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Isobaric Binary and Ternary Vapor–Liquid Equilibria of *N*-Methylpyrrolidone with Water and Toluene at 760 mmHg

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Isobaric vapor–liquid equilibrium data have been generated for water–*N*-methylpyrrolidone, toluene–*N*-methylpyrrolidone, and water–toluene–*N*-methylpyrrolidone systems at 760 mmHg. The data were correlated satisfactorily through NRTL, Wilson, UNIQUAC, UNIFAC, and three constant Redlich–Kister equations.

Introduction

In the industrial extraction of aromatics from naphtha streams like reformates, hydrogenated pyrolysis gasolines, and straight run naphthas, *N*-methylpyrrolidone (NMP) is used as a solvent. This solvent is always used with water as an antisolvent in concentrations varying from 10% to 20% by weight. In the process there are steps like extractive distillation, solvent recovery, and/or stripping. For designing, revamping, or optimization of these steps, vapor–liquid equilibrium (VLE) data are essential on systems of interest.

The VLE data for water–toluene–NMP ternary are not available in the literature. However, some isobaric and isothermal VLE data for water–NMP and toluene–NMP binaries are reported in the literature (*1–7*).

In the present study the VLE data for water–NMP, toluene–NMP, and water–toluene–NMP systems have been determined and correlated by different solution models.

Experimental Section

Materials. Pure toluene and NMP were obtained from M/s BDH, India, ane M/s Aldrich Chemicals, USA, respectively. Toluene was used as such, and NMP was distilled under vacuum and its heart cut was collected and used in the study. The purities of these chemicals were checked by measuring their densities and refractive indices which corresponded to a minimum of 99%.

Experimental Procedure. The VLE studies for the binary and ternary systems were carried out in a modified Smith and Bonner (*8*) type of still provided with a magnetic stirrer. The experimental details are described in an earlier paper (*9*). For ternary VLE determination of water–toluene–NMP in the miscible region, the liquid-phase compositions were chosen from a ternary equilibrium solubility diagram determined at 25 °C by a titration method (*10*).

Analysis of Vapor Phase. The binary water–NMP is a miscible system, and there is a wide difference in the refractive indices of the two components. The vapor samples for this system were, therefore, analyzed by a calibrated RI composition chart prepared at 20 °C. The accuracy of measurements of the compositions was found to be within ±0.5%.

For toluene–NMP binary, the vapor-phase samples were analyzed by gas chromatography (GC).

The vapor samples of water–toluene–NMP ternary always formed two liquid phases on condensation. These vapor samples were made homogeneous by the addition of a known amount of anhydrous sulfolane. The homogeneous samples were then analyzed by GC using a Perkin-Elmer Sigma 300 gas chromatograph with a thermal conductivity detector and LCI-100 laboratory computing integrator. The analysis was carried out on a Tenax-GC column (1 × 2 mm) with hydrogen as a carrier gas. This column was also used for toluene–NMP samples. The accuracy of analysis for GC was found to be about 2% in both cases.

Table I. Experimental VLE Data for Water (1)–*N*-Methylpyrrolidone (3) at 760.0 mmHg: Temperature, t, and Liquid-Phase, x_1, and Vapor-Phase, y_1, Mole Fraction Compositions

t/°C	x_1	y_1	t/°C	x_1	y_1
100.0	1.0	1.0	106.0	0.7830	0.9885
100.5	0.9799	0.9989	109.0	0.7004	0.9822
101.2	0.9550	0.9977	114.7	0.5713	0.9685
102.0	0.9261	0.9963	128.5	0.3495	0.9225
102.9	0.8898	0.9944	144.5	0.1964	0.8373
104.0	0.8438	0.9920	202.8	0.0	0.0

Table II. Experimental VLE Data for Toluene (2)–*N*-Methylpyrrolidone (3) at 760.0 mmHg: Temperature, t, and Liquid-Phase, x_2, and Vapor-Phase, y_2, Mole Fraction Compositions

t/°C	x_2	y_2	t/°C	x_2	y_2
110.6	1.0	1.0	137.2	0.4154	0.9035
114.0	0.9044	0.9918	145.6	0.3141	0.8527
117.5	0.8113	0.9828	155.5	0.2157	0.7747
121.0	0.7115	0.9712	170.5	0.1125	0.6080
125.0	0.6125	0.9565	202.8	0.0	0.0
130.2	0.5168	0.9302			

Table III. Experimental VLE Data for Water (1)–Toluene (2)–*N*-Methylpyrrolidone (3) at 760.0 mmHg: Temperature, t, and Liquid-Phase, x_1, x_2, and Vapor-Phase, y_1, y_2, Mole Fraction Compositions

t/°C	x_1	x_2	y_1	y_2
97.5	0.3804	0.2207	0.5157	0.4696
97.6	0.6441	0.0502	0.5731	0.4121
97.6	0.1846	0.4893	0.5801	0.4037
98.4	0.2182	0.4240	0.5663	0.4166
98.5	0.4922	0.1242	0.5050	0.4775
101.6	0.5795	0.0553	0.5667	0.4141
103.1	0.2309	0.3353	0.5205	0.4575
106.2	0.4926	0.0634	0.5900	0.3810
109.8	0.2188	0.2662	0.5268	0.4420
111.5	0.2291	0.2263	0.5321	0.4327
112.5	0.5277	0.0163	0.8138	0.1504
114.1	0.3792	0.0742	0.6461	0.3144
119.0	0.2261	0.1797	0.5516	0.4005
127.2	0.2351	0.0864	0.5860	0.3361
136.6	0.2158	0.0448	0.6886	0.2015

Results and Discussion

The experimental VLE data for water–NMP, toluene–NMP and water–toluene–NMP systems are presented in Tables I, II, and III, respectively. The binary liquid-phase activity coefficients required for the estimation of binary parameters were calculated using the classical relation (*11*).

