Experimental Measurements of Phase Equilibrium Properties for Systems Containing *n*-Heptane, Benzene, *N*-Methylpyrrolidone, and Monoethanolamine. Representation by the NRTL Equation

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Phase equilibrium data are reported for the systems of *n*-heptane, benzene, *N*-methylpyrrolidone, and monoethanolamine in the 20–100 °C temperature range. All data available are reduced by the NRTL equation.

The separation of aromatic and saturated hydrocarbons is performed on a large scale in industry for the recovery of pure aromatic hydrocarbons from petroleum fractions. These separations are achieved by various techniques, which often require the addition of a solvent (extractive distillation, liquid–liquid extraction). The design of separation processes requires experimental information on phase equilibria and related thermodynamic properties. The determination of many thermodynamic data describing a quaternary system of two solvents and two hydrocarbons is also of theoretical interest for testing the qualities of the representation of these experimental quantities by a model of solution. Excess enthalpies (*5*), liquid–liquid equilibrium data (*5*), vapor–liquid equilibrium data (*1, 6, 18*) of mixtures of *n*-heptane, benzene, and two solvents, *N*-methylpyrrolidone (NMP) and monoethanolamine (MEA), were measured to complement the data already available in the literature cited. NMP is one of the industrially accepted solvents for aromatic hydrocarbon separation, it is sometimes used in a mixture with another solvent.

Chemicals

Benzene was Merck spectroscopy grade, used without any further purification. *n*-Heptane was Phillips Petroleum Co., ASTM lot no. 1359; it was redistilled in a high efficiency packed column. Ethanolamine and *N*-methylpyrrolidone were Merck products, dried over 4 Å molecular sieves. The determination of residual water in *N*-methylpyrrolidone was performed by gas–liquid chromatography, with a 1.20 m × ⅛ in. column filled with Porapack support. After treatment by molecular sieves, it was found that the water content did not exceed 500 ppm in *N*-methylpyrrolidone.

Apparatus and Procedure

For vapor–liquid equilibrium measurements the same static still described by Gustin and Renon (*6*) was used. Other experimental data points were obtained with a recirculation still, described in ref 10. In all cases temperature was read on precision Brooklyn thermometers, with an accuracy of 0.05 °C. The composition of binary mixtures was measured with a Zeiss-Jena refractometer, equipped with thermoprisms giving a resolution of 10^{-5} on refractive index.

Liquid–liquid equilibria were measured in the thermostated glass cell shown on Figure 1. The mixture is stirred by a magnetic stirrer and the cell is equipped with baffles. Two different methods of measurement are possible. First the pure components can be added and mixed until equilibrium is reached between the phases; after settling, each phase is withdrawn: the upper phase with a syringe, the lower phase through the sampling stopcock, type Rotaflo TF 6/13; a small dead space made of cappillary tubing connects the cell and the stopcock; it is always empty before sampling. Multicomponent samples are then analyzed by gas–liquid chromatography, using a Hewlett-Packard chromatograph 5750 G, equipped with an electronic integrator 3370 A. A good separation of the four components was obtained on a 1.40 m × ⅛ in. column, packed with chromosorb WAW 80/100 QDMCS coated with carbowax 20 M, using a 20 cm^3 flow rate of helium as carrier gas. A temperature programming from 60 to 150 °C was necessary, the detection was carried out by thermal conductivity. Quantitative results were obtained by using two internal standards: toluene and pyrrolidone. The relative accuracy of mole fraction measurements is about 0.5% for hydrocarbons, and 1% for NMP. The MEA mole fraction was not directly measured because it was strongly inaccurate; it was deduced from a mass balance on each phase.

