Liquid−Liquid Equilibria of Hydrocarbons with *N*-Formylmorpholine

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Liquid−liquid equilibria of *N*-formylmorpholine (NFM) with alkanes (*n*-hexane, *n*-heptane, isononane), aromatics (benzene, *p*-xylene, toluene), and water were investigated. The experiments were conducted by considering binary, ternary, and quaternary systems at different temperatures (20−60 °C) and initial mixture compositions in the range of mole fraction equal to 0.3−0.6 for NFM, 0.23−0.4 for alkanes, 0.11−0.4 for aromatics, and 0.072−0.24 for water, respectively. The results are used to estimate the interaction parameters of the UNIQUAC expression, for the pairs NFM/*n*-hexane, NFM/*n*-heptane, NFM/isononane, NFM/benzene, NFM/*p*-xylene, NFM/toluene, and NFM/water whose values were not available in the literature.

Introduction

In the chemical industry, the extraction of aromatics from various feedstocks using *N*-formylmorpholine (NFM) as a solvent constitutes an important separation process (Al Qattan et al., 1995). The goal of controlling and optimizing the extraction units where NFM is employed may be achieved using suitable mathematical models (Weinstein et al., 1998). In addition to the difficulty of modeling important aspects related to hydrodynamics and mass transfer of countercurrent liquid−liquid extraction columns, it is widely recognized that an accurate simulation of phase equilibria is mandatory.

To our knowledge, information related to liquid−liquid equilibria involving NFM and hydrocarbons are scarce in the literature (Al Qattan et al., 1995; Marusina et al., 1995). This is also true if one looks for vapor−liquid equilibrium data involving NFM (cf. Park and Gmehling (1989)) from which the interaction parameters of miscible pairs participating in liquid−liquid equilibria can be obtained (cf. Sørensen and Arlt (1979)).

With the aim of contributing to the knowledge of liquid−liquid equilibria with NFM, in the present work we focus our attention on binary, ternary, and quaternary systems where alkanes, aromatics, and water are involved. The results are used to estimate the interaction parameters of the UNIQUAC expression (cf. Abrams and Prausnitz (1975)), for the pairs NFM/*n*-hexane, NFM/*n*-heptane, NFM/isononane, NFM/benzene, NFM/*p*-xylene, NFM/toluene, and NFM/water whose values were not available in the literature.

Table 1. Purity of Chemicals Used in this Work

chemical	supplier	purity %
n-hexane	Merck	99.63
n-heptane	Synthesis Parma	99.5
isononane	EniChem (Certichim−ISO 9002)	98.14
toluene	EniChem (Certichim−ISO 9002)	99.98
p-xylene	EniChem (Certichim−ISO 9002)	99.53
benzene	EniChem (Certichim−ISO 9002)	99.98
NFM	EniChem (Certichim−ISO 9002)	99.1

Experimental Section

The chemicals used in this work are described in Table 1. In addition, twice-distilled water is employed to perform the study of quaternary systems and to separate NFM from hydrocarbons as described below.

The experimental setup is schematically shown in Figure 1. The jacketed glass cell of 2 L equipped with a stirrer was maintained at the desired temperature through forced circulation of water. The temperature in the cell was controlled with an electronic device (Yokogawa) within ±0.1 K. The reactor temperature was continuously recorded during the experimental runs through a mercury thermometer (±0.2 K). The cell was also equipped with a condenser to ensure complete condensation and recycling of evaporated compounds. In a typical experimental run, once the cell reached a specified temperature, the desired mixture was charged into it and then stirred for about 40 min and left to settle for about 30 min. Increasing agitation or settling times did not affect the accuracy of measurements, thus indicating that equilibrium was attained.

When this condition was reached, the compositions of the two phases were obtained by analyzing samples taken from each phase in the cell as follows. For binary systems considered in this work, NFM content in the light phase was determined using ANTEK, i.e., a chemiluminescent nitrogen system, after dilution with a proper quantity of toluene, to guarantee the complete solubilization of the NFM/alkane mixture even at ambient conditions and the

