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Vapor Liquid Equilibrium for the Binary Systems of 2-Methylpropane + Ethanenitrile and 2-Methylpropene + Ethanenitrile at 358 K

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Isothermal vapor liquid equilibrium data were measured for two binary systems, 2-methylpropane + ethanenitrile and 2-methylpropene + ethanenitrile, at 358 K. The experimental method incorporates automated vapor- and liquid-phase sampling. The results were correlated by the Soave-Redlich-Kwong equation of state and the Wilson activity coefficient model.

Introduction

Vapor liquid equilibrium (VLE) data must be available in order to be able to design distillation columns with the required accuracy. Estimation methods such as UNIFAC or ASOG are useful when no data are available, but when the system shows a major deviation from ideal behavior, estimation methods do not provide enough accuracy for process design purposes.

Data for systems with ethanenitrile and C4 hydrocarbons are needed for simulation of ethanenitrile behavior in the 2-methyl-2-methoxypropane (MTBE) processes. Ethanenitrile acts as a catalyst poison for ion-exchange catalysts used in the MTBE processes (Marston, 1994).

Experimental Section

Materials. The 2-methylpropane (99.5 mol %) and 2-methylpropene (99+ mol %) were supplied by AGA Oy. The ethanenitrile was provided by Rathburn Chemicals (HPLC grade, 99.5 mol %). The hydrocarbons were used without further purification. The ethanenitrile was dried over molecular sieves and degassed.

Apparatus. A DB Robinson Jefri sapphire glass cell was used for measuring the VLE data (Figure 1). The volume of the cylinder is approximately 66 cm^3. Mixing of the cell contents was done by using a metal mixer, which is moved up and down by a U-shaped magnet moving outside the cylinder.

Temperature measurement was done with a calibrated Systemteknik 1223-R (Frontec) temperature meter (resolution 0.01 K and calibration accuracy 0.05 K). The pressure measurement was done with a pressure transducer (Gems 6600) and a Druck DPI 262 pressure display with the accuracy of 9 kPa. The pressure measurement system was calibrated against a Beamex PC-105 EPM40 pressure calibrator.

Analysis. A vapor and liquid analysis system was built. The vapor and liquid phases were analyzed with a gas chromatograph (HP 5890 II+). The GC had two flame ionization detectors (FIDs), two injectors, and two columns, one for the liquid-phase sample and one for the vapor-phase sample.

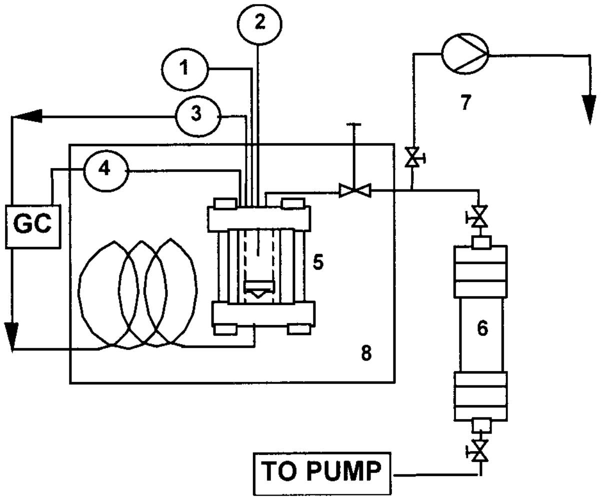

Figure 1. Sapphire cell apparatus: (1) temperature display; (2) pressure display; (3) liquid recirculation pump; (4) vapor sampling system; (5) sapphire glass cylinder; (6) feed cylinder; (7) vacuum pump; (8) thermostated air bath.

The sampling system for the liquid phase consisted of a recirculation pump (Waters 590 HPLC), and the sampling and injection were performed made with a four-port sampling valve attached to the GC. The liquid-phase sample volume was 0.5 μL, and the effect of liquid-phase sampling on the equilibrium is negligible. The liquid sampling line was electrically traced and the temperature held at a temperature approximately 5 K below the equilibrium cell temperature in order to keep the sample in the liquid phase. Before re-entering the equilibrium cell, the temperature of the liquid flow rises to the equilibrium cell temperature in the transfer line part which is situated in the thermostated air bath.

