THE CALCULATION OF TERNARY LIQUID EQUILIBRIA FROM THE BINARY DATA*

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The calculation is presented of the liquid–liquid phase equilibria using the NRTL equation in 8 systems of the hydrocarbon A–hydrocarbon B–solvent type. In seven systems examined the hydrocarbon A is n-heptane and once 1-hexene. Hydrocarbon B is either benzene or toluene and once cyclohexane. The solvents used were acetonitrile, aniline, dimethylformamide, dimethyl sulfoxide and diethylene glycol. A good agreement has been achieved in 6 cases between the calculated and experimentally found course of the phase diagram.

The calculation (prediction) of ternary liquid equilibria from the binary data using the NRTL equation has been tested to date on the following hydrocarbon–solvent systems: *1)* isooctane–n-hexane–furfural, $t = 30°C$ (ref.[1,2]); *2)* n-octane–1-octene–nitroethane, $t = 0°C$ (ref.[1]) *3)* n-octane–isooctane–nitroethane, $t = 25°C$ (ref.[3]), $t = 35°C$ (ref.[1]); *4)* n-heptane–cyclohexane–aniline, $t = 25°C$ (ref.[4]); *5)* n-heptane–heptene–perfluordecaline, $t = 10°C$ (ref.[4]); *6)* n-heptane–heptene–perfluormethylcyclohexane, $t = 10°C$ (ref.[4]).

This paper reports on the computed results of equilibria in additional hydrocarbon–solvent systems using the NRTL parameters of the binary systems presented earlier[5,6]. The binary parameters in homogeneous systems were obtained from the isothermal vapour pressure *versus* composition curves $(P - x)$; in heterogeneous systems either from mutual solubilities, or from mutual solubilities plus the limiting activity coefficients extrapolated from $P - x$ diagrams in the homogeneous region of concentration.

Part of the calculated systems has been described in the literature. These are: n-heptane(1)–benzene(2)–acetonitrile(3), $t = 45°C$ (ref.[7]); n-heptane(1)–benzene(2)–diethylene glycol(3), $t = 75°C$ (ref.[8]); n-heptane(1)–cyclohexane(2)–dimethylformamide(3), $t = 20°C$ (ref.[9]); n-heptane(1)–toluene(2)–aniline(3), $t = 40°C$ (ref.[10]); 1-hexene(1)–benzene(2)–dimethylsulfoxide(3), $t = 25°C$ (ref.[11]). Other systems were investigated experimentally in this work: n-heptane(1)–benzene(2)–dimethylsulfoxide(3), $t = 40°C$; n-heptane(1)–toluene(2)–acetonitrile(3), $t = 40°C$; n-heptane(1)–toluene(2)–dimethylformamide(3), $t = 40°C$.

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EXPERIMENTAL AND RESULTS

The binodal curves for the three above listed systems were determined by the turbidity method[6] and the equilibrium phase composition using the method of Nikurashina and Merclin[12]. Thermostated equilibrium vessels of volume 37 cm^3 were filled with 25 cm^3 of solution which ensured efficient mixing in the shaking machine and negligible changes of composition of the sample due

TABLE I

Binodal Data (in mole fraction) for n-Heptane(1)–Toluen(2)–Acetonitrile(3) System at $t = 40°C$

x_1	x_2	x_3	x_1	x_2	x_3
0·073	0·047	0·880	0·481	0·198	0·321
0·114	0·106	0·780	0·550	0·184	0·226
0·182	0·155	0·663	0·641	0·153	0·206
0·255	0·178	0·567	0·745	0·102	0·153
0·323	0·192	0·485	0·838	0·045	0·117
0·400	0·201	0·399			

TABLE II

Equilibrium Phase Composition for n-Heptane(1)–Toluene(2)–Acetonitrile(3) System at $t = 40°C$

In phase 1			In phase 2		
$x_1^{(1)}$	$x_2^{(1)}$	$x_3^{(1)}$	$x_1^{(2)}$	$x_2^{(2)}$	$x_3^{(2)}$
0·855	0·032	0·113	0·059	0·015	0·926
0·815	0·061	0·124	0·064	0·028	0·908
0·744	0·086	0·140	0·070	0·041	0·889
0·731	0·110	0·159	0·078	0·056	0·866
0·711	0·120	0·169	0·082	0·063	0·855
0·687	0·132	0·181	0·087	0·070	0·843
0·665	0·142	0·193	0·091	0·077	0·832
0·644	0·152	0·204	0·097	0·084	0·819
0·629	0·158	0·213	0·104	0·093	0·803
0·602	0·168	0·230	0·108	0·098	0·794
0·590	0·172	0·238	0·109	0·100	0·791