The second possible utilization of the liquid–liquid cell is the determination of the cloud point of a solution, by progressive decreasing of the temperature. The optic determination of the opacification of the solution was improved by using the experimental equipment shown on Figure 2. A low voltage lamp (l) is

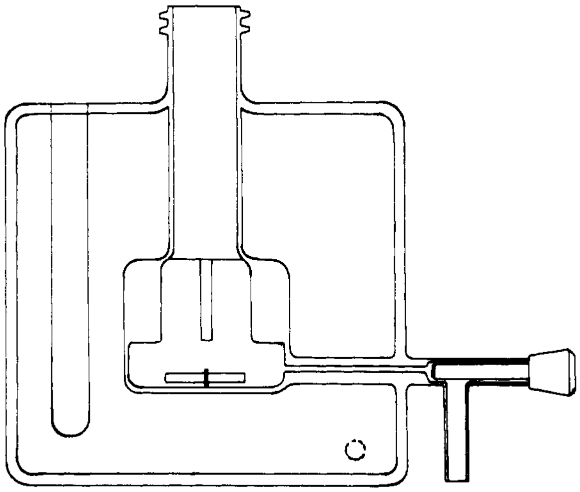

Figure 1. Liquid–liquid equilibrium cell.

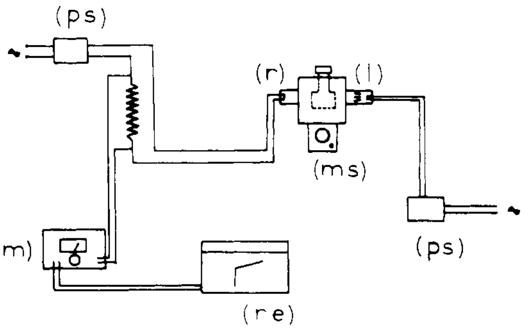

Figure 2. Experimental device for determining the cloud point of a mixture: ps, power supply; ms, magnetic stirrer; vm, voltmeter; re, recorder; r, photoresistor; l, lamp.

Table I. References of Data on the Binary Systems, Used for the Calculation of the NRTL Parameters

System	Type of data	Ref	Temp range, °C
Benzene–NMP	Vapor–liquid equilibrium	This work	20–90
	Heats of mixing	5	
	Limiting activity coefficients	17, this work	
n-Heptane–NMP	Vapor–liquid equilibrium	This work	20–100
	Liquid–liquid equilibrium	5, this work	
	Heats of mixing	5	
	Limiting activity coefficients	This work	
Benzene–MEA	Vapor–liquid equilibrium	6	20–50
	Liquid–liquid equilibrium	5, this work	
	Heats of mixing	5	
	Limiting activity coefficients	This work	
n-Heptane–MEA	Vapor–liquid equilibrium	6	20–50
	Liquid–liquid equilibrium	5, this work	
	Heats of mixing	5	
	Limiting activity coefficients	This work	
Benzene–*n*-heptane	Vapor–liquid equilibrium	2, 3, 7, 12, 13, 16	20–100
	Heats of mixing	4, 8, 9	
NMP–MEA	Vapor–liquid equilibrium	6	20–40
	Heats of mixing	5	

Table II. Experimental Vapor–Liquid Equilibrium Data for the Binary System: Benzene (1)–*N*-Methylpyrrolidone (2)

x_1 mole fraction	*P*, mmHg	*T*, °C
Static still σ_{x_1} = 0.004	σ_P = 0.07 mmHg	σ_T = 0.05 °C
0.164	12.34	19.50
0.164	15.27	23.67
0.164	17.31	26.19
0.191	15.04	20.13
0.191	17.77	23.37
0.191	19.77	25.60
0.363	30.27	21.15
0.363	38.12	26.05
0.466	36.16	20.01
0.466	47.23	25.51
0.542	42.07	20.18
0.542	54.93	25.80
0.762	74.54	25.39
0.762	57.86	20.05
0.914	69.36	20.15
0.914	82.93	23.91
Dynamic still σ_{x_1} = 0.002	σ_P = 0.1 mmHg	σ_T = 0.1 °C
0.680	751.8	91.3
0.712	752.0	90.5
0.773	751.8	88.0
0.908	751.9	82.9

