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Phase Equilibria of Binary Systems Formed by Hydrocarbons from Petroleum Fractions and the Solvents *N*-Methylpyrrolidone and *N*,*N*-Dimethylformamide. 1. Isobaric Vapor−Liquid Equilibria

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Isobaric vapor−liquid equilibrium data at 101.33 kPa are reported for binary systems formed by *N*-methylpyrrolidone (NMP) and *N*,*N*-dimethylformamide (DMF) with benzene, heptane, hexane, or cyclohexane. Data reduction based on the Van Laar, Wilson, NRTL, and UNIQUAC models provides a correlation for the liquid-phase activity coefficients. All the systems, except for the ones formed with benzene, are strongly nonideal, yielding two phases at low temperatures.

Introduction

Recovery of pure aromatic and saturated hydrocarbons from petroleum fractions is of particular interest in the petroleum industry (Bland and Davidson, 1967). Several processes, such as extractive distillation and liquid−liquid extraction, are used to carry out separations of the petroleum fractions into their pure components. These processes require the addition of a separating agent (Lo et al., 1983; Oliver, 1966), and a suitable selection is needed for a successful separation. Several authors (Brignole et al., 1986; Macchietto et al., 1990; Pretel et al., 1994; Shelley et al., 1993) have studied the optimization and design of appropriate solvents to be used as separating agents for extractive distillation and liquid−liquid extraction.

This work is part of a study aimed at separating hydrocarbon mixtures obtained from cracking of naphthas. The number of components in such mixtures is rather high, and therefore, a model mixture containing benzene, heptane, hexane, and cyclohexane has been chosen.

The solvents tested as separating agents are *N*-methylpyrrolidone (NMP) and *N*,*N*-dimethylformamide (DMF). Addition of the solvents NMP or DMF to the model mixture makes its phase behavior fairly complex, so that in order to design efficient large-scale separation processes in the petroleum industry, experimental information on phase equilibria and related thermodynamic properties is required (Prausnitz et al., 1980; Walas, 1985).

In this work, experimental isobaric (101.33 kPa) vapor−liquid equilibria (VLE) of the binary systems formed by NMP and DMF with the components of the synthetic mixture are reported. Seven binary systems have been experimentally determined: NMP with benzene, cyclohexane, hexane, and heptane and DMF with benzene, cyclohexane, and hexane. The systems benzene + DMF and benzene + NMP have been previously reported by Zaretskii et al. (1971) from Gmehling et al. (1996) at 101.33 kPa, but neither of the two systems is thermodynamically consistent. Delzene (1953) determined the system benzene + DMF, and Gupta et al. (1989) the system benzene + NMP, both at 101.33 kPa. Both systems were thermodynamically consistent. In this work, some more equilibrium data points for a wider range of compositions have been determined. Data for the system heptane + DMF at 101.33 kPa have been previously reported by Zemlyanskaya et al. (1977) from Gmehling et al. (1996), and the results of data reduction are reported in Table 8. Isothermal measurements on some of the systems studied in this work have been previously reported, and a compilation can be found in the data bases for VLE (Gmehling et al., 1996). A quantitative comparison of the thermodynamically consistent isobaric systems previously reported and the results of this work is presented in the Results and Discussion section.

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

	ρ(298.15 K)/ kg m^{-3}		n(D,298.15 K)		T_b(101.33 kPa)/K	
compound	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.[a]
benzene	873.5	873.60	1.4978	1.49792	353.25	353.244
cyclohexane	773.7	773.89	1.4236	1.42354	353.85	353.880
hexane	654.3	654.84	1.3721	1.37226	341.80	341.886
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
DMF	944.0	943.87	1.4283	1.42817	426.15	426.20

[a] Riddick et al., 1986.

