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Vapor–Liquid Equilibria of the Ternary System Benzene + *n*-Heptane + *N*-Methylpyrrolidone (NMP) at 101.33 kPa

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Isobaric vapor–liquid equilibrium data of the ternary system benzene + *n*-heptane + *N*-methylpyrrolidone (NMP) have been measured with a Röck and Sieg recirculation still at 101.33 kPa. The experimental data reported were thermodynamically consistent when tested by the McDermott–Ellis method. Data were correlated with the Wilson and NRTL, equations for the liquid-phase activity coefficients. Activity coefficients of the components in the mixture indicate positive deviations from Raoult's law. Experimental results show that NMP is a good extractive solvent that reverses the volatility of the binary system benzene + *n*-heptane.

Introduction

Processes in the petrochemical industry for the separation of mixtures of aromatic and saturated hydrocarbons are usually carried out by liquid–liquid extraction or extractive distillation. In extractive distillation, a solvent is added to increase the relative volatility of the components to be separated. The solvent selectivity, and hence the separation efficiency, depends on the molecular interactions among the mixture components and the solvent.

In choosing a solvent for extractive distillation, among potential candidates, some methods for “solvent design” have been developed, such as group contribution methods¹ or computer simulation.^{2–4} However, these prediction techniques cannot replace actual experimentation.⁵

This work has been carried out as part of a project to study the feasibility of separation of aromatic and saturated hydrocarbons in a pyrolysis gasoline fraction by extractive distillation using polar solvents.^{6,7} The objective of the present paper is to determine vapor–liquid equilibrium (VLE) data for a mixture formed by an aromatic hydrocarbon (benzene), a saturated one (*n*-heptane), and the polar extractive solvent NMP at 101.33 kPa. Benzene is the most abundant aromatic component in the gasoline stream considered, and *n*-heptane was chosen as representative of the nonaromatic components, as it shows the most unfavorable conditions for the separation, because it exhibits the largest liquid–liquid immiscibility gap with NMP^{8,9} and the lowest relative volatility with benzene.⁶ A literature review¹⁰ of this system shows that only scarce data covering a narrow concentration range are available.^{9,11–14} The interaction parameters for this system were obtained by reduction of the experimental data through the Wilson and NRTL equations.

Experimental Section

Chemicals. The chemicals used in this work were supplied by Merck with the following guaranteed purity:

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Table 1. Density, ρ , Refractive Index, n , and Boiling Point, T_b , of the Pure Compounds

compound	$\rho(298.15\text{ K})/(\text{kg}\cdot\text{m}^{-3})$		$n(D, 298.15\text{ K})$		$T_b(101.33\text{ kPa})/\text{K}$	
	exptl	lit. ^a	exptl	lit. ^a	exptl	lit. ^a
benzene	873.5	873.60	1.4978	1.49792	353.25	353.244
<i>n</i> -heptane	679.4	679.46	1.3851	1.38511	371.50	371.574
NMP	1028.4	1025.90	1.4681	1.4675	475.10	475.15

^a Riddick et al.¹⁶

NMP 99.9%, benzene 99.9%, and *n*-heptane 99.5%. To prevent the absorption of water, which is an impurity that significantly modifies the phase behavior of the mixtures,^{9,15} NMP was dried and kept over 3 Å molecular sieves, and benzene and *n*-heptane were stored with threaded sodium.¹⁶ Gas chromatography and Karl-Fisher analyses (Mitsubishi Kasei CA-20) were used to check the purity of the above chemicals, which was found to be higher than 99.99% in all cases. Physical properties of all pure compounds were measured and compared with values reported in the literature, as shown in Table 1.