The vapor-phase sampling system was constructed from two six-port sampling valves and a sampling piston (Figure 2). The sampling piston enables us to take representative and reproducible samples from the equilibrium cell into the sampling loop of the six-port sampling valve. The volume of the vapor sample loop was 250 μL. The sample was transported with a carrier gas (He) from the vapor sampling loop to a second six-port sampling valve which injected the vapor sample into the GC. The sampling

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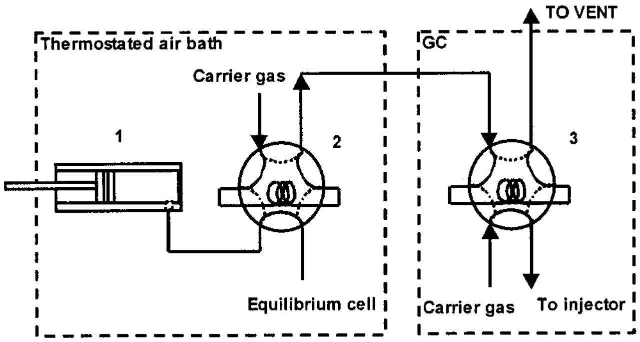

Figure 2. Vapor sampling configuration in the sample-transfer position: (1) sampling piston; (2) six-port vapor sampling valve in the thermostated air bath; (3) six-port vapor sampling valve in the GC.

Table 1. Ethanenitrile Response Factors *Q*, Average Deviations of the Response Factors Avedev. *Q*, Number of Calibration Points *n*, Average of the Average Deviations of the Repeated Samples *K* for the Liquid-Phase *x* and Vapor Phase *y*, and Maximum Average Deviations of Samples *M* for the Systems 2-Methylpropane + Ethanenitrile at 358 K (System 1) and 2-Methylpropene + Ethanenitrile at 358 K (System 2)

system		*Q*	Avedev. *Q*	*K*	*M*
1	*x*	1.80 (n=5)	0.17	0.0053	0.0426
	y			0.0023	0.0068
2	*x*	1.75 (n=6)	0.05	0.0009	0.0018
	y			0.0024	0.0032

valves, the transfer lines, and the carrier gas were heated by electrical tracing to a temperature which is higher than the equilibrium cell temperature in order to avoid condensation. The sampling system was automated and controlled with the GC software.

GC Calibration. GC calibration was done gravimetrically with sample bombs attached to the liquid sampling valve. The sample bombs were pressurized with nitrogen to approximately 2 MPa in order to maintain the hydrocarbon in the liquid phase. Liquid-phase response factors were also used for the vapor-phase analysis. Response factors and average deviations of the response factors are presented in Table 1. For the calibration of the 2-methylpropane + ethanenitrile a solvent (propanenitrile) had to be used because a miscibility gap was detected at temperatures below 320 K. The miscibility gap was detected visually in the equilibrium cell.

Liquid-phase and vapor-phase response factors were checked and found identical within the experimental uncertainty with the 2-methyl-2-butene + ethanenitrile system. Sample vials and manual syringe injection were used in the response factor check.

Procedure. The hydrocarbon was introduced into the sapphire glass cylinder and the pure component vapor pressure was measured. The feed cylinder containing the hydrocarbon was exchanged with a feed cylinder containing degassed ethanenitrile. Some ethanenitrile was transferred into the cell, and the mixing was started simultaneously with the liquid-phase recirculation pump (2 cm^3/min). The liquid was circulated from the top to the bottom of the cell. After 1 h the mixing was terminated and the sample was left for an additional hour to settle. Sampling was repeated four times, and the averages of the recorded temperature, pressure, and composition values were used. After sampling, some of the cell content was removed through the venting line in order to have sufficient volume for an ethanenitrile addition and to remove the small amount of helium gas which was introduced during the vapor-phase sampling. The procedure is repeated for the measurement points to follow. The average deviations of the repeated samples are presented in Table 1. The largest average deviation of the sampling in the 2-methylpropane + ethanenitrile system was at x(2-methylpropane) = 0.4013. The large deviations in the liquid sampling can be due to a miscibility gap at approximately 353 K and below. However, at the temperature 358 K two liquid phases were not observed in the equilibrium cell.