Table 2. Refractive Indexes n(D,298.15 K) for the Binary System Benzene (1) + DMF (2) as a Function of the Mole Fraction x_1

x_1	n	x_1	n
0.0000	1.4283	0.5339	1.4687
0.0786	1.4340	0.6411	1.4759
0.1669	1.4411	0.7541	1.4830
0.2539	1.4478	0.8571	1.4895
0.3394	1.4531	1.0000	1.4978
0.4341	1.4614		

Experimental Section

Chemicals. All chemicals were purified and maintained in special conditions before their use. NMP (Merck, p.s.) and DMF (Merck, p.a.) were kept dried with 3 Å molecular sieves, and benzene (Merck, p.s.), cyclohexane (Panreac, p.a.), hexane (Merck, p.a.), and heptane (Merck, p.a.) with sodium wire. Chemical purity was checked by gas chro-

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Table 3. Density ρ(298.15 K) for the Binary Systems Benzene (1) + NMP (2), Cyclohexane (1) + NMP (2), Hexane (1) + NMP (2), Heptane (1) + NMP (2), Cyclohexane (1) + DMF (2), and Hexane (1) + DMF (2) as a Function of the Mole Fraction x_1

benzene (1) + NMP (2)		cyclohexane (1) + NMP (2)		hexane (1) + NMP (2)		heptane (1) + NMP (2)		cyclohexane (1) + DMF (2)		hexane (1) + DMF (2)	
x_1	ρ/kg m^{-3}	x_1	ρ/kg m^{-3}	x_1	ρ/kg m^{-3}	x_1	ρ/kg m^{-3}	x_1	ρ/kg m^{-3}	x_1	ρ/kg m^{-3}
0.0000	1028.4	0.0000	1028.4	0.0000	1028.4	0.0000	1028.4	0.0000	944.0	0.0000	944.0
0.1342	1013.2	0.1093	996.6	0.0498	1005.4	0.0142	1021.5	0.0390	935.1	0.0105	938.8
0.2458	997.4	0.2011	970.7	0.0988	982.9	0.0268	1010.3	0.0657	927.6	0.0337	927.8
0.3461	984.7	0.3029	942.5	0.1336	967.6	0.0577	1000.0	0.1384	911.1	0.0576	920.1
0.4464	970.3	0.3935	918.5	0.9079	678.6	0.0939	985.7	0.9553	777.2	0.0955	901.4
0.5463	956.0	0.4941	892.6	0.9570	666.3	0.1128	965.6	0.9778	775.6	0.9413	663.4
0.6413	940.1	0.6015	865.6	0.9837	658.8	0.9032	708.4	0.9952	774.1	0.9622	659.6
0.7255	926.6	0.6975	842.3	1.0000	654.3	0.9423	692.2	1.0000	773.7	0.9806	656.7
0.7932	913.7	0.8037	817.0			0.9535	689.8			1.0000	654.3
0.8640	900.1	0.9047	793.8			0.9793	684.2				
1.0000	873.5	1.0000	773.7			1.0000	679.4				

Table 4. Experimental Vapor Pressure Data, Temperature *T*, and Pressure *P*, for Benzene, Cyclohexane, Hexane, Heptane, NMP, and DMF

benzene		cyclohexane		hexane		heptane		NMP		DMF	
T/K	P/kPa	T/K	P/kPa	T/K	P/kPa	T/K	P/kPa	T/K	P/kPa	T/K	P/kPa
350.70	93.64	349.15	87.33	340.65	98.16	364.25	81.44	414.45	16.66	376.70	21.40
351.20	95.14	350.15	90.54	341.80	101.32	369.55	95.43	419.10	19.53	385.75	29.27
352.05	97.69	351.05	92.77	341.95	102.31	369.95	96.92	422.05	21.60	387.65	31.16
352.50	98.97	353.85	101.30	343.00	105.23	370.85	99.41	425.35	24.54	390.55	34.62
353.25	101.32	354.70	104.08	343.75	108.01	371.50	101.33	428.55	26.93	393.40	37.96
354.05	103.77	355.45	106.22	345.20	112.15	372.20	103.40	433.05	30.99	395.25	40.50
354.85	106.43	357.55	112.81	346.40	116.79	372.85	105.41	435.10	33.21	398.40	44.53
356.05	110.45	359.45	119.80	347.10	119.07	374.35	110.27	438.00	36.17	398.95	45.51
357.45	115.18	360.75	124.32	347.75	121.12	375.40	113.54	442.30	41.36	406.80	57.68
358.85	120.15	362.00	128.72	348.70	124.56	377.10	119.47	444.15	43.38	410.20	64.09
360.25	125.17	362.80	132.24	349.30	127.23	378.15	122.91	446.40	46.96	414.65	73.22
361.45	129.61			350.50	131.20	379.20	126.75	448.90	50.33	419.80	84.45
362.10	132.09							475.10	101.32	426.15	101.31

