Isothermal liquid—vapour equilibrium in the systems *n*-heptane—toluene and toluene—dimethylformamide at 40°C

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The values of total vapour pressure were determined over liquid solutions of known composition of the binary systems *n*-heptane—toluene and toluene—dimethylformamide at 40°C are presented. By using the coexistence equation the equilibrium composition in vapour phase as well as the activity coefficients of the components in liquid solutions have been calculated.

With the view of studying the thermodynamic properties of ternary systems of the type hydrocarbon—polar solvent, the $P-x$ relationship was measured for the binary solutions *n*-heptane—toluene and toluene—dimethylformamide over the whole concentration range at constant temperature. The experimental data were used for the calculation of isothermal liquid—vapour equilibrium and for the determination of the activity coefficients of the components in the liquid phase.

Experimental

Preparation of substances

Analytical grade toluene and chemical grade *n*-heptane were purified by twofold rectification on a column with the efficiency of 70 theoretical plates. For the preparation of dimethylformamide (DMFA) a pure chemical was used, purified by twofold rectification *in vacuo* on a column with the efficiency of *ca.* 10 theoretical plates.

The physical properties of the substances thus prepared are compared with the literature data in Table 1.

Table 1

Physical properties of the used substances

Substance	Refractive index n_D^{20}		Density at 20°C [g cm^{-3}]	
	Exper.	Ref.	Exper.	Ref.
n-Heptane	1.3876	1.38765 [1]	0.6834	0.68368 [1]
Toluene	1.4967	1.49693 [1]	0.8665	0.86693 [1]
DMFA	1.4305	—	0.9556	—

Measurements of vapour pressure

The static method was used for the measurement of total vapour pressure over the liquid solution of known composition. A detailed description of the apparatus used and the scheme of its wiring are available in the original paper [2]. The total pressure was determined with the accuracy of $\pm 0.1-0.2$ torr at the constant temperature of $40 \pm \pm 0.05$°C.

The results of measurements of total pressure are compiled in Tables 2 and 3.

Table 2

Experimental values of vapour pressure in the system *n*-heptane (1)—toluene (2) at 40°C

x_1	P [torr]
0	59.2
0.103	66.8
0.195	72.0
0.291	76.0
0.388	80.5
0.483	82.8
0.595	86.3
0.697	88.1
0.793	89.9
0.832	90.9
0.908	91.9
1.0	92.1

Table 3

Experimental values of vapour pressure in the system toluene (1)—DMFA (2) at 40°C

x_1	P [torr]
0	9.75
0.042	14.3
0.102	18.9
0.199	27.0
0.285	32.7
0.356	36.4
0.463	40.7
0.498	43.4
0.575	46.1
0.663	49.2
0.758	51.1
0.821	54.1
0.894	56.1
0.948	57.2
1.0	59.2

Interpretation of the experimental data

To express the $P-x$ dependence the following relationship was applied

$$P = P_1^0 x_1 + P_2^0 x_2 + P^E, \tag{1}$$

The excess pressure P^E was correlated by means of a polynomial

$$\frac{P^E}{x_1 x_2} = \sum_{j=0}^{k} A_j (x_1 - x_2)^j. \tag{2}$$

The coefficients A_j occuring in eqn (2) were calculated by the method of least squares and the most proper degree of polynomial was determined by the F test.

The following characteristic of the $P-x$ relationship was obtained for the system n-heptane (1)—toluene (2)

$$P = 92.10\, x_1 + 59.20\, x_2 + x_1 x_2[31.35 - 10.45(x_1 - x_2) +$$
$$+ 0.188(x_1 - x_2)^2 - 0.246(x_1 - x_2)^3 + 15.92(x_1 - x_2)^4].$$

For the system toluene (1)—DMFA (2) another relationship is convenient

$$P = 59.20\, x_1 + 9.75\, x_2 + x_1 x_2[35.84 - 10.48(x_1 - x_2) -$$
$$- 10.31(x_1 - x_2)^2 - 119.37(x_1 - x_2)^3 + 23.63(x_1 - x_2)^4 +$$
$$+ 384.69(x_1 - x_2)^5 - 16.35(x_1 - x_2)^6 - 319.36(x_1 - x_2)^7].$$

The average deviation of the correlated values from the measured values of total pressure in the systems n-heptane—toluene and toluene—DMFA is ± 0.17 torr and ± 0.16 torr, respectively. The maximum deviation in both systems is 0.4 torr.