Table 2. VLE Data, Liquid Phase x_1, Vapor Phase y_1, Mole Fractions, Pressure *P*, Temperature *T*, Activity Coefficients γ_i, and ln(γ_1/γ_2) for the 2-Methylpropane (1) + Ethanenitrile (2) System

x_1	y_1	P/MPa	T/K	γ_1	γ_2	ln(γ_1/γ_2)
0.0000	0.0000	0.111	358.08			
0.0299	0.6872	0.410	358.07	7.90	1.06	2.00
0.0310	0.6935	0.420	358.07	7.86	1.07	2.00
0.0565	0.7868	0.633	358.06	7.08	1.08	1.88
0.0814	0.8201	0.803	358.07	6.29	1.12	1.72
0.0898	0.8259	0.853	358.05	6.04	1.15	1.66
0.1055	0.8397	0.933	358.06	5.62	1.15	1.59
0.1475	0.8584	1.092	358.07	4.66	1.18	1.37
0.1681	0.8645	1.153	358.06	4.29	1.20	1.28
0.2262	0.8753	1.268	358.05	3.47	1.25	1.02
0.4013	0.8928	1.390	358.10	2.13	1.45	0.38
0.5810	0.8957	1.417	358.12	1.49	2.03	−0.31
0.6563	0.9014	1.426	358.13	1.34	2.35	−0.56
0.7740	0.9061	1.449	358.10	1.15	3.43	−1.09
0.8534	0.9213	1.473	358.20	1.07	4.46	−1.42
0.9147	0.9337	1.491	358.25	1.02	6.49	−1.85
0.9646	0.9636	1.497	358.09	1.01	8.67	−2.15
1.0000	1.0000	1.491	358.14			

Table 3. VLE Data, Liquid Phase x_1, Vapor Phase y_1, Mole Fractions, Pressure *P*, Temperature *T*, Activity Coefficients γ_i, and ln(γ_1/γ_2) for the 2-Methylpropene (1) + Ethanenitrile (2) System

x_1	y_1	P/MPa	T/K	γ_1	γ_2	ln(γ_1/γ_2)
0.0000	0.0000	0.109	357.83			
0.0614	0.7012	0.401	357.82	4.09	1.04	1.37
0.1069	0.7860	0.568	357.83	3.61	1.05	1.23
0.1352	0.8111	0.655	357.85	3.34	1.08	1.13
0.1599	0.8283	0.721	357.84	3.14	1.09	1.06
0.2459	0.8564	0.891	357.85	2.53	1.19	0.75
0.2962	0.8653	0.962	357.84	2.26	1.26	0.58
0.3627	0.8721	1.030	357.83	1.96	1.39	0.35
0.4519	0.8854	1.100	357.80	1.69	1.51	0.11
0.5849	0.8941	1.167	357.85	1.38	1.90	−0.33
0.6703	0.9052	1.210	357.88	1.25	2.19	−0.56
0.7965	0.9233	1.264	357.89	1.11	2.95	−0.98
0.8989	0.9463	1.313	357.91	1.03	4.25	−1.41
0.9532	0.9669	1.344	357.99	1.01	5.72	−1.73
1.0000	1.0000	1.366	357.84			

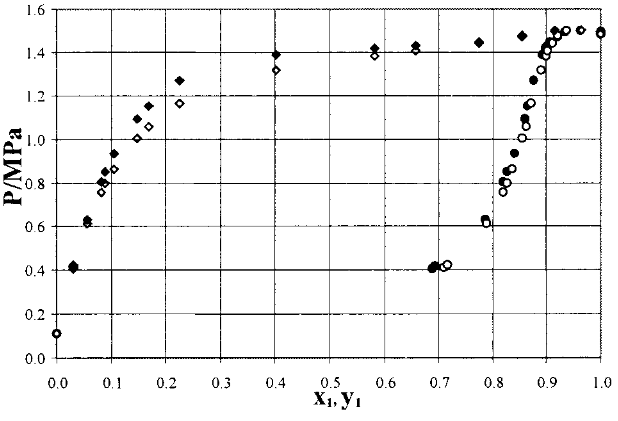

Figure 3. Pressure−composition diagram for the 2-methylpropane (1) + ethanenitrile (2) system at 358 K: (◆) x_1; (●) y_1; (◇) x_1 calculated; (○) y_1 calculated.