Table III. Experimental Vapor–Liquid Equilibrium Data for the Binary System: *n*-Heptane (1)–*N*-Methylpyrrolidone (2)

x_1 mole fraction	*P*, mmHg	*T*, °C
Homogeneous Liquid Phase, Static Still		
σ_{x_1} = 0.004	σ_P = 0.07 mmHg	σ_T = 0.05 °C
0.050	21.31	20.54
0.050	24.89	24.78
Static Still, at Vapor–Liquid–Liquid Equilibrium		
σ_{x_1} = 0.005	σ_P = 0.07 mmHg	σ_T = 0.05 °C
0.1247	33.53	19.73
0.9300		
0.1280	35.09	20.67
0.9275		
0.1290	35.63	20.90
0.9270		
0.1335	38.09	22.27
0.9240		
0.1380	40.63	23.54
0.9205		
0.1438	43.73	25.00
0.9170		
0.1492	47.04	26.52
0.9127		
0.1505	47.80	26.85
0.9120		

x_1	y_1	*P*, mmHg	*T*, °C
Dynamic Still			
σ_{x_1} = 0.0004	σ_{y_1} = 0.0004	σ_P = 0.1 mmHg	σ_T = 0.1 °C
0.9530	0.9886	749.0	98.5
0.9631	0.9909	749.0	98.3

placed on one side of the equilibrium cell so that the light beam passing through the solution is focused on a photoresistor (r). With decreasing temperature the growth of small drops of the dispersed liquid phase causes a diffusion of light, resulting in a variation of the electric resistance of (r). This variation is detected by means of a simple circuit where it is transformed into a voltage variation, measured by a microvoltmeter (vm), Keithley 150 B, coupled with a recorder (re). For the binary system *n*-heptane–NMP, it was observed that a 1% variation of the output signal near the cloud point of the solution was related to a temperature variation of about 0.05 °C. The optic determination of the cloud point temperature without this equipment is less accurate by 0.1 to 0.2 °C. The composition of the mixture may be changed by adding one of the pure components with a calibrated precision microburet Tacussel "electroburap".

Limiting activity coefficients of hydrocarbons in both solvents and their mixture were determined by using the chromatographic method of retention time with the apparatus described by Sannier and Renon (*15*) for three temperatures: 25, 40, and 55 °C.

Results and Discussion

Table I summarizes the origin of all experimental equilibrium properties of the six binary systems used in the simultaneous reduction presented further. The experimental data obtained in this work for these systems are presented in Tables II–VI with the a priori estimated error σ on each variable. For the system *n*-heptane–NMP vapor–liquid equilibrium measurements were partly obtained at vapor–liquid–liquid equilibrium; in this particular case the compositions in both liquid phases were determined from liquid–liquid equilibrium at the same temperature. Table IV shows a discrepancy between the composition of the *n*-heptane rich phase determined by the cloud point method and

Table IV. Liquid–Liquid Equilibrium Data for the Binary System: *n*-Heptane (1)–*N*-Methylpyrrolidone (2)

x_1	T, °C
Cloud Point Method, Visual Determination	
$\sigma_{x_1} = 0.0005$	$\sigma_T = 0.2$ °C
0.1279	20.0
0.1436	25.0
0.1598	30.1
0.1892	35.0
0.2187	40.0
0.2479	45.0
0.9537	15.0
0.9264	25.5
0.9106	29.7
0.8957	34.1
0.8189	45.9
0.7444	51.5
Cloud Point Method, Optical Determination	
$\sigma_{x_1} = 0.0005$	$\sigma_T = 0.04$ °C
0.1266	20.94
0.1462	26.62
0.1557	29.43
Mixer-Settler, Chromatographic Analysis	
$\sigma_{x_1} = 0.001$	$\sigma_T = 0.03$ °C
0.145	25.00
0.888	25.00

