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Isothermal Vapor–Liquid Equilibria for the *n*-Hexane–Cyclohexane–Tetralin System

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Total pressure data are presented for the ternary *n*-hexane–cyclohexane–tetralin system and for binary mixtures composed of its constituents at 283.15 K. Experimental total pressures are compared with values calculated by the Wilson equation and good agreement between calculated and experimental values is obtained. Selectivity of tetralin for separating *n*-hexane and cyclohexane is discussed.

Introduction

Vapor–liquid equilibrium data are useful not only for the design of separation processes but also for the study of the properties of solutions of liquid mixtures. It is also important to know the behavior of solutions for systems which are difficult to separate by distillation.

This paper presents the total pressures for the binary systems *n*-hexane–cyclohexane, *n*-hexane–tetralin, and cyclohexane–tetralin and for the ternary *n*-hexane–cyclohexane–tetralin system at 283.15 K.

Some works have been published on the vapor–liquid equilibria for the *n*-hexane–cyclohexane system (*1–4*). Li et al. (*1*) have reported the total pressure data for the *n*-hexane–cyclohexane system at 0–25 °C. However, the data for other binary systems and for the ternary system at low pressure are hardly available in the literature.

Data for the binary systems are correlated by the Wilson equation, and the predicted values for the ternary system are calculated by using the binary parameters and compared with observed values.

Experimental Section

The total pressures are measured by the static method, and the experimental apparatus and procedure were similar to those of the previous paper (*5*). Pressure measurements were made with a Zimmerli manometer and a cathetometer and are reproducible to within ±50 Pa. The equilibrium cell was immersed in a water bath and controlled by a thermostat with a cooling unit. The temperature of the water bath was determined by using 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 mole fraction was evaluated from the total (liquid + vapor) weight of each material and their respective material balance in the liquid and vapor phases. The compositions of the vapor phases were first calculated from Raoult's law and then by the iterative calculation procedure discussed later, until successive iterations yielded almost the same values ($\Delta x < 0.0001$). The amount of tetralin in the vapor phase could be neglected because of the very low concentrations in the range of this experiment. The liquid compositions were estimated within ±0.001.

Commercially available guaranteed-reagent *n*-hexane and cyclohexane were used after further purification in a laboratory distillation column where only the middle half of the distillate was recovered. Spectrograde tetralin (Nakarai Chemicals, Ltd.) was used with no further purification. The boiling points of distilled *n*-hexane and cyclohexane agreed with literature values, and the vapor pressures of *n*-hexane and cyclohexane at 293.15 K are 16 150 Pa (16 165 Pa (*6*), 16 145 Pa (*7*)), and 10 330 Pa (10 336 Pa (*6*)), and the densities (in g cm^{-3}) of *n*-hexane, cyclohexane, and tetralin at 293.15 K are 0.6591 (0.659 37 (*8*)), 0.7787 (0.778 55 (*8*)), and 0.9698 (0.9702 (*8*)), respectively.

Results and Discussion

The equilibrium equation for each component i containing a vapor phase and a liquid phase, both at the same temperature T and total pressure P, is

$$\phi_i y_i P = \gamma_i x_i \phi_i^{\mathrm{s}} P_i^{\mathrm{s}} \exp\{(P - P_i^{\mathrm{s}}) v_i / RT\} \tag{1}$$

where ϕ_i is the vapor-phase fugacity coefficient, γ_i is the liquid-phase activity coefficient, P_i^{s} is the pure-component vapor pressure, and v_i is the pure-component saturated liquid volume. The fugacity coefficient ϕ_i is given by

$$\ln \phi_i = \frac{2}{v}\sum_{j=1}^{N} y_j B_{ij} - \ln z \tag{2}$$

To correlate the vapor–liquid equilibrium data, it is necessary to evaluate the liquid activity coefficients. From many expressions, the Wilson equation (*9*) was used. The excess Gibbs free energy is given by

$$\frac{g^{\mathrm{E}}}{RT} = -\sum_{i=1}^{N} x_i \ln \left[\sum_{j=1}^{N} x_j \Lambda_{ij}\right] \tag{3}$$

The liquid activity coefficient is expressed in the form of

$$\ln \gamma_i = 1 - \ln \left[\sum_{j=1}^{N} x_j \Lambda_{ij}\right] - \sum_{k=1}^{N} \frac{x_k \Lambda_{ki}}{\sum_{j=1}^{N} x_j \Lambda_{kj}} \tag{4}$$

where

$$\Lambda_{ij} = \frac{v_j}{v_i} \exp[-(\lambda_{ij} - \lambda_{ii})/RT] \tag{5}$$

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Table I. Total Pressures for the Binary Systems at 298.15 K

x_i	P, kPa	x_i	P, kPa	x_i	P, kPa
		n-Hexane (i)–Tetralin			
0.0	0.016[a]	0.3894	5.44	0.7974	8.38
0.0730	1.63	0.4830	6.22	0.9198	9.32
0.1731	3.21	0.5722	6.85		
0.3051	4.69	0.6565	7.40		
		Cyclohexane (i)–Tetralin			
0.1151	1.15	0.5499	3.99	0.8384	5.44
0.2162	1.97	0.5716	4.08	0.9382	6.00
0.3751	3.05	0.7149	4.85	1.0	6.32
		n-Hexane (i)–Cyclohexane			
0.0977	6.89	0.3338	7.94	0.6376	8.99
0.2221	7.45	0.4366	8.26	0.8131	9.57
0.3176	7.85	0.5682	8.72	1.0	10.11

[a] Calculated value.