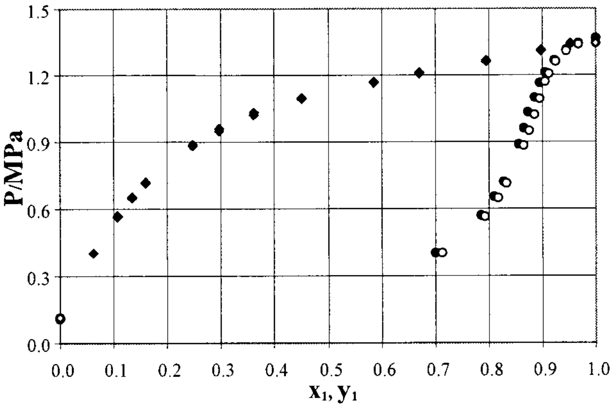

Figure 4. Pressure–composition diagram for the 2-methylpropene (1) + ethanenitrile (2) system at 358 K: (◆) x_1; (●) y_1; (◇) x_1 calculated; (○) y_1 calculated.

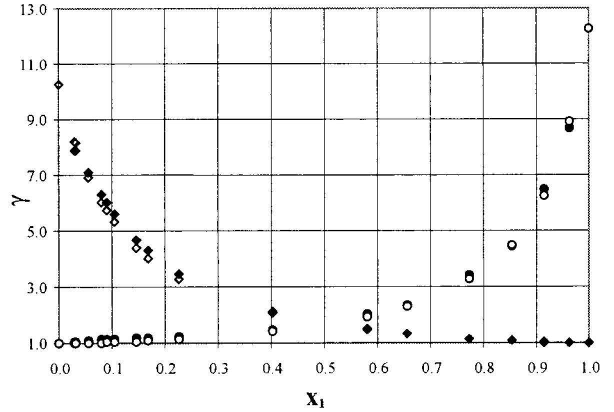

Figure 5. Activity coefficient–composition diagram for the 2-methylpropane (1) + ethanenitrile (2) system at 358 K: (◆) γ_1 from data; (●) γ_2 from data; (◇) γ_1 model; (○) γ_2 model.

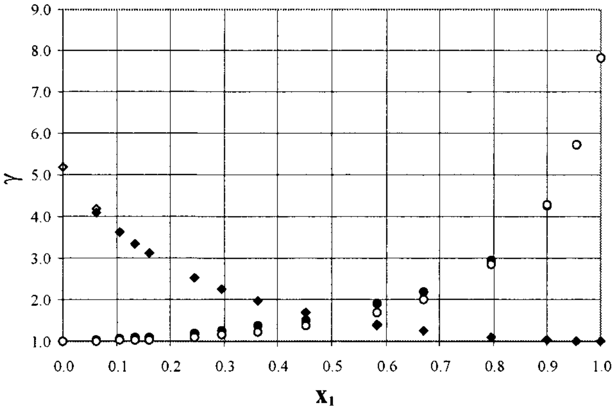

Figure 6. Activity coefficient–composition diagram for the 2-methylpropene (1) + ethanenitrile (2) system at 358 K: (◆) γ_1 from data; (●) γ_2 from data; (◇) γ_1 model; (○) γ_2 model.

Table 4. Critical Temperature T_c, Critical Pressure P_c, Acentric Factor ω, Liquid Molar Volume (Used for Fitting the Wilson Equation Parameters) v_i, Pure Component Vapor Pressure Correlation Parameters for the Antoine Equation A, B, and C, Pure Component Vapor Pressure Correlation Parameters for the Wagner Equation a_i, (i = 1–4) and Recommended Temperature Range of the Pure Component Vapor Pressure Correlations T_{min}, T_{max}

	ethanenitrile[f]	2-methylpropane[g]	2-methylpropene[g]
T_c/K	545.5[a]	408.1[b]	417.9[c]
P_c/MPa	4.830[a]	3.648[b]	3.999[c]
V_c/cm^{-3}·mol^{-1}	173.0[a]	262.7[b]	238.9[c]
ω	0.327[a]	0.183[a]	0.194[a]
v_i/cm^{-3}·mol^{-1}	52.86[d]	104.3[d]	94.46[d]
A or a_1	−7.365[e]	−6.956[a]	−6.955[a]
B or a_2	2945[e]	1.501[a]	1.357[a]
C or a_3	49.15[e]	−2.527[a]	−2.452[a]
a_4		−1.498[a]	−1.461[a]
T_{min}/K	260.0[e]	165.0[a]	170.0[a]
T_{max}/K	390.0[e]	408.2[a]	417.9[a]