Table V. Liquid–Liquid Equilibrium Data for the Binary System: Benzene (1)–Monoethanolamine (2)

x_1	T, °C
Mixer-Settler, Chromatographic Analysis	
$\sigma_{x_1} = 0.0005$	$\sigma_T = 0.03$ °C
0.1214	25.00
0.9882	25.00

Table VI. Liquid–Liquid Equilibrium Data for the Binary System: *n*-Heptane (1)–Monoethanolamine (2)

x_1	T, °C
Mixer-Settler, Chromatographic Analysis	
$\sigma_{x_1} = 0.0001$	$\sigma_T = 0.03$ °C
0.0012	25.00
0.9998	25.00

the chromatographic analysis at liquid–liquid equilibrium, at 25 °C. This difference is much larger than the experimental errors, it may be due to the presence of water traces in NMP during the measurement by the cloud point method. In this case the microburet used for adding the pure component to the mixture contains pure NMP. Although the NMP tank connected with the precision microburet is not directly exposed to the atmosphere, the diffusion of water to NMP, which is highly hygroscopic, remains possible. The effect of water traces in the solvent on the

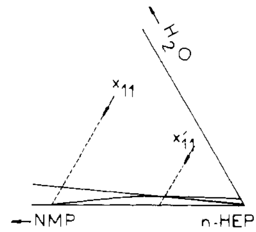

Figure 3. Liquid–liquid equilibrium diagram of the ternary system NMP–*n*-heptane–water in the hydrocarbon rich region: x_{11} is the *n*-heptane mole fraction determined with pure NMP, x_{11}' corresponds to a determination when the solvent contains traces of water.

Table VIII. Liquid–Liquid Equilibrium Data at 25 °C for the Ternary Systems and for the Quaternary System

x_{11}	x_{21}	x_{31}	x_{12}	x_{22}	x_{32}
n-Heptane (1)–Benzene (2)–NMP (3)					
0.796	0.060	0.144	0.166	0.079	0.755
0.745	0.091	0.164	0.190	0.113	0.697
0.615	0.148	0.237	0.268	0.169	0.563
0.592	0.152	0.256	0.283	0.172	0.545
0.577	0.160	0.263	0.306	0.175	0.519
n-Heptane (1)–Benzene (2)–MEA (3)					
0.8258	0.1663	0.0079	0.0014	0.0176	0.9810
0.4415	0.5441	0.0144	0.0015	0.0590	0.9395
0.2817	0.7123	0.0060	0.0014	0.0777	0.9209
MEA (1)–NMP (2)–Benzene (3)					
0.7684	0.0490	0.1826	0.0708	0.0581	0.8711
0.7039	0.0672	0.2289	0.1171	0.0834	0.7995
0.6715	0.0722	0.2563	0.1577	0.0880	0.7543
MEA (1)–NMP (2)–*n*-Heptane (3)					
0.8417	0.1541	0.0042	0.0410	0.0124	0.9466
0.3497	0.6081	0.0422	0.0368	0.0525	0.9107
0.1830	0.7342	0.0828	0.0186	0.0750	0.9064

x_{11}	x_{21}	x_{31}	x_{41}	x_{12}	x_{22}	x_{32}	x_{42}
Benzene (1)–*n*-Heptane (2)–NMP (3)–MEA (4)							
0.2423	0.7087	0.0460	0.0029	01156	0.0219	0.3183	0.5442
0.4020	0.4959	0.0856	0.0165	0.1970	0.0293	0.2685	0.5052

mutual solubility is shown on the liquid–liquid equilibrium diagram for the system NMP–water–hydrocarbon (Figure 3). For pure NMP the hydrocarbon mole fraction in the hydrocarbon rich phase is x_{11}. If the solvent contains traces of water, the experimental determination leads to a much larger value x_{11}'. So the determination of mutual solubilities for a hydrocarbon–hygroscopic solvent system needs special care, and the direct analysis of both phases is recommended when possible.