Apparatus and Procedure. An all glass vapor–liquid–equilibrium apparatus, manufactured by Fritz GmbH (Normag) (Hofheim, Germany), was used for the VLE determinations. It is a recirculation still of the Gillespie type, as modified by Röck and Sieg, that has been described previously and used to obtain VLE data.^{6–7,17–18} Recirculation stills are designed for determination of VLE data of totally miscible mixtures. However, the system investigated in this work shows an immiscibility liquid–liquid region at low benzene concentrations and low temperatures.⁹ Therefore, only VLE data for mixtures containing enough benzene in the vapor phase to avoid immiscibility when condensation occurs were measured.

All the variables necessary to describe VLE, i.e., temperature, pressure, and compositions of the liquid and vapor phases, have been measured. The pressure (± 0.01 kPa) was measured with a dibutylphthalate manometer and was automatically adjusted to the desired value by injecting or releasing dry nitrogen inside the still. An inert

Table 2. Experimental Vapor–Liquid Equilibrium Data for the Ternary System Benzene (1) + *n*-Heptane (2) + NMP (3) at 101.33 kPa^a

<i>T</i> /K	<i>x</i> ₁	<i>x</i> ₂	<i>y</i> ₁	<i>y</i> ₂	γ_1	γ_2	γ_3
364.55	0.379	0.372	0.550	0.443	1.051	1.455	1.218
364.65	0.487	0.197	0.682	0.310	1.011	1.917	1.063
364.70	0.441	0.250	0.621	0.371	1.015	1.805	1.114
364.75	0.384	0.348	0.555	0.438	1.041	1.529	1.121
364.75	0.335	0.408	0.515	0.479	1.107	1.426	1.002
364.90	0.423	0.319	0.597	0.393	1.012	1.490	1.651
364.95	0.519	0.138	0.729	0.262	1.006	2.293	1.117
365.25	0.314	0.417	0.496	0.496	1.122	1.423	1.246
365.90	0.249	0.507	0.431	0.561	1.208	1.299	1.331
365.95	0.542	0.096	0.775	0.215	0.996	2.627	1.123
366.40	0.221	0.569	0.400	0.593	1.246	1.206	1.322
366.45	0.581	0.057	0.849	0.141	1.004	2.860	1.098
367.65	0.583	0.032	0.889	0.095	1.015	3.315	1.561
368.45	0.556	0.035	0.882	0.105	1.033	3.274	1.151
368.80	0.273	0.294	0.458	0.523	1.083	1.920	1.555
369.05	0.248	0.383	0.415	0.565	1.073	1.581	1.898
369.55	0.548	0.046	0.846	0.135	0.976	3.103	1.610
370.50	0.283	0.221	0.476	0.498	1.038	2.317	1.718
371.00	0.272	0.218	0.474	0.496	1.061	2.307	1.883
372.05	0.307	0.165	0.518	0.460	1.000	2.744	1.275
372.75	0.302	0.151	0.533	0.435	1.027	2.781	1.732
373.85	0.300	0.132	0.575	0.403	1.084	2.858	1.095
374.55	0.303	0.120	0.561	0.397	1.028	3.038	1.988
375.50	0.301	0.110	0.568	0.398	1.023	3.236	1.514
375.95	0.293	0.107	0.554	0.416	1.013	3.435	1.287
376.30	0.316	0.099	0.600	0.375	1.008	3.315	1.084
376.35	0.306	0.101	0.590	0.385	1.023	3.331	1.067
377.90	0.309	0.093	0.592	0.374	0.977	3.369	1.344
378.25	0.175	0.165	0.372	0.589	1.076	2.962	1.372
379.10	0.281	0.083	0.583	0.368	1.027	3.597	1.726
379.75	0.082	0.176	0.181	0.759	1.077	3.437	1.753
380.45	0.282	0.077	0.605	0.360	1.027	3.658	1.158
381.40	0.277	0.068	0.620	0.347	1.047	3.893	1.027
382.35	0.275	0.066	0.618	0.345	1.027	3.889	1.099
383.85	0.255	0.067	0.598	0.361	1.034	3.854	1.111
383.85	0.187	0.098	0.455	0.480	1.073	3.504	1.663
383.95	0.208	0.087	0.498	0.431	1.054	3.535	1.834
384.25	0.232	0.076	0.556	0.389	1.047	3.624	1.433
384.55	0.252	0.060	0.609	0.340	1.048	3.981	1.322
387.60	0.093	0.117	0.241	0.677	1.046	3.758	1.624
387.60	0.260	0.049	0.655	0.278	1.016	3.685	1.524
388.20	0.111	0.109	0.305	0.636	1.093	3.732	1.159
388.50	0.277	0.035	0.723	0.219	1.031	3.973	1.280
388.65	0.234	0.049	0.617	0.314	1.038	4.053	1.450
389.05	0.305	0.023	0.801	0.150	1.024	4.084	1.085
389.50	0.235	0.043	0.647	0.300	1.062	4.319	1.071
391.45	0.105	0.102	0.312	0.617	1.097	3.566	1.204
393.60	0.145	0.064	0.450	0.481	1.091	4.202	1.080
394.85	0.128	0.061	0.435	0.478	1.162	4.250	1.263
395.85	0.106	0.070	0.368	0.537	1.161	4.061	1.304
398.55	0.110	0.056	0.409	0.479	1.172	4.245	1.370
401.55	0.120	0.044	0.474	0.415	1.167	4.362	1.212
402.15	0.137	0.039	0.530	0.356	1.128	4.163	1.235
405.45	0.148	0.028	0.591	0.283	1.086	4.274	1.210
407.70	0.155	0.018	0.673	0.199	1.127	4.443	1.131
409.35	0.108	0.032	0.488	0.370	1.134	4.479	1.136