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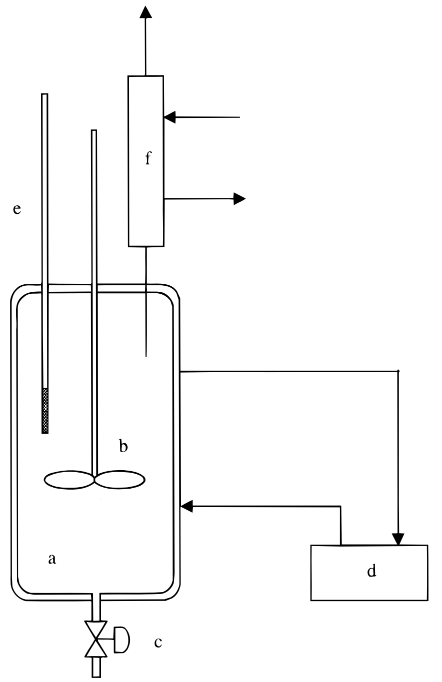

Figure 1. Schematic diagram of the experimental apparatus (a = jacketed cell; b = stirrer; c = drain valve; d = control unit; e = thermometer; f = condenser).

Table 2. Operating Conditions for the Experimental Runs

run	system	T, °C	mole fraction	run	system	T, °C	mole fraction
1	NFM	20.4	0.6	21	NFM	38	0.5134
	n-hexane		0.4		*n*-heptane		0.3547
2	NFM	25.7	0.6		toluene		0.1319
	n-hexane		0.4	22	NFM	38	0.4566
3	NFM	30.3	0.6		*n*-heptane		0.3150
	n-hexane		0.4		toluene		0.2284
4	NFM	40	0.6	23	NFM	38	0.4107
	n-hexane		0.4		*n*-heptane		0.2827
5	NFM	45.2	0.6		toluene		0.3066
	n-hexane		0.4	24	NFM	38	0.3717
6	NFM	50	0.6		*n*-heptane		0.2564
	n-hexane		0.4		toluene		0.3719
7	NFM	62.2	0.6	25	NFM	38	0.5244
	n-hexane		0.4		*n*-heptane		0.3618
8	NFM	25.1	0.63		*p*-xylene		0.1138
	n-heptane		0.37	26	NFM	38	0.4708
9	NFM	29.2	0.63		*n*-heptane		0.3252
	n-heptane		0.37		*p*-xylene		0.2040
10	NFM	38.1	0.63	27	NFM	38	0.4277
	n-heptane		0.37		*n*-heptane		0.2944
11	NFM	45	0.63		*p*-xylene		0.2779
	n-heptane		0.37	28	NFM	38	0.3909
12	NFM	61.9	0.63		*n*-heptane		0.2697
	n-heptane		0.37		*p*-xylene		0.3394
13	NFM	25.1	0.69	29	NFM	38	0.3901
	isononane		0.31		*n*-heptane		0.2773
14	NFM	38	0.69		*p*-xylene		0.2609
	isononane		0.31		water		0.0717
15	NFM	44.8	0.69	30	NFM	38	0.3512
	isononane		0.31		*n*-heptane		0.2582
16	NFM	59.8	0.69		*p*-xylene		0.2437
	isononane		0.31		water		0.1469
17	NFM	38	0.5043	31	NFM	38	0.3277
	n-heptane		0.3472		*n*-heptane		0.2470
	benzene		0.1485		*p*-xylene		0.2330
18	NFM	38	0.4391		water		0.1923
	n-heptane		0.3023	32	NFM	38	0.3019
	benzene		0.2586		*n*-heptane		0.2341
19	NFM	38	0.3888		*p*-xylene		0.2210
	n-heptane		0.2678		water		0.2430
	benzene		0.3434				
20	NFM	38	0.3489				
	n-heptane		0.2402				
	benzene		0.4109				

appropriate range of nitrogen concentration required by ANTEK. The NFM content in the heavy phase was measured by introducing the thermostated sample into a gas chromatograph (HP 5890) equipped with a inovax capillary column (i.d., 0.32 mm; column length, 60 m; layer thickness, 0.3 μm) and a flame ionization detector (FID). The carrier gas was hydrogen (285 cm^3/min). The injector temperature was kept at 250 °C, while that of the detector was kept at 270 °C. The detector was fed with air and hydrogen with a split ratio equal to 1/250. The working temperature was set at 220 °C. The alkane concentrations in the light and heavy phases were obtained from the constraint that the sum of mole fractions should be equal to 1 in each of the two phases.