Table 5. Characteristics of the Components Used in VLE Data Regression: UNIQUAC Parameters *r* and *q*, Critical Temperature T_c, Critical Pressure P_c, Critical Volume V_c, O'Connell Characteristic Volume Parameter VSTR, Rackett Equation Parameter ZRA, Mean Radius of Gyration R_D, Dipole Moment μ, and Association Parameters η; Fitted Antoine Equation[a] Parameters *A*, *B*, and *C*, Correlation Coefficient R^2, and Root-Mean-Square Deviation of the Experimental and Literature Values of Pressure RMSD(*P*)

	UNIQUAC parameters										Antoine constants				
compound	r	q	T_c/K	P_c/ kPa	$V_c \times 10^3$/ m^{3}mol^{-1}	VSTR $\times 10^3$/ m^{3}mol^{-1}	ZRA	$R_D \times 10^{10}$/m	μ/D	η	A	B	C	R^2	RMSD (P)/kPa
benzene	3.19[b]	2.40[b]	562.16[b]	4898[b]	0.260[b]	0.255[b]	0.2696[b]	3.004[b]	0.00[b]	0.00[b]	6.0206	1201.52	−54.003	0.999 98	2.05[d]
cyclohexane	3.97[b]	3.01[b]	553.54[b]	4075[b]	0.308[b]	0.311[b]	0.2729[b]	3.261[b]	0.00[b]	0.00[b]	6.4209	1476.19	−19.553	0.999 77	0.26[d]
hexane	4.50[b]	3.86[b]	507.43[b]	3012[b]	0.363[b]	0.369[b]	0.2635[b]	3.812[b]	0.00[b]	0.00[b]	6.3869	1460.54	−8.316	0.999 43	0.37[d]
heptane	5.17[b]	4.40[b]	540.26[b]	2736[b]	0.426[b]	0.425[b]	0.2611[b]	4.267[b]	0.00[b]	0.00[b]	6.4815	1549.21	−25.352	0.999 94	0.33[d]
NMP	3.98[c]	3.20[c]	712.03[c]	4866[c]	0.311[c]	0.300[c]	0.2517[c]	3.000[c]	4.09[d]	0.90[e]	6.3213	1709.28	−79.040	0.999 72	1.23[d]
DMF	3.09[c]	2.74[c]	596.60[d]	5220[d]	0.249[d]	0.240[c]	0.2634[c]	1.600[c]	3.24[d]	0.50[c]	6.9755	2062.41	−11.210	0.999 93	0.29[d]

solvation parameters: benzene + NMP = 0.50[e]
nonaromatics + NMP = 0[c]
benzene + DMF = 0.50[c]
nonaromatics + DMF = 0[c]

[a] Antoine equation: $\log(P/\text{kPa}) = A - B/[(T/\text{K}) + C]$. [b] Prausnitz et al., 1980. [c] Data base of the PRO/II® simulation program (Simulation Sciences INC.). [d] Riddick et al., 1986. [e] Gupta et al., 1989.

matography being higher than 99.9% in all cases. Residual water in NMP was measured with a gas chromatograph (Perkin Elmer, model Sigma 4B) equipped with a thermal conductivity detector. The water content was below 0.01 mass %. Experimental values obtained for the physical properties of the pure compounds are reported in Table 1, along with literature values.

Apparatus and Procedure. Vapor−liquid equilibria and vapor pressures for the pure components were measured with an all-glass circulation still of the Gillespie type as modified by Röck and Sieg (1955). Circulation stills are the most widely used apparatus for determination of VLE. One of their features is the vapor-phase condensation before circulation to the still. This feature does not cause any problem when determining VLE of totally miscible systems. However, in systems with partial liquid inmiscibility, the vapor phase may condense into a two-phase mixture, and the condensate cannot be returned to the still with the two liquid phases in the appropriate ratio. In this work, the inmiscibility concentration range was reduced as much as possible by condensation at the highest possible temperatures to avoid phase splitting of the vapor phase (Linek et al., 1996). Raising the condensation temperature widens the one-phase region in all the partially miscible systems studied, since all of them present an upper critical solution temperature (UCST). Liquid mixtures are homogeneous at their boiling point in all cases since the UCST is lower than the boiling temperature of the liquid phase in the still for all systems studied in the entire composition range.