The second virial coefficients B_{ij} were calculated by Pitzer–Curl's correlation as modified by Tsonopoulos (*12*). The critical constants and acentric factors for water and toluene were taken from the literature (*13*), and for NMP they were calculated

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Table IV. Coefficients *a*, *b*, and *c* in Liquid Molar Volume *V* Correlation[a] and Antoine Constants *A*, *B*, and *C*[b]

component	*a*	*b*	$c/10^{-4}$	*A*	*B*	*C*
water	22.8882	–0.036 425	0.6857	7.966 81	1682.21	228.0
toluene	98.865	–0.557 8	2.770	6.953 34	1343.943	219.377
NMP	102.635	–0.117 94	3.2323	7.362 566	1874.715	215.508

[a] $V_i^L/(\text{cm}^3\ \text{mol}^{-1}) = a + b(T/\text{K}) + c(T/\text{K})^2$. [b] $\log (p_i^S/\text{mmHg}) = A - B/((t/°\text{C}) + C)$.

Table V. Correlation Parameters for the Constituent Binaries and Root Mean Square Deviations in Vapor-Phase Mole Fractions, RMSD(y_1)

parameter	water (1)– toluene (2)	water (1)– NMP (3)	toluene (2)– NMP (3)
1. NRTL (Three-Parameter)			
$\Delta g_{12}/R$	881.052 K	-23.054 K	-219.615 K
$\Delta g_{21}/R$	2488.456 K	89.7835 K	420.185 K
α_{12}	0.2	0.3	0.3
RMSD(y_1)		0.0048	0.0071
2. Wilson (Two-Parameter)			
λ_{12}/R		290.071 K	38.683 K
λ_{21}/R		131.614 K	81.276 K
RMSD(y_1)		0.0091	0.0070
3. UNIQUAC (Two-Parameter)			
$\Delta u_{12}/R$	3131.712 K	-124.236 K	20.827 K
$\Delta u_{21}/R$	552.168 K	9.013 K	28.266 K
RMSD(y_1)		0.0335	0.0113
4. UNIFAC			
RMSD(y_1)		0.0081	0.0073
5. Redlich–Kister (Three-Constant)			
B_{12}		0.037 80	0.126 77
C_{12}		0.027 25	0.009 32
D_{12}		0.048 78	0.040 11
RMSD(y_1)		0.003 4	0.007 0

Table VI. Root Mean Square Deviations (RMSD) in Vapor-Phase Mole Fraction (y_i) Values for the Prediction of Ternary VLE by Different Model Equations

	RMSD(y_i)		
equation	water	toluene	NMP
NRTL	0.0234	0.0167	0.0150
UNIQUAC	0.0340	0.0332	0.0142
UNIFAC	0.0492	0.0450	0.0171

by the method of Hakuta and Hirata (*14*). The liquid molar volumes V_i^L for water and toluene at three different temperatures were taken from the literature (*13*), and for NMP they were calculated from the experimental density values and fitted to a quadratic equation with coefficients *a*, *b*, and *c* given in Table IV. The pure component vapor pressures P_i^S were calculated from Antoine constants *A*, *B*, and *C* available in the literature (*15*, *3*) and are also reported in Table IV.

The experimental VLE data for the binary mixtures of water–NMP and toluene–NMP were correlated through Wilson (*16*), NRTL (*17*), and UNIQUAC (*18*) equations using the Simplex optimization technique (*19*). These two binaries were further correlation by UNIFAC (*20*, *21*) and three parameter Redlich–Kister (*22*) equations. The binary parameters for partially miscible water–toluene binary were calculated by NRTL and UNIQUAC equations from the mutual solubility data reported in the literature (*23*) at 99.4 °C. The estimated binary parameters along with the root mean square deviation (RMSD) betwen experimental and calculated vapor-phase compositions are presented in Table V. The binary data satisfy the Herington's (*24*) area consistency test (water–NMP, $D = 12.07$, $J = 41.0$; toluene–NMP, $D = 23.36$, $J = 37.73$).

From the calculated constituent binary parameters of NRTL and UNIQUAC models, the ternary VLE data were calculated using their ternary forms. The ternary data were also calculated from the UNIFAC model from the t–x data. The comparative results are given in Table VI.

It is obvious from Table V that water–NMP and toluene–NMP binaries are best represented by three constant Redlich–Kister, NRTL, and UNIFAC equations.

Glossary

n	number of data points
P^S_i	pure component saturated vapor pressures, mmHg
P	total pressure, mmHg
R	molar gas constant, cal mol^{-1} K^{-1}
RMSD-(y_i)	$(\sum_{i=1}^{n}(y_{i,\text{exptl}} - y_{i,\text{calcd}})^2/n)^{1/2}$
t	temperature, °C
T	absolute temperature, K
V^L_i	pure component liquid molar volume, cm^3 mol^{-1}
x_i	liquid-phase mole fraction of component i.
y_i	vapor-phase mole fraction of component i.

Subscripts

i	component i
calcd	calculated value
exptl	experimental value

Registry No. NMP, 872-50-4; toluene, 108-88-3.

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