^a Liquid-phase mole fractions, *x*_{*i*}, vapor-phase mole fractions, *y*_{*i*}, temperature, *T*, and activity coefficients, γ_i .

atmosphere was maintained until thermodynamic equilibrium was reached. Atmospheric pressure was measured with a Lambrecht type barometer. Temperature (± 0.05 K) was measured with a digital thermometer (Ertco-Hart, Model 850) and vapor and liquid-phase compositions were determined by gas–liquid chromatography (GLC) (Perkin-Elmer, Autosystem). The chromatographic column used was a capillary column (15 m by 0.25 mm, coated with a 0.25 μ m film of MFE–1000) whose temperature profile went from 328 to 423 K at a 20 K·min^{−1} rate. An internal standard (*p*-xylene) was used for peak area quantification. Two different calibration curves were used for the analysis

Table 3. Ternary System Benzene (1) + *n*-Heptane (2) + NMP (3)^a

	Wilson	NRTL
Parameters of Activity Coefficient Equations		
<i>A</i> ₁₂	872.679	4152.195
<i>A</i> ₂₁	1305.356	−1738.856
<i>A</i> ₁₃	57.508	2728.937
<i>A</i> ₃₁	218.151	−1888.035
<i>A</i> ₂₃	3413.521	3345.603
<i>A</i> ₃₂	3536.011	2959.826
Mean Deviations		
<i>P</i> /kPa	3.92	2.75
<i>T</i> /K	1.45	1.02
<i>y</i> ₁	0.013	0.013
<i>y</i> ₂	0.013	0.010
<i>y</i> ₃	0.006	0.006

^a Correlation parameters, *A*_{*ij*} and *A*_{*ji*}, (J·mol^{−1}) for the Wilson and NRTL activity coefficient equations, and mean deviation for pressure, *P*, temperature, *T*, vapor composition, *y*_{*i*}.

of the vapor and liquid phases, to minimize the effect that the large difference of NMP composition in the two phases might have on the chromatographic peaks. The polynomial fitting of the calibration curves gave a correlation coefficient *R*² higher than 0.999. The reproducibility of concentration measurements was better than ± 0.001 for the liquid phase and ± 0.002 for the vapor phase.

