The NRTL parameters were assumed to be temperature dependent by

$$\frac{g_{12} - g_{22}}{R} = C_1 + D_1T \tag{8a}$$

$$\frac{g_{21} - g_{11}}{R} = C_2 + D_2T \tag{8b}$$

The nonrandomness parameter α was taken as 0.20, as suggested by Renon and Prausnitz (1968). The energy parameters of the NRTL equation given in Table 6 were obtained by minimizing the following objective function.

$$F = \sum_{j=1}^{n}\sum_{i=1}^{2}\left(1 - \frac{y_{i,\mathrm{cal}}}{y_{i,\mathrm{exp}}}\right)_j^2 \tag{9}$$

The calculated values of T, x_1, and y_1 are shown in Table 6 and Figures 4 and 5 along with the experimental data.

Correlation of Liquid−Liquid Equilibrium. The basic equations of the LLE are

$$\gamma_i^{\alpha}x_i^{\alpha} = \gamma_i^{\beta}x_i^{\beta} \tag{10a}$$

$$\sum x_i^{\alpha} = 1 \tag{10b}$$

$$\sum x_i^{\beta} = 1 \tag{10c}$$

The liquid-phase activity coefficients were correlated with the NRTL equation with $\alpha = 0.20$. The two energy parameters of the NRTL equation given in Table 7 were obtained by minimizing the following objective function.

$$F = \sum_{j=1}^{n}\sum_{i=1}^{2}\left(1 - \frac{\gamma_i^{\beta}x_i^{\beta}}{\gamma_i^{\alpha}x_i^{\alpha}}\right)_j^2 \tag{11}$$

The differences between the experimental values and the correlation values are given in Table 7.

Summary

Experimental results show that the octane + maleic anhydride system is partially miscible with very small mutual solubilities. Vapor−liquid−liquid equilibrium occurs at approximately 122.6 °C, which can be obtained from VLE, LLE data and analysis of experimental phenomena. In the data reduction procedure, because this system is strongly nonideal, the virial equation of state was used to calculate the vapor-phase fugacity coefficient, and the liquid-phase activity coefficient was correlated by the NRTL equation. The liquid-phase activity coefficients varied with temperature. The temperature dependences of the two energy parameters of the NRTL equation were determined.

Acknowledgment

The authors also express our thanks to Li Xiangjie, Wang Wuqian, Wang Gonghua, Wang Xiaonuan, and Liu Fei for assistant with the measurements.

Literature Cited

Daubert, T. E.; Danner, R. P. *Data compilation of tables of properties of pure compounds*; AIChE, DIPPR: New York, 1993.

Gmehling, J.; Onken, U. *Vapor liquid equilibrium data collection, aqueous organic systems*, Vol. 1, Part 1; DECHEMA: Frankfurt, 1977.

Huang, R. R.; Gu, F. Y.; Zhang, B.; Hou, Y. J. Phase equilibria for the binary system of water-isobutyl aldehyde. *Huagong Xuebao (Chin. Ed.)* **1985**, *1*, 85−92.

Lide, D. R. *CRC Handbook of Chemistry and Physics*, 74th ed.; Chemical Rubber Publishing Company: Tokyo, 1993−1994.

Prausnitz, J. M.; Lichtenthaler, R. N.; Azevedo, E. G. *Molecular Thermodynamics of Fluid Phase Equilibria*; Prentice Hall Inc.: Englewood Cliffs, NJ, 1986.

Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed; McGraw-Hill Book Company: New York, 1987.

Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J*. **1968**, *14*, 135−144.

Tsonopoulos, C. An emperical correlation of second virial coefficients. *AIChE J*. **1974**, *20*, 263−271.

Zhang, Zh. X.; Zhang, R. G. *Quantitative analysis of organic functional groups (China)*; Chemical Engineering and Industry Press: Beijing, 1990.

Received for review December 20, 2000. Accepted April 30, 2001. The authors would like to express appreciation for the financial support of Design Institute for Physical Property Data of AIChE.

JE000383G