TABLE III

Binodal Data for n-Heptane(1)–Toluene(2)–Dimethylformanide(3) System at $t = 40°C$

x_1	x_2	x_3	x_1	x_2	x_3
0·141	0·042	0·818	0·431	0·149	0·420
0·158	0·067	0·776	0·526	0·146	0·328
0·186	0·095	0·719	0·614	0·131	0·255
0·256	0·130	0·614	0·721	0·096	0·183
0·369	0·145	0·496	0·821	0·051	0·129

TABLE IV

Equilibrium Phase Composition for n-Heptane(1)–Toluene(2)–Dimethylformamide(3) System at $t = 40°C$

In phase 1			In phase 2		
$x_1^{(1)}$	$x_2^{(1)}$	$x_3^{(1)}$	$x_1^{(2)}$	$x_2^{(2)}$	$x_3^{(2)}$
0·874	0·025	0·101	0·129	0·025	0·846
0·803	0·060	0·137	0·149	0·057	0·794
0·741	0·088	0·171	0·168	0·078	0·754
0·680	0·112	0·208	0·189	0·098	0·713
0·641	0·124	0·235	0·203	0·109	0·689
0·579	0·139	0·282	0·234	0·123	0·643
0·558	0·142	0·300	0·243	0·126	0·631

to evaporation. The temperature was held constant with the accuracy ±0·05 °C. The refractive index was measured to within $\pm 2 \cdot 10^{-5}$. The obtained data are summarized in Tables I–VI.

Calculation of Ternary Liquid–Liquid Equilibria

The parameters of the NRTL equation obtained from the binary data were used to calculate the ternary phase equilibria as follows[13]: For six mole fractions, determining composition of the two liquid phases in equilibrium in the three-component system, one can write the following five equations

$$\sum_{i=1}^{3} x_i^{(1)} = 1 \,, \tag{1}$$

$$\sum_{i=1}^{3} x_i^{(2)} = 1 \,, \tag{2}$$

$$a_i^{(1)} = a_i^{(2)} \,; \quad \mathrm{i} = 1, 2, 3 \,, \tag{3}$$

where the activity, or the activity coefficients, are given by Eq. (*1*) of the preceding paper[5] (the NRTL equation). The calculation routine is initiated by an arbitrarily chosen value of one of the mole fractions. The iteration procedure based on incrementing the initial guesses of the remaining five mole fractions is terminated when the condition in Eq. (*3*) is met, or when that condition is met with sufficient accuracy.

The agreement between the calculated and experimental equilibrium compositions for the best set of parameters in Tables VII–XIV is assessed from the arithmetic mean:

$$\delta x_\mathrm{i} = (x_\mathrm{i}^\mathrm{C} - x_\mathrm{i}^\mathrm{Ex})/N \,, \tag{4}$$

TABLE V

Binodal Data for n-Heptane(1)–Benzene(2)–Dimethylsulfoxide(3) System at t = 40°C

x_1	x_2	x_3	x_1	x_2	x_3
0·691	0·287	0·022	0·060	0·326	0·614
0·537	0·412	0·051	0·040	0·242	0·718
0·386	0·493	0·121	0·022	0·126	0·852
0·111	0·429	0·460			

TABLE VI

Equilibrium Phase Composition for n-Heptane(1)–Benzene(2)–Dimethylsulfoxide(3) System at t = 40°C

In phase 1			In phase 2		
$x_1^{(1)}$	$x_2^{(1)}$	$x_3^{(1)}$	$x_1^{(2)}$	$x_2^{(2)}$	$x_3^{(2)}$
0·485	0·446	0·069	0·051	0·296	0·653
0·553	0·401	0·046	0·043	0·264	0·693
0·618	0·351	0·031	0·037	0·222	0·741
0·698	0·280	0·022	0·028	0·167	0·805
0·785	0·200	0·015	0·022	0·111	0·867
0·881	0·109	0·010	0·017	0·055	0·928

where x_i^C and x_i^{Ex} stand respectively for the calculated and experimental values of the mole fraction in the liquid phase under consideration and N is the number of the data pairs. Parenthesized data in these tables are the maximum deviations $\Delta x_i = x_i^C - x_i^{Ex}$.