Limiting activity coefficients of benzene and *n*-heptane in the mixture of solvents are reported in Table VII.

The liquid–liquid equilibrium data obtained for all the ternary systems at 25 °C and for the four-component system are given in Table VIII, while the vapor–liquid equilibrium data relative to

Table VII. Activity Coefficients and Selectivity at Infinite Dilution of Two Hydrocarbons *n*-Heptane (1) and Benzene (2) in the Binary Mixture of the Solvents NMP and MEA

Mol fraction (x_3) of MEA in the solvent mixture	25 °C			40 °C			55 °C		
	γ^∞			γ^∞			γ^∞		
	Benzene	*n*-Heptane	S^∞	Benzene	*n*-Heptane	S^∞	Benzene	*n*-Heptane	S^∞
0 (NMP)	1.05	19.1	18.2	1.08	17.2	15.9	1.07	12.6	11.8
0.328	2.20	53.7	24.4	2.02	40.	19.8	1.91	28.	14.6
0.645	3.78	112.	29.6	3.85	92.	24.0	4.02	83.	20.6
0.874	9.89	332.	33.6	9.14	248.	27.1	8.9	210.	23.8
1. (MEA)	17.7	624.	35.2	15.1	444.	29.4	14.7	341.	23.2

Table IX. Vapor–Liquid Equilibrium Data for the Ternary and Quaternary Systems

x_1	x_2	x_3	x_4	T, °C	P, mmHg
		n-Heptane (1)–Benzene (2)–NMP (3)			
0.124	0.587	0.289		20.25	58.17
				20.45	58.74
				20.75	59.58
				21.24	61.10
				21.66	62.38
				22.54	65.02
				24.17	70.08
0.508	0.270	0.222		20.40	48.64
				20.86	49.73
				21.72	51.77
				22.63	54.08
				23.55	56.50
0.425	0.457	0.118		20.83	60.18
				22.11	63.97
				23.90	69.64
				24.38	71.07
				25.13	73.53
				25.15	73.62
		MEA (1)–NMP (2)–Benzene (3)			
0.086	0.685	0.229		22.00	21.84
				22.24	22.08
				22.85	22.76
		Benzene (1)–*n*-Heptane (2)–NMP (3)–MEA (4)			
0.314	0.066	0.587	0.033	20.45	42.21
				21.00	43.25
				21.96	45.16

the ternary systems *n*-heptane–benzene–NMP, MEA–NMP–benzene, and the quaternary system are reported in Table IX.

The representation of the data by a generalized equation for g^E ($\bar{x}$, T, $\bar{C}$) is useful for computer calculations. It is interesting also to test the ability of a given expression of g^E to represent all data and possibly to predict ternary and quaternary system properties from binary and if necessary ternary system properties. The NRTL equation (*14*) is used assuming a linear variation with the temperature of its three parameters C_{ij}, C_{ji}, α_{ij}, because it can represent properties of strongly nonideal systems. The binary parameters were adjusted in two different ways: from binary data only and from miscibility data. Nonideality correction for the vapor phase was calculated by the correlation of O'Connel and Prausnitz (*11*). The first set of parameters is obtained by reduction of all known properties of binary systems. It is reported in Table X. Table XI gives the standard deviation obtained on the vapor mole fraction y_1, the total pressure P at given T and x_1, the mutual solubility x_S at given T, and the heat of mixing h^E at given T and x_1 for each system. The representation of the thermodynamic properties is generally satisfactory; only for the system *n*-heptane–MEA is the agreement of the experimental pressure at vapor–liquid equilibrium with the calculated total pressure poor; that may be due to the fact that the composition of the liquid phase is not known with sufficient accuracy because of the very low mutual solubility. Prediction of ternary and quaternary vapor–liquid equilibrium is good (Table XI); it is less satisfactory for the system MEA–NMP–benzene for which the number of experimental data points is reduced. For these parameters the binodal curves were calculated for the four ternary systems at 25 °C and are shown on diagrams A, B, C, and D of Figure 4. The prediction of tie lines is generally poor. The second set of NRTL parameters given in Table XII corresponds to the best representation of miscibility data (binary and ternary data). The agreement between the experimental liquid–liquid data and the calculated tie-lines is improved for two ternary systems: *n*-heptane (1)–benzene (2)–NMP (3) and *n*-heptane (1)–benzene (2)–MEA (3) (diagrams A and B of Figure 4), but we find a limitation of the model in the case of the two systems containing the mixture of polar solvents where large deviations subsist.