Table 6. Vapor−Liquid Equilibrium Data for Binary Systems with *N*-Methylpyrrolidone (NMP) at 101.33 kPa: Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature *T*, Activity Coefficients γ_i, and Fugacity Coefficients ϕ_i

x_1	y_1	T/K	γ_1	γ_2	ϕ_1	ϕ_2
		Benzene (1) + NMP (2)				
0.000	0.000	475.10		0.999	0.995	0.970
0.052	0.530	448.45	1.271	0.997	0.988	0.965
0.085	0.674	437.85	1.175	0.977	0.985	0.964
0.118	0.790	426.20	1.215	0.938	0.983	0.962
0.205	0.901	406.65	1.165	0.957	0.980	0.959
0.250	0.931	398.65	1.169	0.951	0.979	0.957
0.407	0.971	381.60	1.110	1.004	0.975	0.952
0.455	0.977	378.50	1.078	0.990	0.974	0.951
0.570	0.986	370.40	1.069	1.096	0.972	0.948
0.673	0.992	365.30	1.045	1.045	0.971	0.946
0.707	0.993	363.45	1.048	1.115	0.971	0.945
0.775	0.995	360.55	1.039	1.194	0.970	0.943
0.870	0.998	357.30	1.018	0.972	0.969	0.942
0.933	0.999	355.30	1.007	1.043	0.968	0.941
1.000	1.000	353.25	1.000		0.968	0.940
		Cyclohexane (1) + NMP (2)				
0.000	0.000	475.10		0.999	0.999	0.970
0.053	0.822	418.20	3.346	0.970	0.979	0.967
0.097	0.917	396.85	3.170	1.027	0.975	0.964
0.159	0.957	381.30	2.896	1.075	0.971	0.962
0.344	0.979	363.60	2.163	1.503	0.966	0.957
0.436	0.983	361.20	1.831	1.590	0.965	0.956
0.490	0.985	360.15	1.681	1.634	0.964	0.956
0.519	0.987	358.55	1.663	1.626	0.964	0.956
0.676	0.991	357.85	1.308	1.731	0.964	0.956
0.757	0.993	356.90	1.202	1.884	0.963	0.956
0.873	0.995	355.85	1.077	2.716	0.963	0.956
0.918	0.996	355.25	1.043	3.470	0.963	0.955
1.000	1.000	353.85	0.999		0.962	0.955
		Hexane (1) + NMP (2)				
0.000	0.000	475.10		0.999	1.003	0.970
0.069	0.943	384.40	4.685	1.137	0.970	0.970
0.107	0.970	370.25	4.290	1.164	0.966	0.968
0.115	0.977	365.85	4.471	1.107	0.965	0.968
0.140	0.984	357.70	4.542	1.181	0.962	0.966
0.174	0.987	352.90	4.158	1.277	0.960	0.965
0.823	0.993	343.25	1.154	5.409	0.956	0.963
0.911	0.995	342.85	1.056	7.861	0.956	0.963
0.941	0.996	342.55	1.033	9.649	0.955	0.963
0.957	0.997	342.20	1.027	10.129	0.955	0.963
0.973	0.998	342.00	1.016	10.878	0.955	0.963
1.000	1.000	341.80	0.997		0.955	0.963
		Heptane (1) + NMP (2)				
0.000	0.000	475.10		0.999	0.993	0.970
0.007	0.128	463.80	2.592	1.211	0.989	0.967
0.011	0.147	459.20	2.038	1.346	0.989	0.966
0.886	0.976	373.85	1.031	6.062	0.953	0.961
0.912	0.982	372.65	1.042	6.198	0.952	0.961
0.930	0.985	372.35	1.034	6.577	0.952	0.961
0.939	0.986	372.20	1.029	7.090	0.952	0.961
0.961	0.988	371.90	1.016	9.629	0.952	0.961
0.982	0.994	371.80	1.003	10.481	0.952	0.961
0.993	0.997	371.55	1.002	13.623	0.952	0.961
1.000	1.000	371.50	0.999		0.952	0.961