When ternary systems are considered, NFM in the light phase was obtained as described above, while alkane and aromatic species involved were first separated from NFM by taking an additional sample and using a suitable amount of water with respect to the sample volume. Thus, these components are practically immiscible with water. The two phases obtained were separated using a separatory funnel. The corresponding mass ratio of alkanes and aromatics is then obtained using a gas chromatograph (HP 5890), equipped with a methyl silicone capillary column (i.d., 0.2 mm; column length, 50 m; layer thickness, 0.5 μm) and a FID. The carrier gas was nitrogen. The detector was fed with air and hydrogen with a split ratio equal to 1/300. The analysis was carried out with the following programmed temperature analysis: an initial temperature of 50 °C was kept for 5 min followed by a temperature gradient of 20 °C/min up to 200 °C; this latter temperature was finally held for 20 min. This procedure was required because of the very low content of NFM in the light phase, which was not accurately detectable by the gas chromatograph. The same strategy as above was followed to obtain the hydrocarbon content of the heavy phase. The only difference was that the NFM content was measured as described for the heavy phase of binary systems.

Quaternary systems involved the presence of water whose content in the two immiscible phases was measured using a Karl Fischer apparatus. For these systems three samples from each phase are taken, while NFM, alkane, and aromatic contents were detected as described previously for ternary systems. For all systems investigated the accuracy of the mole fraction measurement is within ±1 wt %.

After the samples had been taken, depending on the system considered, the two phases were collected from the cell using a stopcock with a narrow neck placed at its bottom which allows one to display the meniscus between the two immiscible phases so that the latter ones could be separated with negligible losses. The masses of the two phases were measured with a suitable balance. The reliability of the obtained results was verified through appropriate material balances.

As summarized in Table 2, the experimental runs were carried out at various temperature levels of industrial interest and different initial mixture compositions for binary, ternary, and quaternary systems. The reproducibility of the experimental runs was verified by repeating each of them at least twice, until the difference between two runs was within the experimental error in the concentration measurement. The results of the two runs are then averaged, and averaged results are reported.

Table 3. Experimental Data for the System NFM (1)/*n*-Hexane (2): $A_{12} = 3.2195 \times 10^2$ J·mol^{-1}; $A_{21} = 3.0227 \times 10^3$ J·mol^{-1}; $\eta = 7.5\%$

	light phase (mole fraction)		heavy phase (mole fraction)	
run	NFM	*n*-hexane	NFM	*n*-hexane
1	0.0086	0.9914	0.9748	0.0252
2	0.0093	0.9907	0.9679	0.0321
3	0.0112	0.9888	0.9709	0.0291
4	0.0153	0.9847	0.9630	0.0370
5	0.0174	0.9826	0.9592	0.0408
6	0.0203	0.9797	0.9525	0.0475
7	0.0219	0.9781	0.9530	0.0470

Model Equations

At a fixed temperature and pressure, liquid−liquid equilibria in multicomponent systems can be quantitatively described on the basis of the following equilibrium conditions

$$\gamma_i^{\mathrm{I}} x_i^{\mathrm{I}} = \gamma_i^{\mathrm{II}} x_i^{\mathrm{II}} \qquad i = 1, N_{\mathrm{C}} \tag{1}$$

coupled with an overall mass balance for ternary and quaternary systems

$$x_i^0 = \alpha x_i^{\mathrm{I}} + (1 - \alpha) x_i^{\mathrm{II}} \qquad i = 1, N_{\mathrm{C}} - 1 \tag{2}$$

and the constraints

$$\sum_{i=1}^{N_{\mathrm{C}}} x_i^{\mathrm{I}} = \sum_{i=1}^{N_{\mathrm{C}}} x_i^{\mathrm{II}} = 1 \tag{3}$$

where x_i^0 represents the molar fraction of the ith component in the initial mixture, x_i^{I} and x_i^{II} are the equilibrium mole fractions of the ith component in the two phases, γ_i^{I} and γ_i^{II} are the corresponding activity coefficients of the ith component in the two phases, α is the ratio between the total number of moles of phase I and the total number of moles of the initial mixture, and N_{C} represents the number of components. The activity coefficients of the ith component in the two phases are computed through the UNIQUAC expression (Abrams and Prausnitz, 1975), which contains two adjustable parameters per binary; i.e., $A_{ij} = u_{ij} - u_{jj}$. For a mixture of given composition, the equations above represent a system of nonlinear algebraic equations which was solved using standard routines (cf. Buzzi Ferraris and Tronconi (1986)). Thus, the ratio α as well as the mole fractions of the ith component in the two phases may be computed. The parameters of the UNIQUAC expression were evaluated by direct comparison of model results with the experimental data as described in the next section.