Table XIII summarizes the limiting activity coefficients of each hydrocarbon in both solvents at 25 °C, calculated from each set of NRTL parameters.

Table X. Best NRTL Parameters to Represent the Thermodynamic Data of all Binary Systems: $C_{ij} = C_{ij}{}^{c} + C_{ij}{}^{T}(T - 273.15)$; $\alpha_{ij} = \alpha_{ij}{}^{c} + \alpha_{ij}{}^{T}(T - 273.15)$

System		NRTL parameters at 0 °C and temperature coefficients						Temp range, °C
(1)	(2)	$C_{21}{}^{c}$	$C_{12}{}^{c}$	$\alpha_{12}{}^{c}$	$C_{21}{}^{T}$	$C_{12}{}^{T}$	$\alpha_{12}{}^{T}$	
Benzene	*n*-Heptane	−97.89	613.63	0.40	−2.3236	0.6061	0	20–100
Benzene	NMP	−412.83	671.66	0.455357	0.2958	1.1960	0	20–90
n-Heptane	NMP	1102.33	1306.17	0.350149	−1.0274	−3.9322	0.000 516	20–100
Benzene	MEA	937.85	2445.24	0.303198	1.3765	−7.4484	0.001 050	20–50
n-Heptane	MEA	3834.48	3538.07	0.301336	−8.0775	−4.7073	0.002 114	20–50
NMP	MEA	−210.91	815.91	0.40	−1.7265	−0.8117	0	20–40

Table XI. Root Mean Square Deviations between Experimental Variables and Those Calculated by Reducing Equilibrium Phase Properties and Excess Enthalpies of the Binary Mixtures with the NRTL Model

System				Root-mean-square deviations				No. of exptl data available		
(1)	(2)	(3)	(4)	δy	$\delta P/P$, %	δx_s	δh^E, cal mol^{-1}	LV	LL	h^E
Benzene	*n*-Heptane	—	—	0.005	0.4	—	9.8	179	—	71
Benzene	NMP	—	—	—	2.3	—	1.5	45	—	28
n-Heptane	NMP	—	—	0.0008	1.6	0.0018	10.7	20	16	8
Benzene	MEA	—	—	—	0.2	0.0020	6.0	11	14	6
n-Heptane	MEA	—	—	—	14.	0.00027	8.3	4	14	4
NMP	MEA	—	—	—	3.8	—	6.9	8	—	33
				Evaluation from Binary Mixtures						
n-Heptane	Benzene	NMP	—	—	1.1	—	—	18	—	—
MEA	NMP	Benzene	—	—	7.1	—	—	3	—	—
Benzene	*n*-Heptane	NMP	MEA	—	1.5	—	—	3	—	—

