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Isothermal Vapor–Liquid Equilibria for the Propane–Propylene–Tetralin System

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Total-pressure data are obtained for the binary systems propane–propylene, propane–tetralin, and propylene–tetralin and for the ternary propane–propylene–tetralin system at 273.15 and 293.15 K. Experimental total pressures are compared with calculated values by the NRTL equation ($\alpha = -1$). The root mean square deviations in relative pressures are 0.11–0.95%.

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 propane–propylene, propane–tetralin, and propylene–tetralin and for the ternary propane–propylene–tetralin system at 273.15 and 293.15 K. Data for the binary systems are correlated by the NRTL 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 (*1*), except for the vapor-phase recirculation by magnetic pump. Pressure measurements were made with a Bourdon pressure gauge which was calibrated with a dead-weight gauge and are reproducible to within ±1 kPa. 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 ($\Delta x < 0.0001$). That of tetralin could be neglected because of the very low concentrations in the range of this experiment. The liquid compositions were estimated within ±0.001.

Research-grade propane (99.9 vol %) and propylene (99.7 vol %) purchased by Takachiho Kagaku Kogyo were used without further purification, and commercially available guaranteed-reagent tetralin was used after further purification in a laboratory distillation column where only the middle half of the distillate was recovered. The boiling point of distilled tetralin was 341.05 K at 0.8 kPa and $n^{20}{}_{D} = 1.5412$. (The literature values are 0.77 kPa at 341.05 K (*2*) and $n^{20}{}_{D} = 1.54135$ (*3*), respectively.)

Results and Discussion

Experimental results for the binary systems are presented in Table I, and those for the ternary system in Table II. The results for the propane–tetralin and propylene–tetralin systems are shown in Figure 1.

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

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

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

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

To correlate the vapor–liquid equilibrium data, it is necessary to evaluate the liquid activity coefficients. From the many expressions which have been reported by several investigators (*4–6*), the NRTL equation, where the nonrandomness parameter α is equal to −1 (*7*, *8*), was chosen. The excess Gibbs free energy is given by

$$\frac{g^E}{RT} = \sum_{j=1}^{N} x_j \sum_{i=1}^{N} \frac{x_i w_{ji}}{\sum_{k=1}^{N} A_{ki} x_k} \qquad (3)$$

The liquid activity coefficient is expressed in the form of

$$\ln \gamma_i = \sum_{j=1}^{N} x_j \left[\frac{w_{ji}}{\sum_{k=1}^{N} x_k A_{ki}} + \frac{w_{ij}}{\sum_{k=1}^{N} x_k A_{kj}} - \sum_{l=1}^{N} \frac{x_l w_{jl} A_{il}}{(\sum_{k=1}^{N} x_k A_{kl})^2} \right] \qquad (4)$$

where

$$A_{ij} = \exp(-w_{ij}) \qquad (5)$$

The parameters w_{ij} were determined in such a way that the summation of the difference between calculated and experi-

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Table I. Total Pressures for the Binary Systems

x_1	P, kPa	x_1	P, kPa
	Propane-Propylene System		
	$T = 273.15$ K		
0.0	584	0.6449	522
0.0652	580	0.7132	513
0.0929	577	0.7582	509
0.1910	567	0.8596	494
0.3114	556	0.9290	484
0.4120	548	1.0	473
0.5290	535		
	$T = 293.15$ K		
0.0	1017	0.6503	915
0.0654	1008	0.7176	899
0.0936	1004	0.7617	892
0.1927	991	0.8619	867
0.3157	971	0.9296	852
0.4047	958	1.0	836
0.5336	936		
	Propane-Tetralin System		
	$T = 273.15$ K		
0.1483	136	0.5515	358
0.1729	153	0.6676	382
0.1900	170	0.7024	391
0.2598	211	0.7434	400
0.2687	222	0.8520	423
0.2893	234	0.9445	450
0.4131	299	0.9617	456
0.4269	304		
	$T = 293.15$ K		
0.1329	197	0.3881	481
0.1479	217	0.6115	624
0.1658	241	0.6408	648
0.2236	320	0.6689	658
0.2503	345	0.8273	725
0.3703	467	0.9411	788
x_2	P, kPa	x_2	P, kPa
	Propylene-Tetralin System		
	$T = 273.15$ K		
0.1268	113	0.5576	401
0.2314	201	0.5723	409
0.2937	246	0.6756	450
0.3036	249	0.7834	491
0.3564	284	0.8855	529
0.3689	299	0.9441	551
0.4344	337	0.9822	571
0.5212	384		
	$T = 293.15$ K		
0.1114	161	0.4555	582
0.1947	275	0.5321	661
0.2555	355	0.6189	729
0.2642	371	0.7554	831
0.2852	385	0.8665	901
0.2999	418	0.9377	957
0.3614	486	0.9621	978
0.4383	567	0.9818	997