Table 7. Vapor−Liquid Equilibrium Data for Binary Systems with *N,N*-Dimethylformamide (DMF) at 101.33 kPa: Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature *T*, Activity Coefficients γ_i, and Fugacity Coefficients ϕ_i

x_1	y_1	T/K	γ_1	γ_2	ϕ_1	ϕ_2
		Benzene (1) + DMF (2)				
0.000	0.000	426.15		1.001	0.988	0.963
0.023	0.142	421.25	1.233	1.003	0.986	0.962
0.105	0.503	405.80	1.294	0.984	0.982	0.958
0.222	0.716	389.75	1.237	1.064	0.977	0.954
0.314	0.812	381.25	1.214	1.060	0.975	0.952
0.395	0.863	374.30	1.222	1.116	0.974	0.950
0.508	0.910	368.40	1.165	1.109	0.972	0.949
0.605	0.934	365.75	1.081	1.121	0.971	0.948
0.740	0.964	360.35	1.060	1.139	0.970	0.946
0.892	0.986	356.35	1.009	1.246	0.969	0.945
0.961	0.995	354.10	1.009	1.347	0.968	0.944
1.000	1.000	353.25	1.000		0.968	0.944
		Cyclohexane (1) + DMF (2)				
0.000	0.000	426.15		1.001	0.995	0.963
0.004	0.065	423.50	3.211	1.009	0.993	0.962
0.281	0.903	356.50	2.980	1.305	0.963	0.961
0.293	0.912	355.60	2.962	1.248	0.963	0.960
0.315	0.917	354.90	2.827	1.249	0.963	0.960
0.816	0.934	354.25	1.132	3.798	0.962	0.960
0.870	0.942	354.10	1.076	4.755	0.962	0.960
0.890	0.948	354.05	1.060	5.050	0.962	0.960
0.940	0.965	353.80	1.029	6.301	0.962	0.960
0.962	0.967	353.75	1.009	9.400	0.962	0.960
0.981	0.982	353.60	1.009	10.327	0.962	0.960
0.989	0.989	353.55	1.010	10.927	0.962	0.960
0.994	0.993	353.75	1.003	12.651	0.962	0.960
1.000	1.000	353.85	1.001		0.962	0.960
		Hexane (1) + DMF (2)				
0.000	0.000	426.15		1.001	0.997	0.963
0.006	0.125	417.35	3.796	1.119	0.993	0.963
0.882	0.948	343.75	1.014	7.224	0.956	0.963
0.926	0.962	342.95	1.002	8.720	0.956	0.963
0.951	0.972	342.50	1.028	10.334	0.955	0.963
0.963	0.977	342.30	0.997	10.867	0.955	0.963
0.975	0.983	342.10	0.996	11.997	0.955	0.963
0.989	0.992	341.95	0.996	12.924	0.955	0.963
0.995	0.996	341.90	0.995	14.252	0.955	0.963
1.000	1.000	341.80	0.996		0.955	0.963

Details of the still used in this work and its operation have been previously described (Blanco et al., 1994). The boiling point was measured with a mercury-in-glass thermometer (0.05 K), calibrated against a standard thermometer. Atmospheric pressure was measured with a Lambrecht type barometer. Nitrogen was injected or released from the equilibrium still for pressure adjustment, keeping an inert atmosphere inside the still during the experiments. A dibutyl phthalate manometer (0.01 kPa) was used to measure pressures around atmospheric, and a mercury manometer (0.07 kPa) was used for lower pressures, as needed to determine vapor pressures for pure components.

Mole fractions of the vapor (±0.002) and liquid (±0.001) phases were determined by gas chromatography (Perkin-Elmer, 990 flame ionization detector) and refractometry (Abbé-type refractometer) or pycnometry. Two of these methods were used for analysis of each sample. No significant difference in composition was found using either method. The chromatographic column used was a 3 m × 0.3 cm Carbowax 20M (10%) on Chromosorb WHP 80/100 for all systems. Chromatographic analyses were carried out at the following column temperatures: systems benzene + DMF and cyclohexane + DMF at 393 K; system hexane + DMF at 413 K; systems benzene + NMP and cyclohexane + NMP at 448 K; system hexane + NMP at 423 K, and system heptane + NMP at 433 K.