[a] Reid et al., 1988. [b] Daubert, 1996. [c] Tsonopoulos and Ambrose, 1996. [d] Gmehling and Onken, 1977. [e] Reid et al., 1977. [f] Antoine equation used as vapor pressure correlation. [g] Wagner equation used as vapor pressure correlation.

Results and Discussion

The data measured, activity coefficients and ln(γ_1/γ_2), are reported in Tables 2 and 3 and Figures 3–6. Azeotropic behavior was observed for the 2-methylpropane (1) + ethanenitrile (2) binary with $x_1 = 0.962$, $T = 358.09$ K, and $p = 1497$ kPa. A miscibility gap was detected visually below 320 K. No miscibility gap was observed visually at the temperature 353 K. Further studies are required to investigate the liquid liquid equilibrium behavior of the 2-methylpropane + ethanenitrile binary.

For the 2-methylpropene + ethanenitrile binary no azeotrope was detected at approximately 357.8 K. It is possible that an azeotrope is situated near the pure 2-methylpropene end. Further studies are required to investigate possible azeotrope formation.

The activity coefficients for species i, γ_i were calculated from eq 1.

$$y_i P \phi_i = \gamma_i x_i P_{vpi} \phi_i^{S} \exp \int_{P_{vpi}}^{P} \frac{v_i^{L}\,dP}{RT} \tag{1}$$

where y_i is the component i vapor phase mole fraction, the system total pressure is P, ϕ_i is the component i fugacity coefficient for the vapor phase, x_i is the component i liquid-phase mole fraction, P_{vpi} is the pure component i vapor pressure, ϕ_i^{S} is the pure component i saturated liquid fugacity coefficient at the system temperature, V_i^{L} is the component i liquid-phase molar volume, T is temperature, K, and R is the universal gas constant (8.314 J K^{-1} mol^{-1}). The Soave–Redlich–Kwong equation of state (Soave, 1972) with the van der Waals one fluid mixing rule was used for vapor-phase calculation, and the liquid phase was modeled with the Wilson equation (Wilson, 1968). Critical temperatures, critical pressures, acentric factors, and the liquid molar volumes used for the Wilson equation fit are presented in Table 4. The vapor pressures of the pure substances were calculated from the Antoine equation for ethanenitrile (eq 2) and the Wagner equation for 2-methylpropane and 2-methylpropene (eqs 3 and 4) (Reid et al., 1988). The pure component vapor pressure equation parameters used, with the recommended temperature range of the parameters of the vapor pressure equations used, are also presented in Table 4. Both systems measured

$$P_{vpi}/\mathrm{MPa} = \exp\left(A - \frac{B}{(\mathrm{T/K}) + \mathrm{C}}\right) \tag{2}$$

$$\ln \frac{P}{P_c} = [a_1\theta + a_2\theta^{3/2} + a_3\theta^3 + a_4\theta^6](1-\theta)^{-1} \tag{3}$$

$$\theta = 1 - \frac{T}{T_C} \tag{4}$$

indicate positive deviation from Raoults law.