DISCUSSION

The determination of liquid–liquid equilibria in the hydrocarbon–hydrocarbon–solvent systems listed above was carried out as follows:

Excepting the system sub *3*) ($t = 35°C$) the calculations was carried out with the aid of the parameters α_{ij} estimated in advance using Renon's rules[2] ($\alpha_{13} = 0\cdot2$),

Table VII

Test of Prediction for n-Heptane(1)–Toluene(2)–Acetonitrile System at $t = 40°C$

No	Set of binary parameters	Source of binary parameters	$\delta x_1^{(1)}$ ($\Delta x_{1\max}^{(1)}$)	$\delta x_2^{(1)}$ ($\Delta x_{2\max}^{(1)}$)	$\delta x_1^{(2)}$ ($\Delta x_{1\max}^{(2)}$)
I.	$\alpha_{12} = 0\cdot2$ $C_{12} = -491\cdot20$ $C_{21} = 937\cdot89$ $\alpha_{23} = 0\cdot4490$ $C_{23} = 427\cdot73$ $C_{32} = 477\cdot31$ $\alpha_{13} = 0\cdot3865$ $C_{13} = 1373\cdot94$ $C_{31} = 1589\cdot14$	*P-x* curve α_{12} estimated in advance from ref.[2] *P-x* curve mutual solubility and limiting activity coefficients from *P-x* data	0·0052 (0·0188)	0·0076 (0·0153)	0·0073 (−0·0150)
II.	$\alpha_{12} = 0\cdot2$ $C_{12} = -491\cdot20$ $C_{21} = 937\cdot89$ $\alpha_{23} = 0\cdot2$ $C_{23} = 403\cdot58$ $C_{32} = 442\cdot36$ $\alpha_{13} = 0\cdot2$ $C_{13} = 770\cdot54$ $C_{31} = 1441\cdot18$	*P-x* curve α_{23} estimated in advance from ref.[2] mutual solubility, α_{13} estimated in advance from ref.[2]	0·0274 (0·0586)	0·0144 (0·0273)	0·0410 (−0·0397)
III.	$\alpha_{12} = 0\cdot2$ $C_{12} = -491\cdot20$ $C_{21} = 937\cdot89$ $\alpha_{23} = 0\cdot2$ $C_{23} = 403\cdot58$ $C_{32} = 442\cdot36$ $\alpha_{13} = 0\cdot3865$ $C_{13} = 1373\cdot94$ $C_{31} = 1589\cdot14$		0·0090 (−0·0128)	0·0134 (0·0234)	0·0117 (−0·0241)

or by trial and error so as to achieve maximum possible agreement between the calculated and experimental ternary equilibrium data (system sub *4*)–*6*)). The parameters C_{ij} and C_{ji} were calculated for the earlier estimated α_{ij} from the solubility data or vapour–liquid equilibria. In some cases it was assumed that the binary hydrocarbon solutions behave ideally. In case of the system listed sub *3*) ($t = 35°C$) we compared the predicted value based on the in advance estimated α_{ij} with that when the equilibrium binary data served to compute all three parameters of the NRTL equation. While the first alternative (two-parameter prediction) failed to provide reasonable

TABLE VIII

Test of Prediction for n-Heptane(1)–Benzene(2)–Acetonitrile(3) System at $t = 45°C$ (ref.[7])