Results and Discussion

Refractive indexes, *n*(D,298.15 K), for the binary mixture benzene + DMF are given in Table 2. Table 3 reports densities for the binary systems formed by NMP with benzene, cyclohexane, hexane, and heptane and by DMF with cyclohexane and hexane. Table 4 shows the data of pressure vs temperature experimentally obtained for the pure compounds. These data were fitted to the Antoine equation to obtain the parameters used in VLE data regression. These parameters, their correlation coefficients, and the comparison of the data obtained in this work with literature values are reported in Table 5. Such comparison is presented as the root mean square deviation of the experimental values of pressure obtained in this

Table 8. Correlation Parameters A_{12}, A_{21}, and α_{12} for Activity Coefficient Models and Root-Mean-Square Deviations for Pressure, Temperature, and Liquid and Vapor Compositions

						root-mean-square deviations			
	A_{12}	A_{21}	α_{12}	γ_1^∞	γ_2^∞	P/kPa	T/K	x_1	y_1
			Benzene (1) + NMP (2)						
Van Laar	0.17	0.40		1.185	1.492	0.01	0.11	0.0030	0.0046
Wilson[a]	−1486.15	3241.17		0.956	1.028	0.01	0.10	0.0028	0.0046
NRTL[a]	3789.35	−2141.51	0.30	1.396	1.919	0.01	0.12	0.0031	0.0046
UNIQUAC[a]	934.20	−603.61		1.492	2.447	0.01	0.10	0.0031	0.0046
			Cyclohexane (1) + NMP (2)						
Van Laar	1.28	2.29		3.597	9.875	0.03	0.36	0.0031	0.0032
Wilson[a]	1299.25	7211.60		3.698	8.851	0.03	0.30	0.0038	0.0031
NRTL[a]	6160.50	728.84	0.30	3.671	9.642	0.05	0.35	0.0030	0.0033
UNIQUAC[a]	3486.01	1149.19		4.311	11.626	0.03	0.29	0.0040	0.0032
			Hexane (1) + NMP (2)						
Van Laar	1.73	3.41		5.641	30.265	0.02	0.22	0.0045	0.0030
Wilson[a]	2339.33	9591.67		6.820	17.507	0.02	0.21	0.0102	0.0025
NRTL[a]	8155.13	1850.23	0.30	5.371	26.409	0.02	0.21	0.0045	0.0029
UNIQUAC[a]	1992.29	−414.16		7.995	41.496	0.02	0.21	0.0044	0.0029
			Heptane (1) + NMP (2)						
Van Laar	1.97	2.72		7.171	15.180	0.02	0.23	0.0015	0.0771
Wilson[a]	2123.13	7507.85		6.311	9.259	0.02	0.23	0.0013	0.0774
NRTL[a]	5883.71	3666.76	0.30	7.596	15.085	0.02	0.23	0.0014	0.0772
UNIQUAC[a]	1499.13	−146.87		11.984	20.263	0.02	0.22	0.0016	0.0771
			Benzene (1) + DMF (2)						
Van Laar	0.33	0.63		1.391	1.878	0.02	0.24	0.0047	0.0063
Wilson[a]	−358.01	2355.66		1.278	1.612	0.02	0.24	0.0048	0.0062
NRTL[a]	3701.17	−1581.98	0.30	1.517	2.115	0.02	0.24	0.0046	0.0063
UNIQUAC[a]	1131.82	−692.50		1.687	2.644	0.02	0.25	0.0054	0.0062
			Cyclohexane (1) + DMF (2)						
Van Laar	1.79	2.63		5.989	13.874	0.01	0.12	0.0014	0.0094
Wilson[a]	7067.99	5861.69		6.205	13.301	0.03	0.32	0.0013	0.0093
NRTL[a]	5833.30	2552.36	0.30	6.131	12.952	0.01	0.14	0.0015	0.0090
UNIQUAC[a]	1427.74	−68.54		6.729	14.349	0.01	0.13	0.0014	0.0091
			Hexane (1) + DMF (2)						
Van Laar	2.35	2.29		10.486	9.875	0.03	0.29	0.0019	0.0294
Wilson[a]	4198.61	4834.20		10.294	7.491	0.03	0.29	0.0018	0.0303
NRTL[a]	3553.17	5108.23	0.30	9.969	8.854	0.03	0.29	0.0019	0.0296
UNIQUAC[a]	935.46	356.30		12.857	9.319	0.03	0.29	0.0019	0.0294
			Heptane (1) + DMF (2)[b]						
Van Laar	1.82	2.19					0.34		0.0166
Wilson[a]	1837.34	7951.78					0.36		0.0132
NRTL[a]	6711.06	5160.82	0.5592				0.71		0.0108
UNIQUAC[a]	3419.99	−689.82					0.40		0.0183

[a] A_{12} and A_{21} are in J mol^{-1}. [b] Zemslyanskaya et al. (1977) from Gmehling et al. (1996).

work and the values obtained through vapor pressure equations in the literature, for a given temperature. All the properties and characteristics of the components used in VLE data regression are also reported in Table 5.