Results and Discussion

The VLE data for the system benzene (1) + *n*-heptane (2) + NMP (3) at 101.33 kPa are listed in Table 2. VLE data include vapor- and liquid-phase compositions (*y*_{*i*} and *x*_{*i*}), temperature (*T*) and liquid-phase activity coefficients (γ_i), whose values indicate that the liquid phase presents positive deviations from Raoult's law. Liquid-phase activity coefficients were calculated taking into account the non-ideal nature of the vapor phase by means of the equation

$$\gamma_i = \frac{y_i \Phi_i^L P}{x_i P_i^s \Phi_i^s} \exp \left[\frac{V_i^L (P_i^s - P)}{RT} \right] \quad (1)$$

where the exponential term (Poynting correction) may be considered negligible at the low pressures of the present study. Vapor pressures for the pure components, *P*_{*i*}^{*s*}, were calculated using the Antoine equation. The Antoine constants used, *A*_{*i*}, *B*_{*i*}, and *C*_{*i*}, have been previously reported.⁶ Vapor-phase fugacity coefficients, Φ_i and Φ_i^s , were estimated by means of the virial equation of state. The Hayden and O'Connell¹⁹ correlation was used for estimation of the second virial coefficients.

The interaction parameters for the activity coefficient equations (Wilson and NRTL) were obtained by correlating several sets of experimental VLE data, that is, the ternary data experimentally obtained in this work and the previously reported binary data for the systems benzene + *n*-heptane²⁰ and benzene + NMP.⁶ The VLE data reported for the system *n*-heptane + NMP⁶ were not included since only a few mixtures, in the range 0.011 > *x*_{*i*} > 0.886, were studied due to experimental limitations.

The parameter α_{ij} in NRTL equation was fixed to the value $\alpha_{ij} = 0.3$ in all cases. The six adjustable binary parameters, *A*_{*ij*} and *A*_{*ji*}, obtained for the two smoothing equations used, Wilson and NRTL, are presented in Table 3 together with the mean deviations for pressure, temperature, and vapor phase compositions. Such parameters were estimated with the computer program PRO/II.²¹ The subroutine REGRESS of this program uses a weighted

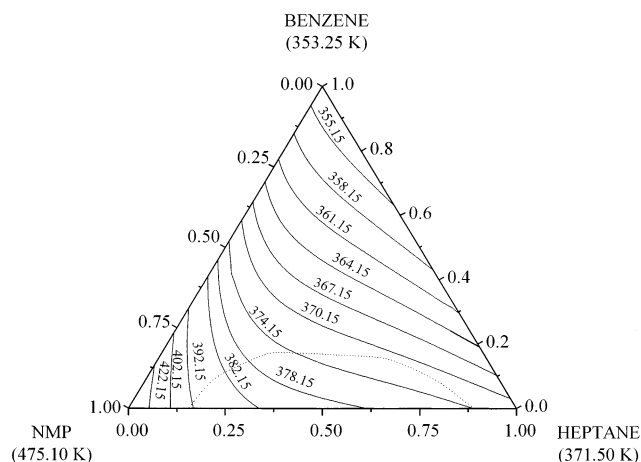


Figure 1. Isotherms for the ternary system benzene (1) + *n*-heptane (2) + NMP (3) at 101.33 kPa, calculated with the NRTL equation.

orthogonal distance regression algorithm developed by the National Institute of Standards and Technology (NIST). This is a powerful, robust package that considers all measured data to have associated measurement errors. The objective function to be minimized was

$$S = \sum_{j=1}^N \sum_{i=1}^{\text{NOC}} \left(1.0 - \frac{K_{ij} \text{ calcd}}{K_{ij} \text{ expt}} \right)^2 \quad (2)$$

where N is the number of data, NOC the number of components, and K_i the equilibrium ratio for component i ($K_i = y_i/x_i$).