No	Set of binary parameters	Source of binary parameters	$\delta x_1^{(1)}$ ($\Delta x_{1\,\max}^{(1)}$)	$\delta x_2^{(1)}$ ($\Delta x_{2\,\max}^{(1)}$)	$\delta x_1^{(2)}$ ($\Delta x_{1\,\max}^{(2)}$)
I.	$\alpha_{12} = 0{\cdot}2$ $C_{12} = -471{\cdot}24$ $C_{21} = 961{\cdot}95$ $\alpha_{23} = 0{\cdot}8904$ $Ca_3 = 458{\cdot}10$ $C_{32} = 460{\cdot}88$ $\alpha_{13} = 0{\cdot}3750$ $C_{13} = 1353{\cdot}87$ $C_{31} = 1522{\cdot}90$	*P-x* curve, α_{12} estimated in advance from ref.[2] *P-x* curve mutual solubility and limiting activity coefficients from *P-x* data	0·0490 (0·0711)	0·0037 (−0·0034)	0·0075 (−0·0100)
II.	$\alpha_{12} = 0{\cdot}2$ $C_{12} = -471{\cdot}24$ $C_{21} = 961{\cdot}95$ $\alpha_{23} = 0{\cdot}2$ $C_{23} = 331{\cdot}07$ $C_{32} = 343{\cdot}00$ $\alpha_{13} = 0{\cdot}3750$ $C_{13} = 1353{\cdot}87$ $C_{31} = 1522{\cdot}90$	*P-x* curve, α_{23} estimated in advance from ref.[2]	0·0120 (0·0164)	0·0126 (0·0255)	0·0205 (−0·0473)
III.	$\alpha_{12} = 0{\cdot}2$ $C_{12} = -471{\cdot}24$ $C_{21} = 961{\cdot}95$ $\alpha_{23} = 0{\cdot}2$ $C_{23} = 331{\cdot}07$ $C_{32} = 343{\cdot}00$ $\alpha_{13} = 0{\cdot}2$ $C_{13} = 859{\cdot}97$ $C_{31} = 1343{\cdot}79$	mutual solubility, α_{13} estimated in advance from ref.[2]	0·0486 (0·0778)	0·0100 (0·0274)	0·0253 (−0·0516)

estimates, the second one (the three-parameter prediction) provided a good agreement between the calculated and the experimental data. The two-parameter estimate produced relatively poor results also for the system sub *2*) in which case, similarly as for the system sub *3*) (t = 35°C), the binodal curve displays a closed course. In all remaining cases of systems with an open binodal curve the two-parameter prediction was satisfactory.

Summarizing the above results as well as the general findings of the authors cited in the preceding papers[5] concerning the hydrocarbon–hydrocarbon–solvent systems

TABLE IX

Test of Prediction for n-Heptane(1)–Benzene(2)–Dimethylsulfoxide(3) System at t = 40°C

No	Set of binary parameters	Source of binary parameters	$\delta x_1^{(1)}$ $(\Delta x_{1\,\mathrm{max}}^{(1)})$	$\delta x_2^{(1)}$ $(\Delta x_{2\,\mathrm{max}}^{(1)})$	$\delta x_1^{(2)}$ $(\Delta x_{1\,\mathrm{max}}^{(2)})$
	α_{12} = 0·2	*P-x* curve,			
	C_{12} = −347·12	α_{12} estimated in advance			
	C_{21} = 773·39	from ref.[2]			
	α_{23} = 0·6418		0·0219	0·0035	0·0163
I.	C_{23} = 787·56	*P-x* curve	(0·0527)	(−0·0069)	(−0·0185)
	C_{32} = 360·32				
	α_{13} = 0·2	mutual solubility,			
	C_{13} = 2559·74	α_{13} estimated in advance			
	C_{31} = 1616·13	from ref.[2]			
	α_{12} = 0·2				
	C_{12} = −347·12				
	C_{21} = 773·39				
	α_{23} = 0·2	*P-x* curve,	0·0086	0·0107	0·0086
II.	C_{23} = 970·21	α_{23} estimated in advance	(0·0133)	(0·0190)	(−0·0203)
	C_{32} = −39·43	from ref.[2]			
	α_{13} = 0·2				
	C_{13} = 2559·74				
	C_{31} = 1616·13				
	α_{12} = 0·2				
	C_{12} = −347·12				
	C_{21} = 773·39				
	α_{23} = 0·2		0·0109	0·0083	0·0015
III.	C_{23} = 970·21		(−0·0213)	(0·0145)	(0·0041)
	C_{32} = −39·43				
	α_{13} = 0·3	mutual solubility,			
	C_{13} = 2792·22	α_{13} estimated in advance			
	C_{31} = 2084·41	from ref.[2]			

one can conclude that a more reliable prediction for systems with closed binodal curve is obtained with that set of the binary solution parameters where all three parameters of the NRTL equation for the binary of limited mutual solubility $(1-3)$ were found by calculation. This indicates that apart from mutual solubilities one needs also the vapour–liquid equilibrium data in the homogeneous region or the azeotropic composition. It may happen that estimates starting from mutual solubilities, *i.e.* from two-parameter description of the system $1-3$, will completely fail. Such case has been described by Joy and Kyle[1].