In view of the relatively low pressures in the systems studied it is possible to use the virial equation of state with secondary coefficients [3] for expressing the volume properties of vapour phase. The coexistence equation allowing the direct calculation of the equilibrium vapour composition at constant temperature assumes thus the following form

$$\frac{dy_1}{dP} = \frac{\Psi - (1 - 2y_1)(y_1 - x_1)(\delta/RT)}{[(y_1 - x_1)/y_1(1 - y_1)] - (y_1 - x_1)(2\delta P/RT)}, \tag{3}$$

where

$$\Psi = \frac{y_1 y_2 \delta - V^L + x_1 B_{11} + x_2 B_{22}}{RT} + \frac{1}{P} \tag{4}$$

and

$$\delta = 2B_{12} - B_{11} - B_{22}. \tag{5}$$

In this study it was assumed $\delta = 0$. The secondary virial coefficients of hydrocarbons and DMFA were calculated according to the correlation put forward by *O'Connell* and *Prausnitz* [4]. The molar volumes of pure components were used for the calculation of the molar volume of liquid solution

$$V^L = x_1 V_1^L + x_2 V_2^L. \tag{6}$$

The values of secondary virial coefficients and the molar volumes of pure components are listed in Table 4.

Table 4

Values of secondary virial coefficients and molar volumes of pure components at 40°C

Substance	B_{ii} [cm^3 mol^{-1}]	V_i^L [cm^3 mol^{-1}]
n-Heptane	−2445	150.4
Toluene	−2100	108.6
DMFA	−3850	63.7

By dividing relationship (*3*) by dx_1 and rearranging we obtain

$$\frac{dy_1}{dx_1} = \frac{\Psi y_1(1 - y_1)}{(y_1 - x_1)} \frac{dP}{dx_1}. \qquad (7)$$

The simplified form of coexistence eqn (*7*) was applied to the calculation of the equilibrium vapour composition by using the procedure described in literature [5].

For the first step in the numerical integration of the differential equation the subsequent approximation was used

$$\frac{dy_1}{dx_1} \doteq \frac{\Delta y_1}{\Delta x_1},$$

where

$$\Delta y_1 = (y_1)_{x_1=\varepsilon} - (y_1)_{x_1=0} = (y_1)_{x_1=\varepsilon}.$$

For calculation of the first value y_1 we obtain eqn (*8*) from relationship (*7*) as a result of the integration steps ε

$$(y_1)_{x_1=\varepsilon} = \left\{ \frac{x_1\left[1 + \left(\frac{dP}{dx_1}\right)\Psi\right]}{1 + x_1\left(\frac{dP}{dx_1}\right)\Psi} \right\}_{x_1=\varepsilon} \qquad (8)$$

The following values y_1 were calculated by solving eqn (*7*) by the method of Runge–Kutta. The numerical integration of coexistence equation, as stated by *van Ness* [6] must always proceed in the direction of increasing total pressure. Our case concerns the systems with a positive deviation from the Raoult's law which do not show any azeotropic point; that is why the calculation starts in the point $x_1 = 0$ and goes on to the point $x_1 = 1$.

The accuracy in the calculation of the values y_1 is also affected by the magnitude of integration step ε. By repeated calculation involving three arbitrary ε values (0.01, 0.005, and 0.001), the same values were obtained for the $y-x$ relationship in the system *n*-heptane–toluene, but in the system toluene–DMFA the deviations of y_1 were as far as the third decimal place.

Table 5

Calculated equilibrium data and activity coefficients of the components in the system *n*-heptane (1)—toluene (2) at 40°C

x_1	P [torr]	y_1	Φ_1	Φ_2	γ_1	γ_2
0.050	63.3	0.110	1.004	1.000	1.518	1.001
0.100	66.7	0.195	1.003	0.999	1.417	1.007
0.150	69.6	0.266	1.003	0.999	1.344	1.014
0.200	72.1	0.328	1.003	0.999	1.287	1.022
0.250	74.5	0.384	1.002	0.998	1.245	1.032
0.300	76.6	0.435	1.002	0.998	1.208	1.042
0.350	78.6	0.482	1.002	0.998	1.177	1.056
0.400	80.4	0.526	1.002	0.998	1.150	1.070
0.450	82.0	0.567	1.001	0.997	1.123	1.088
0.500	83.5	0.606	1.001	0.997	1.100	1.108
0.550	84.8	0.643	1.001	0.997	1.077	1.133
0.600	86.0	0.679	1.001	0.997	1.058	1.162
0.650	87.0	0.715	1.001	0.997	1.040	1.193
0.700	88.0	0.753	1.001	0.997	1.028	1.220
0.750	89.0	0.793	1.000	0.997	1.022	1.241
0.800	89.9	0.834	1.000	0.997	1.018	1.256
0.850	90.7	0.875	1.000	0.996	1.014	1.272
0.900	91.5	0.915	1.000	0.996	1.010	1.309
0.950	92.0	0.954	1.000	0.996	1.003	1.424