Table 5. Pure Component Measured Vapor Pressures *P*, Calculated Vapor Pressures P_{vpi}, Deviation Δ*P*

component	*T*/K	*P*/kPa	P_{vpi}/kPa	Δ*P*/kPa
ethanenitrile	357.83	109	114	−5
ethanenitrile	358.08	111	114	−3
2-methylpropane	358.14	1491	1467	24
2-methylpropene	357.84	1366	1345	21

Table 6. Wilson Equation Parameters $\lambda_{ij}-\lambda_{ii}$ for the Mixtures and Averages of the Vapor Fraction Residuals Δ*y* and the Pressure Residuals Δ*P* for the Wilson Fit

component	$\lambda_{12}-\lambda_{11}$/ J·mol^{-1}	$\lambda_{21}-\lambda_{22}$/ J·mol^{-1}	Δ*y*	Δ*P*/kPa
2-methylpropane (1) + ethanenitrile (2)	2466.7	7175.8	0.0043	36
2-methylpropene (1) + ethanenitrile (2)	880.0	6113.6	0.0063	6.7

Table 7. Results of Integral Test for the Binary Systems Methylpropane + Ethanenitrile and Methylpropane + Ethanenitrile at 358 K

binary pair	D^a/%	test result
2-methylpropane + ethanenitrile	2.7	pass
2-methylpropene + ethanenitrile	8.1	pass

[a] The criterion for passing the test is $D < 10\%$ (Gmehling and Onken, 1977).

Comparison between the measured vapor pressures of the pure substances and the calculated vapor pressures of the pure substances is presented in Table 5.

The objective function O.F. used for fitting of the Wilson equation parameters is presented in eq 5 (Aittamaa et al., 1995). Wilson parameters for the mixtures with the averages of the vapor fraction residuals and the pressure residuals for the fitted data are presented in Table 6.

$$\text{O.F.} = \frac{1}{N \cdot NC} \sum_{i=1}^{N} \sum_{j=1}^{NC} (\gamma_{i,j}^{\text{model}} - \gamma_{i,j}^{\text{fromdata}})^2 \tag{5}$$

where *N* is the number of points used in the fit and *NC* is the number of components used in the fit. The measured data were tested for thermodynamic consistency with the integral test (Gmehling and Onken, 1977). The results of the integral test are presented in Table 7. The data measured passed the integral test (Figures 7 and 8).

Conclusions

A sampling system was built on a sapphire cell apparatus. The sampling system is not recommended to be used for mixtures with a miscibility gap. Isothermal vapor liquid equilibria at 358 K were measured for the binary pairs 2-methylpropane + ethanenitrile and 2-methylpropene + ethanenitrile. Azeotropic behavior was observed for the 2-methylpropane + ethanenitrile binary. A miscibility gap was observed visually for the binary pair 2-methylpropane + ethanenitrile at 320 K but not at the temperature 358 K. For the 2-methylpropene + ethanenitrile binary azeotropic behavior was not observed at 358 K. As a consistency test, the integral test was applied, and both systems measured passed the test.

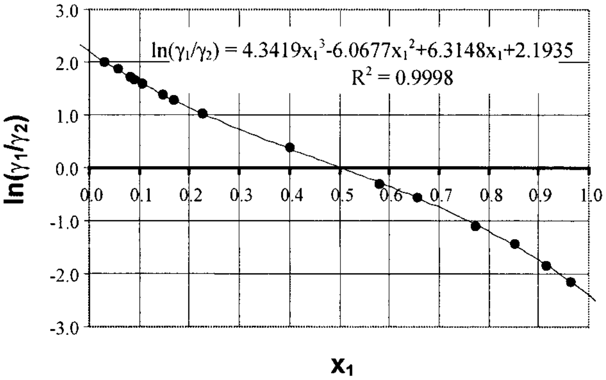

Figure 7. Integral test for the 2-methylpropane + ethanenitrile system at 358 K.

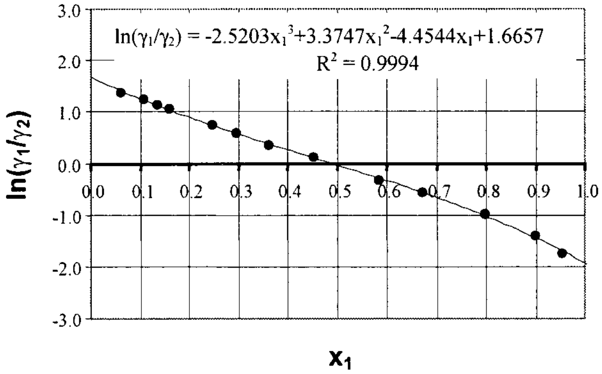

Figure 8. Integral test for the 2-methylpropene + ethanenitrile system at 358 K.

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