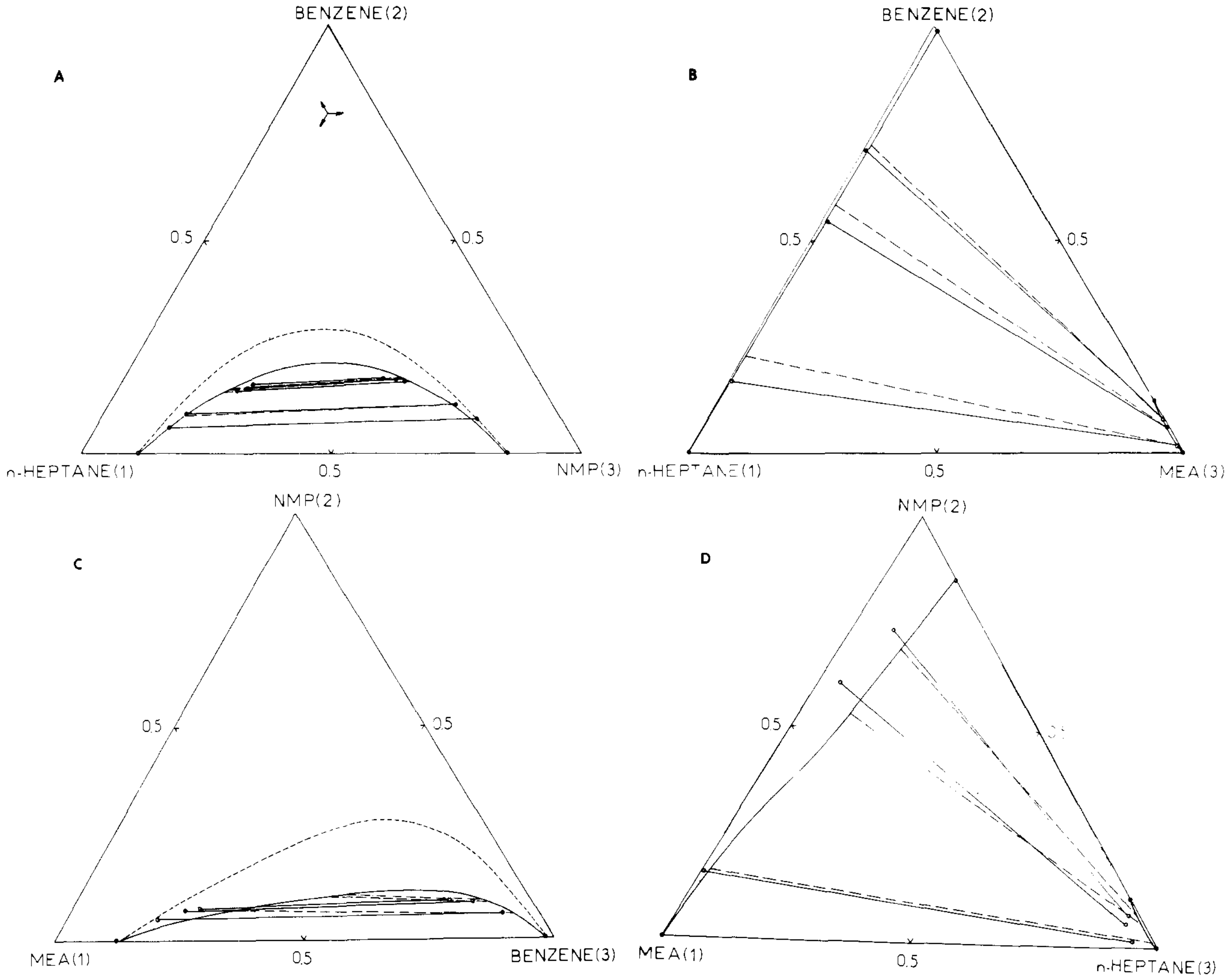

Figure 4. Liquid–liquid equilibrium diagrams at 25 °C for all ternary systems: A, *n*-heptane (1)–benzene (2)–NMP (3); B, *n*-heptane (1)–benzene (2)–MEA (3); C, MEA (1)–NMP (2)–benzene (3); D, MEA (1)–NMP (2)–*n*-heptane (3); binodal curves, interrupted line corresponds to the prediction with parameters obtained from all binary data (Table XII), continuous line corresponds to the best representation obtained by listing all experimental miscibility data to parameters (Table XII); tie lines, continuous lines are experimental tie lines, interrupted lines are calculated with parameters adjusted on all experimental miscibility data.