Table 6

Calculated equilibrium data and activity coefficients of the components in the system toluene (1)—DMFA (2) at 40°C

x_1	P [torr]	y_1	Φ_1	Φ_2	γ_1	γ_2
0.050	14.9	0.371	1.005	0.999	1.877	1.011
0.100	18.8	0.521	1.005	0.998	1.662	1.024
0.150	22.8	0.627	1.004	0.997	1.617	1.024
0.200	26.9	0.701	1.004	0.997	1.599	1.028
0.250	30.6	0.751	1.003	0.996	1.558	1.038
0.300	33.6	0.785	1.003	0.995	1.489	1.053
0.350	36.3	0.811	1.003	0.995	1.425	1.077
0.400	38.7	0.832	1.002	0.994	1.363	1.105
0.450	41.1	0.851	1.002	0.994	1.316	1.135
0.500	43.4	0.868	1.002	0.993	1.275	1.167
0.550	45.5	0.882	1.002	0.993	1.234	1.215
0.600	47.2	0.894	1.001	0.993	1.190	1.273
0.650	48.6	0.903	1.001	0.992	1.142	1.371
0.700	49.9	0.913	1.001	0.992	1.101	1.472
0.750	51.3	0.923	1.001	0.992	1.067	1.607
0.800	53.0	0.937	1.001	0.991	1.049	1.698
0.850	54.9	0.952	1.001	0.991	1.039	1.786
0.900	56.4	0.965	1.000	0.991	1.022	2.006
0.950	57.3	0.975	1.000	0.990	0.994	2.911

At the end the activity coefficients of components γ_1 and γ_2 were calculated by means of the formula

$$\gamma_i = \frac{P\, y_i\, \Phi_i}{P_i^0\, x_i} \tag{9}$$

where Φ_i is defined by eqn (*10*)

$$\ln \Phi_i = \frac{(P_i^0 - P)\,(V_i^L - B_{ii})}{RT} . \tag{10}$$

The calculated values of y_1, γ_1, γ_2, Φ_1, and Φ_2 are presented in Tables 5 and 6.

Symbols

x_i	mole fraction of the component in liquid
y_i	mole fraction of the component in vapour
P_i^0	pressure of the saturated vapour of pure component
P	total pressure
P^E	excess pressure
A_j	coefficient of polynomial
B_{ii}	secondary virial coefficient of pure component
R	gas constant
T	absolute temperature
V_i^L	molar volume of pure liquid component
V^L	molar volume of liquid solution
γ_i	activity coefficient of the component in liquid
δ	$2B_{12}-B_{11}-B_{22}$, function of the secondary virial coefficients
Φ_i	correction factor expressed by eqn (*10*)
Ψ	defined by eqn (*4*)
ε	integration step
j	exponent expressing the degree of polynomial

Subscripts 1, 2, and i denote more volatile component, less volatile component, and component i, respectively.

References

1. Rossini, D., *Selected Values of Properties of Hydrocarbons*. Circular C 641. National Bureau of Standards, Washington, 1947.
2. Surový, J., *Habilitation Thesis*. Slovak Technical University, Bratislava, 1969.
3. Prausnitz, J. M., Eckert, C. A., Orye, R. V., and O'Connell, J. P., *Computer Calculations for Multicomponent Vapor—Liquid Equilibria*. Prentice-Hall, Englewood Cliffs, New York, 1967.
4. O'Connell, J. P. and Prausnitz, J. M., *Ind. Eng. Chem., Process Design Develop.* **6**, 245 (1967).
5. Chang, S. D. and Lu B. C. Y., *Can. J. Chem. Eng.* **46**, 273 (1968).
6. Van Ness, H. C., *AICHE J.* **16**, 18 (1970).

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