The objective function to perform the fitting of model parameters is given by

$$F = \sum_{k=1}^{N_{\mathrm{S}}} \sum_{j=1}^{2} \left[\sum_{i=1}^{N_{\mathrm{C}}-1} \left(\frac{x_{ik\mathrm{c}}^{j} - x_{ik\mathrm{s}}^{j}}{x_{ik\mathrm{c}}^{j}} \right)^2 \right] \tag{4}$$

where the significance of the symbols is reported in Notation.

Table 4. Experimental Data for the System NFM (1)/*n*-Heptane (2): $A_{12} = 2.85 \times 10^2$ J·mol^{-1}; $A_{21} = 2.9316 \times 10^3$ J·mol^{-1}; $\eta = 4.3\%$

	light phase (mole fraction)		heavy phase (mole fraction)	
run	NFM	*n*-heptane	NFM	*n*-heptane
8	0.0129	0.9871	0.9761	0.0239
9	0.0131	0.9869	0.9748	0.0252
10	0.0172	0.9828	0.9704	0.0296
11	0.0214	0.9786	0.9696	0.0304
12	0.0244	0.9756	0.9637	0.0363

Table 5. Experimental Data for the System NFM (1)/Isononane (2): $A_{12} = -6.1404 \times 10^1$ J·mol^{-1}; $A_{21} = 3.1936 \times 10^3$ J·mol^{-1}; $\eta = 7.2\%$

	light phase (mole fraction)		heavy phase (mole fraction)	
run	NFM	isononane	NFM	isononane
13	0.0135	0.9865	0.9867	0.0133
14	0.0209	0.9791	0.9819	0.0181
15	0.0235	0.9765	0.9802	0.0198
16	0.0337	0.9663	0.9786	0.0214

Table 6. Experimental Data for the System NFM (1)/*n*-Heptane (2)/Benzene (3): $A_{13} = 8.092\,27 \times 10^2$ J·mol^{-1}; $A_{31} = 7.186\,43 \times 10^1$ J·mol^{-1}; $\eta = 2.0\%$

	light phase (mole fraction)			heavy phase (mole fraction)		
run	NFM	*n*-heptane	benzene	NFM	*n*-heptane	benzene
17	0.0297	0.7876	0.1827	0.8246	0.0525	0.1229
18	0.0504	0.6618	0.2878	0.6995	0.0621	0.2384
19	0.0710	0.5358	0.3932	0.6019	0.0807	0.3174
20	0.1066	0.4558	0.4376	0.5026	0.1051	0.3923

Table 7. Experimental Data for the System NFM (1)/*n*-Heptane (2)/Toluene (3): $A_{13} = 5.068\,91 \times 10^2$ J·mol^{-1}; $A_{31} = 3.970\,74 \times 10^2$ J·mol^{-1}; $\eta = 6.2\%$

	light phase (mole fraction)			heavy phase (mole fraction)		
run	NFM	*n*-heptane	toluene	NFM	*n*-heptane	toluene
21	0.0305	0.7906	0.1789	0.8553	0.0418	0.1029
22	0.0467	0.6562	0.2971	0.7713	0.0520	0.1767
23	0.0862	0.5343	0.3795	0.6781	0.0728	0.2491
24	0.1200	0.4300	0.4500	0.6000	0.0978	0.3022

Table 8. Experimental Data for the System NFM (1)/*n*-Heptane (2)/*p*-Xylene (3): $A_{13} = 3.2967 \times 10^1$ J·mol^{-1}; $A_{31} = 6.895\,39 \times 10^2$ J·mol^{-1}; $\eta = 3.2\%$

	light phase (mole fraction)			heavy phase (mole fraction)		
run	NFM	*n*-heptane	*p*-xylene	NFM	*n*-heptane	*p*-xylene
25	0.0325	0.7968	0.1707	0.8901	0.0396	0.0703
26	0.0509	0.6543	0.2948	0.8311	0.0447	0.1242
27	0.0768	0.5414	0.3818	0.7732	0.0517	0.1751
28	0.1160	0.449	0.4350	0.7104	0.0626	0.2270

Results and Discussion

The experimental data for binary systems are given in Tables 3−5 together with the interaction parameters of the UNIQUAC equation as well as the average percentage error η arising from the fitting procedure. We did not follow the method proposed in the literature (cf. Sørensen and Arlt (1979)), i.e., the fitting of the interaction parameters at each temperature level investigated. We have instead shown that the temperature dependence of the UNIQUAC equation allows us to describe quantitatively the equilibrium behavior of binary systems at least within the temperature range considered, i.e., 20−60 °C.