Table XII. Values of Parameters of the NRTL Model at 25 °C Calculated by Reduction of Equilibrium Properties Measured for the Binary Systems (BD) and all Liquid–Liquid Equilibrium Data (TD)

Type of adjustment	*i–j*	C_{ij}	C_{ji}	α_{ij}
	System *n*-Heptane (1)–Benzene (2)–NMP (3)			
BD	1–2	−155.98	628.78	0.40
	1–3	1207.87	1076.65	0.363
	2–3	701.56	−405.44	0.455
TD	1–2	−155.98	628.78	0.40
	1–3	1207.87	1076.65	0.363
	2–3	225.43	−224.42	0.455
	System *n*-Heptane (1)–Benzene (2)–MEA (3)			
BD	1–2	−155.98	628.78	0.40
	1–3	3420.39	3632.54	0.354
	2–3	2259.03	972.26	0.329
TD	1–2	−361.11	1277.90	0.40
	1–3	3420.39	3632.54	0.354
	2–3	2059.70	1274.51	0.383

Type of adjustment	*i–j*	C_{ij}	C_{ji}	α_{ij}
	System MEA (1)–NMP (2)–Benzene (3)			
BD	1–2	−254.07	795.62	0.40
	1–3	972.26	2259.03	0.329
	2–3	−405.44	701.56	0.455
TD	1–2	491.03	−114.35	0.40
	1–3	1274.51	2059.70	0.383
	2–3	−224.42	225.43	0.455
	System MEA (1)–NMP (2)–*n*-Heptane (3)			
BD	1–2	−254.07	795.62	0.40
	1–3	3632.54	3420.39	0.354
	2–3	1076.65	1207.87	0.363

Conclusion

The representation of vapor–liquid equilibrium of a complex multicomponent system can be easily achieved by a unique thermodynamic excess function for the liquid phase, containing only binary interaction parameters obtained from binary data.

The representation of liquid–liquid equilibrium is much more difficult and cannot be obtained with a good accuracy for mixtures containing two polar solvents by using the same function. The data assembled here may serve as a test of flexibility and significance of models of liquid phase nonideality.

Table XIII. Activity Coefficients at Infinite Dilution at 25 °C of the Two Hydrocarbons: *n*-Heptane and Benzene in the Solvents NMP and MEA, Calculated from the NRTL Model by Reducing: (1) Properties of the Binary Mixtures (BD), (2) Ternary Liquid-Liquid Equilibrium Data (TD)

Type of data used in the reduction	Solute		Solvent	Ternary system used in the reduction of liquid-liquid equilibrium data
	n-Heptane	Benzene		
BD	16.28	1.007	NMP	—
BD	971.	15.31	MEA	
TD	16.28	0.94	NMP	*n*-Heptane-benzene-NMP
TD	—	0.94	NMP	MEA-NMP-benzene
TD	971.	21.52	MEA	*n*-Heptane-benzene-MEA
Exptl γ^∞	19.1	1.05	NMP	—
Exptl γ^∞	624.	17.7	MEA	—

Acknowledgment

Mm. Sannier and Kikic are acknowledged for their contribution to experimental work.

Glossary

$\bar{C}$	parameter vector
C_{ij}	NRTL parameter, cal g-mol^{-1}
g^E	excess Gibbs energy, cal mol^{-1}
P	total pressure, mmHg
T	temperature, °C
$\bar{x}$	composition vector
x_i	mole fraction of component i in the liquid phase
x_{ij}	mole fraction of component i in the phase j
y_i	mole fraction of component i in the vapor phase
S_{12}^∞	selectivity at infinite dilution for solutes 1 and 2

Greek Letters

α_{ij}	NRTL parameter (dimensionless)
δ	standard deviation
γ_i^∞	activity coefficient of component i at infinite dilution
σ	standard error

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