Table II. Total Pressures for the Propane-Propylene-Tetralin System

x_1	x_2	$y_{1,\text{calcd}}$	$y_{2,\text{calcd}}$	P, kPa
		$T = 273.15$ K		
0.0356	0.1379	0.215	0.785	153
0.0600	0.1058	0.375	0.625	148
0.0786	0.2972	0.212	0.788	300
0.0985	0.3653	0.213	0.787	349
0.1167	0.2030	0.370	0.630	260
0.1250	0.0974	0.571	0.429	192
0.1593	0.2733	0.368	0.632	328
0.1610	0.0452	0.786	0.214	179
0.1612	0.5899	0.204	0.796	468
0.2348	0.1791	0.564	0.436	313
0.2601	0.1958	0.565	0.435	334
0.2777	0.4666	0.354	0.641	455
0.2809	0.0777	0.782	0.218	278
0.3818	0.1030	0.780	0.220	339
0.4402	0.3279	0.545	0.455	446
0.6071	0.1636	0.764	0.236	428
		$T = 293.15$ K		
0.0300	0.1209	0.211	0.789	217
0.0507	0.0935	0.369	0.631	210
0.0700	0.2686	0.212	0.788	459
0.0786	0.3041	0.209	0.791	502
0.1030	0.1824	0.370	0.630	394
0.1081	0.0866	0.570	0.430	279
0.1282	0.2267	0.367	0.633	467
0.1403	0.0401	0.787	0.213	259
0.1545	0.5548	0.208	0.792	780
0.2180	0.1659	0.570	0.430	494
0.2282	0.1609	0.588	0.412	492
0.2535	0.0703	0.786	0.214	431
0.2653	0.4372	0.362	0.638	761
0.3221	0.0866	0.787	0.213	513
0.4288	0.3119	0.556	0.444	755
0.5894	0.1545	0.773	0.227	730

mental total pressures was at a minimum. The technique used for the data fitting was similar to that of Prausnitz et al. (*9*).

The most probable second virial coefficients for the pure substances and the mixtures have been taken from the literature (*10*) or calculated from the correlation of Tsonopoulos (*11*). The vapor pressures of tetralin are estimated by extrapolation (*2*).

The data for the propane–propylene system have been reported by many authors (*12*, *13*) and are correlated by Bae et al. (*14*) and by Howat and Swift (*15*). The present data have been calculated by the Howat–Swift correlation with errors of 0.2–0.4%, and these errors are comparable with others (*15*). The pure-vapor pressures of propane and propylene agree with the Manley–Swift data (*13*) within ±2 kPa.

Table III lists the parameters and the root mean square deviations in relative total pressures. Table III shows that the predicted values are within the expected experimental error.

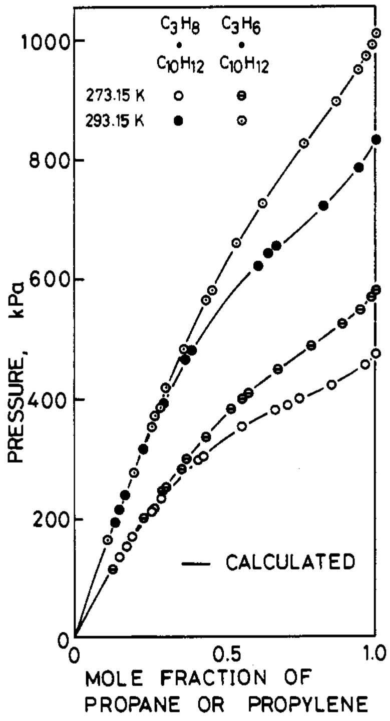

Figure 1. Total vapor pressure for the systems propane–tetralin and propylene–tetralin.