TABLE X

Test of Prediction for 1-Hexene(1)–Benzene(2)–Dimethylsulfoxide(3) System at $t = 25°C$

No	Set of binary parameters	Source of binary parameters	$\delta x_1^{(1)}$ $(\Delta x_{1\,\max}^{(1)})$	$\delta x_2^{(1)}$ $(\Delta x_{2\,\max}^{(1)})$	$\delta x_1^{(2)}$ $(\Delta x_{1\,\max}^{(2)})$
I.	$\alpha_{12} = 0{\cdot}2$ $C_{12} = -300{\cdot}16$ $C_{21} = 617{\cdot}02$ $\alpha_{23} = 0{\cdot}5726$ $C_{23} = 792{\cdot}11$ $C_{32} = 340{\cdot}27$ $\alpha_{13} = 0{\cdot}2$ $C_{13} = 3307{\cdot}31$ $C_{31} = 832{\cdot}11$	*P-x* curve, α_{12} estimated in advance from ref.[2] *P-x* curve mutual solubility α_{13} estimated in advance from ref.[2]	0·0367 (0·0706)	0·0192 (−0·0378)	0·0096 (−0·0253)
II.	$\alpha_{12} = 0{\cdot}2$ $C_{12} = -300{\cdot}16$ $C_{21} = 617{\cdot}02$ $\alpha_{23} = 0{\cdot}2$ $C_{23} = 962{\cdot}95{\cdot}$ $C_{32} = -1937$ $\alpha_{13} = 0{\cdot}2$ $C_{13} = 3307{\cdot}31$ $C_{31} = 832{\cdot}11$	*P-x* curve α_{23} estimated in advance from ref.[2]	0·0298 (0·0500)	0·0192 (−0·0241)	0·0113 (−0·0283)
III.	$\alpha_{12} = 0{\cdot}2$ $C_{12} = -300{\cdot}16$ $C_{21} = 617{\cdot}02$ $\alpha_{23} = 0{\cdot}2$ $C_{23} = 962{\cdot}95$ $C_{32} = -19{\cdot}37$ $\alpha_{13} = 0{\cdot}3$ $C_{13} = 3263{\cdot}92$ $C_{31} = 1425{\cdot}98$	mutual solubility α_{13} estimated in advance from ref.[2]	0·0283 (0·0433)	0·0232 (−0·0308)	0·0049 (−0·0149)

TABLE XI

Test of Prediction for n-Heptane(1)–Cyclohexane(2)–Dimethylformamide(3) System at $t = 20°C$ (ref.[11])

No	Set of binary parameters	Source of binary parameters	$\delta x_1^{(1)}$ $(\Delta x_{1\max}^{(1)})$	$\delta x_2^{(1)}$ $(\Delta x_{2\max}^{(1)})$	$\delta x_1^{(2)}$ $(\Delta x_{1\max}^{(2)})$
I.	$\alpha_{12} = 0·2$ $C_{12} = -318$ $C_{21} = 279$ $\alpha_{23} = 0·2$ $C_{23} = 1461·62$ $C_{32} = 455·95$ $\alpha_{13} = 0·2$ $C_{13} = 1990·58$ $C_{31} = 754·17$	taken from Renon[13] mutual solubility α_{23} estimated in advances from ref.[2] mutual solubility α_{13} estimated in advance from ref.[2]	0·014 (0·037)	0·018 (−0·042)	0·005 (−0·007)
II.	$\alpha_{12} = 0·2$ $C_{12} = -318$ $C_{21} = 279$ $\alpha_{23} = 0·3$ $C_{23} = 1394·98$ $C_{32} = 738·80$ $\alpha_{13} = 0·2$ $C_{13} = 1990·58$ $C_{31} = 754·17$	mutual solubility, α_{23} estimated	0·018 (0·026)	0·010 (−0·030)	0·006 (−0·007)

TABLE XII

Test of Prediction for n-Heptane(1)–Benzene(2)–Diethylene Glycol(3) System at $t = 75°C$ (ref.[8])

