Isothermal Vapour—Liquid Equilibrium Data for the System Toluene—N-Methylpyrrolidone at 40°C, 50°C, and 60°C

E. GRACZOVÁ and J. SUROVÝ

Department of Chemical and Biochemical Engineering, Faculty of Chemical Technology,
Slovak University of Technology, SK-812 37 Bratislava

Sets of isothermal vapour—liquid equilibrium data are presented for the system toluene—N-methylpyrrolidone at 40°C, 50°C, and 60°C, measured by a static method. The binary parameters of equations for the concentration dependence of the excess Gibbs energy (NRTL, Wilson, van Laar equations, and the Redlich—Kister 4th-order expansion) were evaluated using a simple objective function based on the maximum likelihood method.

For the extraction of aromatic hydrocarbons by N-methylpyrrolidone or its mixed solvents it is necessary to know binary vapour—liquid equilibria for the system aromate—N-methylpyrrolidone. To our knowledge, these data are not available in the literature. In this paper we report on the measurement of equilibrium data of the binary system toluene—N-methylpyrrolidone at temperatures close to temperatures employed in the commercial extraction.

In principle there are many methods available for a thermodynamic description of solutions [1, 2]. More about identification parameters of equations for the excess Gibbs energy (G^E equations) can be found in paper [3].

Starting from the maximum likelihood method [1] the objective function F for the set of isothermal $P—x$ equilibrium data can be written in the following form

$$F = \sum_n \left[\left(\frac{x_1 - x_{\text{calc},1}}{\sigma_x^2} \right)^2 + \left(\frac{P - P_{\text{calc}}}{\sigma_P^2} \right)^2 + \left(\frac{T - T_{\text{calc}}}{\sigma_T^2} \right)^2 \right]_n \quad n = 1, 2, \ldots, N \quad (1)$$

where P is total pressure, T thermodynamic temperature, and x_i mole fraction of component i in the liquid; σ_P, σ_T, and σ_x are standard deviations of the abovementioned variables; subscript calc denotes calculated values.

On the basis of our results [4], the objective function (1) for an isothermal system can be written in the form

$$F = \sum_n \left[(P - P_{\text{calc}})^2 + \left(\frac{\partial P_{\text{calc}}}{\partial x_1} \right)^2 (x_1 - x_{\text{calc},1})^2 \right]_n \quad (2)$$

The objective function (2) divides deviations of measured variables P and x_1 in such a manner that they contribute by equal mass to the inaccuracy of the expression $P = f(x)$.

For the evaluation of independent variables x_1 we suggested an iteration method for the calculation of $x_{\text{calc},1}$ in the minimum of the objective function (2). From the condition

$$\left(\frac{\partial F}{\partial x_1} \right)_n = 0 \quad (3)$$

and considering that following equalities approximately hold

$$x_{\text{calc},1} = x_{\text{calc},1}^\circ + \Delta x_1$$
$$P_{\text{calc}} = P_{\text{calc}}^\circ + \left(\frac{\partial P_{\text{calc}}}{\partial x_1} \right)^\circ \Delta x_1 \quad (4)$$
$$P_{\text{calc}}^\circ = P(x_1 - x_{\text{calc},1}^\circ)$$

the following expression can be derived for the increment Δx_1 of the n-th measurement

$$\Delta x_1 = \left[(x_1 - x_{\text{calc},1}^\circ) \left(\frac{\partial P_{\text{calc}}}{\partial x_1} \right)^\circ + (P - P_{\text{calc}}) \right] \bigg/ 2 \left(\frac{\partial P_{\text{calc}}}{\partial x_1} \right)^\circ \quad (5)$$

By the superscripts ° are denoted the values from the last iteration.

EXPERIMENTAL

N-Methylpyrrolidone (NMP) was prepared from a technical product used in the oil refinery Slovnaft, by double vacuum rectification. Toluene (anal. grade, Lachema, Neratovice) was redistilled in an atmospheric column with about 20 theoretical plates.

The chromatographic purity of NMP was higher than 99.8 %, in the case of toluene this value reached 99.6 %.

Isothermal liquid—vapour equilibrium data of the binary system toluene—NMP at 40 °C, 50 °C, and 60 °C were measured by a static method in the modified apparatus described in [5]. The pressure was measured by a precise manometer with the accuracy of ± 0.03 mm of the mercury column height, *i.e.* with the accuracy of about ± 4 Pa. The liquid sample was prepared using an analytical weight with the accuracy of ± 5 × 10^{-4} g, *i.e.* with the accuracy of about ± 2 × 10^{-4} mole %. The sets of equilibrium data for the system toluene—NMP at 40 °C, 50 °C, and 60 °C are listed in Table 1.