Isotherms for the ternary system benzene (1) + *n*-heptane (2) + NMP (3), shown in Figure 1, have been calculated with the NRTL equation. The binodal curve in Figure 1 was taken from the literature⁹ and indicates the miscibility limit of the three liquid components at 298.15 K.

The ternary system was found to be thermodynamically consistent as tested by the McDermott–Ellis method²² as modified by Wisniak and Tamir.²³ According to these methods, two experimental points a and b are considered to be thermodynamically consistent if $D < D_{\max}$, where D is a local deviation and D_{\max} a maximum deviation, both related to the equilibrium data a and b . Values calculated of $D_{\max} - D_i$ were greater than zero for every experimental point with a mean value of 0.048, which indicates that the system is thermodynamically consistent.

Figure 2 shows the equilibrium data for the system benzene (1) + *n*-heptane (2) + NMP (3), plotted on a NMP free basis diagram, for two different narrow NMP concentration ranges. It can be observed that the solvent, NMP, reverses the volatility of the binary system in such a way that the composition of the more volatile component (benzene) is higher in the liquid than in the vapor phase. That is, *n*-heptane would be obtained as the overhead product in the extractive distillation column, with benzene and the extractive solvent NMP as the bottoms product. Volatility reversibility has been widely studied.^{24–26} Such behavior is explained on the basis of chemical affinity between the extractive solvent and the components to be separated. The component with stronger intermolecular forces with the extractive solvent (benzene, in this case) is recovered as the bottoms product.

One factor that strongly influences the effectiveness of an extractive distillation solvent is the modification of the relative volatility of the components in the mixture.²⁷

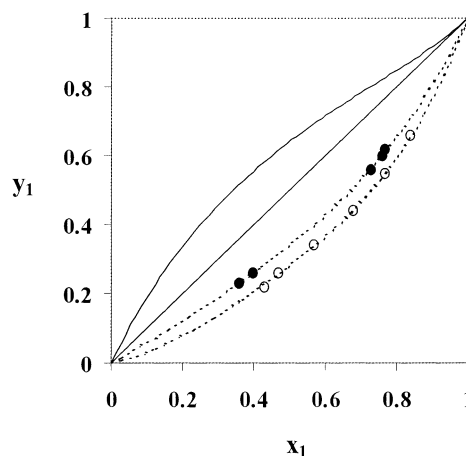


Figure 2. VLE data plotted on a NMP free basis for the system benzene (1) + *n*-heptane (2) + NMP (3): continuous line, $x_{\text{NMP}} = 0.00$;²⁰ (●) $x_{\text{NMP}} \approx 0.60$; (○) $x_{\text{NMP}} \approx 0.82$; Dashed lines were calculated with the NRTL equations for $x_{\text{NMP}} = 0.60$ and $x_{\text{NMP}} = 0.82$.

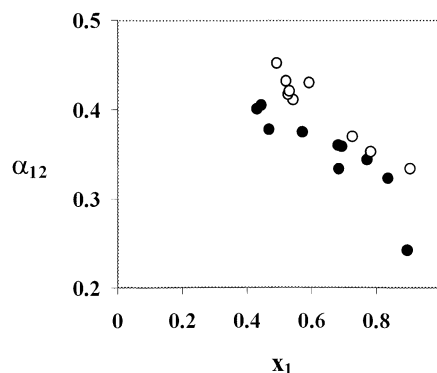


Figure 3. Relative volatility, α , of the system benzene (1) + *n*-heptane (2) in the presence of a solvent (3). x_1 was calculated on a solvent free basis; x_3 was chosen in a narrow range around $x_3 = 0.80$: (●) NMP; (○) DMF.

Figure 3 shows the relative volatility of the system benzene + *n*-heptane when DMF⁷ (*N,N*-dimethylformamide) and NMP are used as extractive solvents. It can be observed that NMP would be a more efficient solvent than DMF. NMP would also be selected for safety reasons.²⁸

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