Glossary

A_{ij}	parameter defined by eq 5
B_{ij}	second virial coefficient, m^3 mol^{-1}
g^E	excess molar Gibbs free energy, J mol^{-1}

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Table III. Parameters and the Root Mean Square Deviations in Relative Pressures

	273.15 K			293.15 K		
	w_{ij}[a]	w_{ji}[a]	rms[b]	w_{ij}[a]	w_{ji}[a]	rms[b]
propane-propylene	−0.0187	0.0830	0.0015	0.0057	0.0458	0.0011
propane-tetralin	0.7742	0.0968	0.0095	0.7434	0.0976	0.0082
propylene-tetralin	0.7427	−0.1773	0.0069	0.7761	−0.2828	0.0085
propane-propylene-tetralin			0.0035			0.0070

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

K	number of data
N	number of component
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}
w_{ij}	adjustable parameter (w_{ii} = 0)
x	liquid mole fraction
y	vapor mole fraction

Greek Letters

γ	activity coefficient
ϕ	fugacity coefficient

Subscripts

1	propane
2	propylene
3	tetralin
i	component i

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Solubility of Urea in Ammonium Polyphosphate Solutions at 0 and 25 °C

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The six-component system $CO(NH_2)_2$–NH_3–H_3PO_4–$H_4P_2O_7$–$H_5P_3O_{10}$–H_2O, along with the subsystem $CO(NH_2)_2$–NH_3–H_3PO_4–$H_4P_2O_7$–H_2O, was studied at 0 and 25 °C to determine the solubility isotherms in the pH range 5–7. All invariant solutions were identified at both temperatures. In the two systems, those solutions containing monoammonium and diammonium orthophosphates in equilibrium had the highest total plant food.

This study of the solubility of urea in the presence of the three basic linear ammonium phosphates was made to complement previous solubility studies of the same phosphates (*1–4*). Determinations of the composition of solutions in the system urea–ammonia–orthophosphoric acid–pyrophosphoric acid–tripolyphosphoric acid–water in the pH range 5.2–7.2 were made at 0 and 25 °C, as well as the subsystem urea–ammonia–orthophosphoric acid–pyrophosphoric acid–water in the pH range 4.4–7.2 at 0 and 25 °C.

The urea and monoammonium and diammonium orthophosphates were reagent grade. Triammonium and tetraammonium pyrophosphates were crystallized from a product of ammoniation of 80% P_2O_5 electric-furnace superphosphoric acid. Pentaammonium tripolyphosphate was prepared from the sodium salt by using cation-exchange resin (Amberlite IR-120 H^+ form) to produce a tripolyphosphoric acid solution and then ammoniating to pH 7.8 before crystallizing the salt by the addition of methyl alcohol to the solution.

Two stock solutions saturated with monoammonium or diammonium orthophosphate were prepared at ambient temperature. Depending upon the desired pH (*5*) for the complex, a portion of one of the stock solutions whose saturating salt is stable at that pH was saturated with the ammonium pyrophosphate that is stable (*2*, *4*) at the desired pH. For the subsystem these ammonium orthophosphate–pyrophosphate mixtures were adjusted to the desired pH with gaseous ammonia or orthophosphoric acid. Urea was added, and the complexes were placed either in a cold room at 0 ± 0.5 °C with periodic manual agitation or in a water bath at 25 ± 0.2 °C and agitated at 4 rpm. This procedure was the same for the main system, except that the orthophosphate–pyrophosphate solutions were saturated with pentaammonium tripolyphosphate before adjusting the pH and saturating with urea.

The approach to equilibrium was followed by petrographic examination of the solid phase of the complexes. When one