Experimental VLE data for the systems studied are reported in Tables 6 and 7. VLE data include vapor- and liquid-phase compositions, temperature, liquid-phase activity coefficients, and vapor-phase fugacity coefficients. All the systems were determined at a pressure of 101.33 kPa. Vapor-phase fugacity coefficients were calculated by means of the virial equation of state, and the Hayden and O'Connell (1975) correlation was used to estimate second virial coefficients. Liquid-phase activity coefficients were calculated taking into account the nonideal nature of the vapor and liquid phases.

Experimental VLE data were correlated by the Van Laar, Wilson, NRTL, and UNIQUAC equations representing the excess Gibbs energy in the liquid phase. The adjustable binary parameters contained in these equations were estimated by a nonlinear regression method, based on the maximum-likelihood principle (Prausnitz et al., 1980). This regression procedure weighs each individual measurement according to its experimental uncertainty. The parameter α_{12} in NRTL equation was fixed to the value $\alpha_{12} = 0.3$ in all cases. Table 8 reports the results of data regression: adjustable parameters A_{12} and A_{21} for the correlation equations, the root-mean-square deviations for pressure, temperature and vapor- and liquid-phase compositions, and the activity coefficients at infinite dilution, γ_1^∞ and γ_2^∞.

Fredenslund's test for thermodynamic consistency (Fredenslund et al., 1977) was applied to the experimental data. The average values for $\Delta y = y_{\text{exp}} - y_{\text{calc}}$ absolute (mole fraction) for the systems studied were Δy(benzene + NMP) = 0.0021, Δy(cyclohexane + NMP) = 0.0031, Δy(hexane + NMP) = 0.0034, Δy(heptane + NMP) = 0.0469, Δy(benzene + DMF) = 0.0089, Δy(cyclohexane + DMF) = 0.0096, and Δy(hexane + DMF) = 0.0245. Systems heptane + NMP and hexane + DMF show average deviations higher than 0.01, which may be due to the large range of compositions in which equilibrium could not be determined, due to phase splitting of the vapor samples after condensation.

The results obtained show two types of system behavior, regarding deviations from ideality. Systems benzene + NMP and benzene + DMF are nearly ideal. The system benzene + DMF shows slightly larger positive deviations from ideality as can be inferred from their activity coefficients, which, for both systems, are close to unity. A point to point comparison between these two systems and the ones previously reported has been made by calculating the root-mean-square deviation (RMSD) of the activity coefficients of the system determined in this work and the systems reported by Delzene (1953) and Gupta et al. (1989) respectively. The results obtained were RMSD(γ_1) = 0.0132 and RMSD(γ_2) = 0.0077 for the system benzene + DMF and RMSD(γ_1) = 0.0199 and RMSD(γ_2) = 0.0173 for the system benzene + DMF.

The other systems studied in this work, formed by a hydrocarbon and NMP or DMF, show large positive deviations from ideality. These deviations are large enough as to cause inmiscibility in a broad composition range. Experimental mutual solubilities for these binary systems have also been determined in our laboratory and will be considered in another publication. Liquid−liquid equilibrium data will permit further discussion on molecular interactions for the systems studied.

Two of the systems studied with DMF show azeotropic behavior: cyclohexane (1) + DMF (2), x_1 = 0.989, T = 353.55 K; heptane (1) + DMF (2), x_1 = 0.915, T = 370.2 K. Azeotropic behavior is not desirable for an extractive solvent; thus, when DMF is used, its composition in the mixture should be far away from the azeotropic one.

Registry Numbers Supplied by the Author. Benzene, 71-43-2; cyclohexane, 110-82-7; hexane, 110-54-3; heptane, 142-82-5; *N*-methylpyrrolidone, 872-50-4; *N*,*N*-dimethylformamide: 68-12-2.

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