Table II. Total Pressures for the n-Hexane (1)–Tetralin (2)–Cyclohexane (3) System at 298.15 K

x_1	x_2	$y_{1,\text{calcd}}$	$y_{2,\text{calcd}}$	P, kPa
0.2482	0.4253	0.5766	0.0015	5.61
0.1549	0.5064	0.4546	0.0020	4.75
0.3037	0.3857	0.6298	0.0013	6.03
0.1842	0.1300	0.3235	0.0005	6.59
0.3605	0.4294	0.7463	0.0014	6.06
0.1520	0.6142	0.5568	0.0025	4.23
0.0868	0.7214	0.4797	0.0038	3.22
0.2457	0.6408	0.8001	0.0024	4.70
0.0963	0.7932	0.6404	0.0046	2.83
0.2384	0.7284	0.9293	0.0029	4.21
0.5046	0.3360	0.8363	0.0011	6.99
0.3874	0.1803	0.5949	0.0006	7.20
0.2202	0.3530	0.4809	0.0013	5.79
0.4054	0.2384	0.6514	0.0008	7.05
0.5708	0.1120	0.7350	0.0004	8.17
0.1368	0.2630	0.2971	0.0010	5.79
0.3927	0.5509	0.9223	0.0018	5.74
0.3159	0.1766	0.5115	0.0006	6.95

The parameters Λ_{ij} were determined in such a way that the summation of the difference between calculated and experimental total pressures was at a minimum. The technique used for the data fitting was similar to that of Prausnitz et al. (*10*).

The most probable second virial coefficients for the pure substances and the mixtures have been taken from the literature (*11*) or calculated from the correlation of Tsonopoulos (*12*). The vapor pressure of tetralin is estimated by extrapolation (*6*).

Experimental results for the binary systems are presented in Table I and those for the ternary system in Table II. The present data for the n-hexane–cyclohexane at 283.15 K are compared with those of Li et al. (*1*), and both data are in good agreement with each other.

Table III lists the parameters and the root mean square deviations in relative total pressures.

Selectivity of tetralin for separating n-hexane and cyclohexane can be discussed by comparing the relative volatility for ternary system with that for the binary one. Figure 1 shows the selectivity of tetralin. As shown in Figure 1, tetralin has a significant effect in changing the relative volatility of n-hexane to cyclohexane; therefore, tetralin may be used as a solvent.

Table III. Parameters and Root Mean Square Deviations in Relative Pressures at 298.15 K

	Λ_{ij}[a]	Λ_{ji}[a]	rms[b]
n-hexane–cyclohexane	0.470	1.517	0.0027
n-hexane–tetralin	0.615	0.584	0.0082
cyclohexane–tetralin	0.939	0.523	0.0067
n-hexane–cyclohexane–tetralin			0.0075

[a] First component is i. [b] rms = $\{\sum_{i=1}^{K}[(P_{\text{calcd}} - P_{\text{exptl}})/P_{\text{exptl}}]_i^2/K\}^{1/2}$.

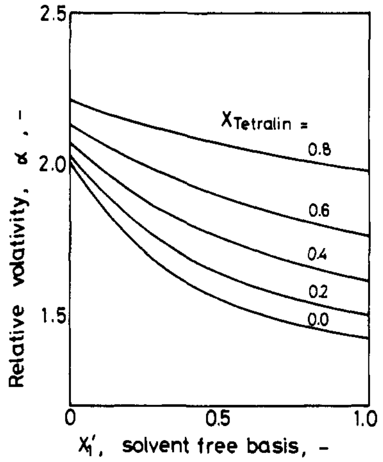

Figure 1. Relative volatility for the n-hexane–cyclohexane system.

Glossary

B_{ij}	second virial coefficient, m^3 mol^{-1}
g^E	excess molar Gibbs free energy, J mol^{-1}
K	number of data
N	number of components
P	total pressure, kPa
P_i^s	vapor pressure of pure component, kPa
R	gas constant, J mol^{-1} K^{-1}
T	absolute temperature, K
v	molar volume of liquid, m^3 mol^{-1}
x	liquid mole fraction
y	vapor mole fraction
z	compressibility factor

Greek Letters

γ	activity coefficient
ϕ	fugacity coefficient
λ	Wilson parameter, J mol^{-1}
Λ	Wilson parameter

Subscripts

1	n-hexane
2	tetralin
3	cyclohexane
i,j,k	component i, j, k

Registry No. Hexane, 110-54-3; tetralin, 119-64-2; cyclohexane, 110-82-7.

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