RESULTS AND DISCUSSION

The measured sets of experimental data were correlated by the NRTL, Wilson, van Laar, and Redlich—Kister equations. The parameters of the above-mentioned G^E equations were calculated using the objective function (2), by the maximum likelihood method utilizing the procedure suggested by *Rod* and *Hančil* [6].

The given problem was solved in two independent iteration cycles [4].

1. With respect to the parameters of G^E equations, simultaneously for all the experimental data (at constant values of the incidental parameters x_{1n}). The

Table 1. Experimental Isothermal Equilibrium Data $P—x_1$ for the System Toluene—NMP at 40 °C, 50 °C, and 60 °C

x_1	P/Pa		
	40 °C	50 °C	60 °C
0.	159	283	522
0.0561	786	1219	1968
0.1114	1337	2098	3289
0.2043	2184	3464	5344
0.2589	2654	4191	6442
0.3524	3536	5530	8395
0.4225	4230	6517	9873
0.5158	4918	7564	11451
0.5785	5355	8281	12542
0.6572	5778	8946	13556
0.7484	6223	9680	14648
0.8081	6700	10408	15728
0.8746	7043	10892	16466
0.9535	7650	11844	17835
1.	7893	12212	18464

total pressure P_{calc} was calculated from the relation

$$P_{calc} = \frac{x_{calc,1}\gamma_1 f_1^{oL}}{\varphi_1^G} + \frac{x_{calc,2}\gamma_2 f_2^{oL}}{\varphi_2^G} \quad [T] \quad (6)$$

taking into account the real behaviour of the liquid—vapour system. The fugacity coefficient φ_i^G of component *i* in vapour phase was calculated according to the equation

Table 2. Values of Parameters of the NRTL, Redlich—Kister, Wilson, and van Laar Equations, Mean Deviations of Mole Fractions and Pressures for the System Toluene—NMP at 40 °C, 50 °C, and 60 °C

θ/°C	Parameters of G^E equations			$d(x)/10^{-2}$	$d(P)$/kPa
NRTL equation					
	τ_{12}	τ_{21}	α_{12}		
40	4.6261	−3.1118	0.0681	0.33	0.024
50	1.1792	−0.2989	0.5622	0.27	0.028
60	0.8795	−0.0110	1.0459	0.25	0.040
Redlich—Kister 4th-order expansion					
	B_{12}	C_{12}	D_{12}		
40	0.4669	0.2412	0.0779	0.32	0.023
50	0.4817	0.2301	0.0948	0.26	0.026
60	0.4952	0.2180	0.1161	0.24	0.037
Wilson equation					
	Λ_{12}	Λ_{21}			
40	1.5184	0.2525		0.34	0.025
50	1.5140	0.2496		0.27	0.028
60	1.5026	0.2505		0.25	0.040
van Laar equation					
	A_{12}	A_{21}			
40	0.3404	0.7875		0.49	0.018
50	0.3407	0.7872		0.34	0.025
60	0.3589	0.7649		0.32	0.032

$$RT \ln \varphi_i^{\mathrm{G}} = (B_{ij} + y_j^2 \delta_{ij})P \qquad (7a)$$

where

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \qquad (7b)$$

For the calculation of the second virial coefficients B *Pitzer* and *Curl* method [7] was used. The critical parameters of NMP were taken from the literature [4]. The critical parameters and parameters for calculation of vapour pressure of toluene are given in literature [8]. The vapour pressures of pure NMP at abovementioned temperatures were extrapolated from data reported in literature [9].

2. With respect to the incidental parameters x_{1n}, separately for each measurement (at constant values of the parameters of G^{E} equations), according to relation (5). The alteration of both the iteration cycles is repeated until the minimum of the objective function (2) with a required tolerance is reached.

The values of parameters of the above-mentioned equations and the corresponding values of mean deviations in mole fractions of the liquid phase and the total pressure are given in Table 2. The values of the mean deviation in total pressure $d(P)$ are ranging within 0.023—0.040 kPa and the values of the mean deviations in mole fractions of the liquid phase $d(x)$ are within 0.0027—0.0049.

SYMBOLS

A_{ij}	parameter of the van Laar equation
B	the second virial coefficient
B_{ij}, C_{ij}, D_{ij}	parameters of the Redlich—Kister equation
d	mean deviation
F	objective function
f_i^{oL}	fugacity of pure component i in liquid
G^{E}	molar excess Gibbs energy
n	number of measurements
N	total number of measurements
P	total pressure
R	gas constant
T	thermodynamic temperature
x_i	mole fraction of component i in liquid
y_i	mole fraction of component i in gas
α_{ij}, τ_{ij}	parameters of the NRTL equation
φ_i^{G}	fugacity coefficient of component i in vapour
γ_i	activity coefficient of component i
δ	parameter of eqn (7)
Λ_{ij}	parameters of the Wilson equation
σ	standard deviation
θ	temperature

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