In Tables 6−8 we report the experimental data for ternary systems, together with the interaction parameters of the pairs NFM/aromatics of the UNIQUAC equation as well as the average percentage error arising from the fitting

Table 9. Interaction Parameters Available in the Literature

pair	interaction param, J·mol^{-1}		refs	temp range, °C
n-heptane/benzene	$A_{23} = 4.860\ 757 \times 10^2$	$A_{32} = -8.074\ 11 \times 10^1$	Gmehling et al., 1979	20−80
n-heptane/toluene	$A_{23} = 2.891\ 42 \times 10^2$	$A_{32} = -9.362\ 997 \times 10^1$	Gmehling et al., 1979	25
n-heptane/*p*-xylene	$A_{23} = -3.938\ 239 \times 10^2$	$A_{32} = -8.318\ 6439 \times 10^1$	Sørensen and Arlt, 1979	25
n-heptane/water	$A_{24} = 9.559\ 142 \times 10^3$	$A_{42} = 5.145\ 8179 \times 10^3$	Sørensen and Arlt, 1979	40
p-xylene/water	$A_{34} = 7.715\ 839 \times 10^3$	$A_{43} = 2.831\ 14544 \times 10^3$	Sørensen and Arlt, 1979	40

Table 10. Experimental Data for the System NFM (1)/*n*-Heptane (2)/*p*-Xylene (3)/Water (4): $A_{14} = 7.017\ 1119 \times 10^2$ J·mol^{-1}; $A_{41} = -1.465\ 9815 \times 10^3$ J·mol^{-1}; $\eta = 6.81\%$

	light phase (mole fraction)				heavy phase (mole fraction)			
run	NFM	*n*-heptane	*p*-xylene	water	NFM	*n*-heptane	*p*-xylene	water
29	0.0634	0.5316	0.4033	0.0017	0.7079	0.0253	0.1211	0.1457
30	0.0520	0.5214	0.4243	0.0023	0.6313	0.0118	0.0753	0.2816
31	0.0446	0.5193	0.4332	0.0029	0.5786	0.0076	0.0575	0.3563
32	0.0414	0.5179	0.4373	0.0034	0.5143	0.0041	0.0422	0.4394

procedure. It should be noted that the interaction parameters of the pair NFM/*n*-heptane, i.e., A_{12} and A_{21} are maintained fixed during the fitting procedure with respect to those obtained from the binary systems previously investigated (cf. Table 4). On the other hand, the interaction parameters of the pairs *n*-heptane/aromatics, i.e., A_{23} and A_{32}, are taken from the literature and are reported in Table 9. It should be noted that we select for each pair the parameter values available in the literature which allow us to obtain a better fitting against the experimental data.

The experimental data for the quaternary system investigated in this work are given in Table 10 together with the interaction parameters of the pair NFM/water of the UNIQUAC equations as well as the average percentage error arising from the fitting procedure. When fitting these data, the interaction parameters of the pairs NFM/*n*-heptane, NFM/aromatics, *n*-heptane/aromatics, *n*-heptane/water, and water/aromatics are taken from Table 4, Tables 6−8, and Table 9, respectively.

Concluding Remarks

In this work, we first estimated the interaction parameters of the UNIQUAC equation for the system NFM/alkane (i.e. *n*-hexane, *n*-heptane, and isononane) from experimental binary liquid−liquid equilibrium data at various temperatures. Next, we obtained the same parameters for the system NFM/aromatic (i.e. toluene, *p*-xylene, and benzene) from experimental ternary liquid−liquid equilibrium data at various initial mixture compositions. Finally, the parameters mentioned above were evaluated for the system NFM/water from experimental quaternary liquid−liquid equilibrium data at various initial mixture compositions. Thus, a quantitative description of liquid−liquid equilibria of industrial interest involving alkanes, aromatics, water, and NFM is available to accurately simulate, optimize, and control the extraction units where these systems are involved.

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Notation

F = objective function
N_c = number of components
N_s = number of runs of the system under investigation
x_i = mole fraction of the ith component

Greek Letters

α = ratio between total number of moles in phase I and total number of moles of the initial mixture
γ_i = activity coefficient of the ith component
η = average percentage error (square root of the minimum value of F given by eq 4 divided by $2N_s$)

Superscripts

I = phase I
II = phase II
0 = initial conditions

Subscripts

c = calculated
s = experimental

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