No	Set of binary parameters	Source of binary parameters	$\delta x_1^{(1)}$ $(\Delta x_{1\max}^{(1)})$	$\delta x_2^{(1)}$ $(\Delta x_{2\max}^{(1)})$	$\delta x_1^{(2)}$ $(\Delta x_{1\max}^{(2)})$
I.	$\alpha_{12} = 0·2$ $C_{12} = -437·17$ $C_{21} = 812·90$ $\alpha_{23} = 0·2$ $C_{23} = 2164·96$ $C_{32} = -164·43$ $\alpha_{13} = 0·2$ $C_{13} = 3166·62$ $C_{31} = 2174·35$	*P-x* curve α_{12} estimated in advance from ref.[2] mutual solubility, α_{13} and α_{23} estimated in advance from ref.[2]	0·0028 (0·0109)	0·0026 (0·0038)	0·0172 (0·0434)

The conclusions following from the presented tests (see Tables VII – XIV) are essentially identical. Yet, in neither of the cases examined did we encounter a similar course of the calculation as the mentioned authors[1]. The worst results of prediction were experienced in tests with closed systems containing aniline or dimethylformamide. The inferior quality of prediction in these systems though is probably not the matter of two-or three-parametr description of the $1-3$ binary but rather caused on hand by the narrow two-phase region (toward the plait point the error of prediction almost always increases) and, on the other hand, by poor reliability of the limiting activity coefficients in the $1-3$ binary. The latter is caused by large relative errors of measuring low values of total pressure in the vapor–liquid equilibrium experiments.

In contrast, other systems yielded very good estimates even with the aid of the two-parametr description of the $1-3$ system (systems with acetonitrile and particularly those with dimethylsulfoxide where, owing to low mutual solubility, it is not even possible to evaluate the limiting activity coefficients from the $P - x$ data).

The systems with acetonitrile and dimethylsulfoxide served to investigate also the effect of using either two- or three-parameter description for the $2-3$ system (Tables VII – X). However, no unambiguous conclusion could be drawn as the three-parameter description improved prediction only for the n-heptane–toluene–acetonitrile system, had no clear effect in case of the n-heptane–benzene acetonitrile system and deteriorated the quality of the prediction in case of two systems containing dimethylsulfoxide. Such behaviour has been reported in literature also in the calculation of the ternary vapor–liquid equilibria: see ref.[7] in the preceding communication[5].

TABLE XIII

Test of Prediction for n-Heptane(1)–Toluene(2)–Dimethylformamide(3) System at $t = 40°C$

No	Set of binary parameters	Source of binary parameters	$\delta x_1^{(1)}$ $(\Delta x_{1\,\mathrm{max}}^{(1)})$	$\delta x_2^{(1)}$ $(\Delta x_{2\,\mathrm{max}}^{(1)})$	$\delta x_1^{(2)}$ $(\Delta x_{1\,\mathrm{max}}^{(2)})$
I.	$\alpha_{12} = 0{\cdot}2$ $C_{12} = -491{\cdot}20$ $C_{21} = 937{\cdot}89$ $\alpha_{23} = 0{\cdot}2$ $C_{23} = 1076{\cdot}01$ $C_{32} = -385{\cdot}47$ $\alpha_{13} = 0{\cdot}3625$ $C_{13} = 1696{\cdot}28$ $C_{31} = 1192{\cdot}88$	*P-x* curve, α_{12} and α_{23} estimated in advance from ref.[2] mutual solubility and limiting activity coefficients from *P-x* data	0·0904 (0·1736)	0·0064 (0·0092)	0·0553 (0·1013)

In accord with the findings from the literature, no such problems occur in systems with open binodal curves (Tables XI – XII) and a good agreement is achieved even with the two-parameter description of the binary of limited mutual solubility.

In some cases it is possible to improve the description of the ternary diagram of liquid–liquid equilibrium by choosing meaningful, but otherwise arbitrary, values for the parameters α_{ij} to correlate the data in the $1-3$ and $2-3$ binary systems and select the combination yielding a minimum deviation from the experimental results. As an example may serve the systems in Tables IX – XI. Such approach, of course, is not a prediction because the analysis of the properties of the NRTL equation indicates so far only that in the hydrocarbon–polar substance systems the value of α_{ij} for the two-parameter processing should be taken equal 0·20. Another side of the problem though is that such a value of a nonrandom parameter in the binary of limited mutual solubility shall be sometimes too small to describe a small two-phase region in the ternary system.

CONCLUSION

Judging from the literature and the results of this study one can expect the prediction of the ternary equilibria from the binary data using the NRTL equation in hydrocarbon–hydrocarbon–solvent systems with closed binodal curve to yield satisfactory results. Particularly so, if the two-phase region is not too narrow. The decisive role is played by the NRTL parameters of the binary of limited mutual solubility. For that binary it is better to avoid drawing all information exclusively from the solubility data, but, instead, to utilize also the vapour–liquid equilibria. The latter data may be condensed into the value of the limiting activity coefficient. In system with open bino-

TABLE XIV

Test of Prediction for n-Heptane(1)–Toluene(2)–Aniline(3) System at $t = 40°C$

No	Set of binary parameters	Source of binary parameters	$\delta x_1^{(1)}$ ($\Delta x_{1\,\max}^{(1)}$)	$\delta x_2^{(1)}$ ($\Delta x_{2\,\max}^{(1)}$)	$\delta x_1^{(2)}$ ($\Delta x_{1\,\max}^{(2)}$)
I.	$\alpha_{12} = 0{\cdot}2$ $C_{12} = -491{\cdot}20$ $C_{21} = 937{\cdot}89$ $\alpha_{23} = 0{\cdot}2$ $C_{23} = 592{\cdot}18$ $C_{32} = 144{\cdot}48$ $\alpha_{13} = 0{\cdot}3750$ $C_{13} = 3149{\cdot}83$ $C_{31} = 1708{\cdot}89$	*P-x* curve, α_{12} and α_{23} estimated in advance from ref.[2] mutual solubility and limiting activity coefficients from *P-x* data	0·192 (0·215)	0·013 (0·024)	0·006 (0·018)

dal curves the prediction from this standpoint is rather less exacting on the input data. For almost all systems examined the error of the calculation increases toward the plait point. This fact, however, does not restrict the applicability of the predicted equilibria (*e.g.* for preliminary choice of a suitable solvent) because the upper part of the binodal curve is usually beyond the region of interest for liquid–liquid extraction.

LIST OF SYMBOLS

$a_i^{(k)}$	activity of *i*-th component in *k*-th liquid phase
$x_i^{(k)}$	mole fraction of *i*-th component in *k*-th phase
x_i^{C}	calculated mole fraction of *i*-th component
x_i^{Ex}	experimental mole fraction of *i*-th component
C_{ij}	parameter of NRTL equation
C_{ji}	parameter of NRTL equation
P	total pressure, Torr
α_{ij}	non-probabilistic parameter in NRTL equation
$\delta x_i^{(k)}$	mean deviation of calculated equilibrium concentration
$\Delta x_i^{(k)}$	maximum deviation of calculated equilibrium concentration

REFERENCES

1. Joy D. S., Kyle B. G.: AICHE J. *15*, 296 (1969).
2. Renon H., Prausnitz J. M.: AICHE J. *14*, 135 (1968).
3. Renon H., Prausnitz J. M.: Ind. Eng. Chem. Process. Des. Develop. *8*, 413 (1969).
4. Soares L. de J. S., Packer L. G., Ellis S. R. M.: Proc. Ist Int. Solvent Extr. Conf. Pap. 38, 9—17, Soc. Chem. Ind., London 1971.
5. Heinrich J.: This Journal *40*, 787 (1975).
6. Heinrich J., Dojčanský J.: This Journal *40*, 940 (1975).
7. Palmer D. A.: *Thesis*. Washington University, Washington 1970.
8. Jonhson G. C., Francis A. W.: Ind. Eng. Chem. *46*, 1662 (1954).
9. Durandet J., Gladel Y. L.: Rev. Inst. Fr. Petrole Ann. Combust. Liquides *11*, 811 (1956).
10. Durandet J., Gladel Y. L.: Rev. Inst. Fr. Petrole Ann. Combust. Liquides *9*, 296 (1954).
11. Dojčanský J.: *Thesis*. Slovak Institute of Technology, Bratislava 1968.
12. Nikurashina R. V., Merclin G. M., Komarova G. M.: Zh. Obshch. Khim. *29*, 345 (1950).
13. Renon H., Asselineau L., Cohen G., Raimbault C.: *Calcul sur Ordinateur des Équilibres Liquide–Vapeur et Liquide–Liquide*. Technip, Paris 1971.
14. Palmer D. A., Smith B. D.: Ind. Eng. Chem. Process. Des. Develop. *11*, 114 (1972).
15. Renon H. M.: *Thesis*. California University, Berkeley 1966.

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