ACTIVITY COEFFICIENTS IN BINARY SYSTEMS OF LIMITED MUTUAL SOLUBILITY*

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The parameters are given of the NRTL equation in 10 hydrocarbon–solvent systems. The parameters were evaluated from the isothermal dependence of total vapour pressure on liquid phase composition and from mutual solubilities of the components. The data were obtained partly from the literature, partly experimentally. The binary NRTL parameters are used to calculate ternary liquid equilibria in hydrocarbon–solvent systems.

The paper presents the data on vapour–liquid and liquid–liquid equilibria in binary systems with limited mutual solubility of the components and the NRTL parameters[1,2] computed from them.

EXPERIMENTAL

The solubility data on the following systems were taken over from the literature: n-Heptane–acetonitrile, $t = 45°C$ (ref.[7]); n-heptane–aniline, $t = 40°C$ (ref.[5]); n-heptane–diethylene glycol, $t = 75°C$ (ref.[3]); n-heptane–dimethylformamide, $t = 20°C$ (ref.[4]); 1-hexene–dimethyl sulfoxide, $t = 25°C$ (ref.[6]); benzene–diethylene glycol, $t = 75°C$ (ref.[3]) and cyclohexane–dimethylformamide, $t = 20°C$ (ref.[5]).

The data on the following systems were obtained experimentally: n-Heptane–acetonitrile, $t = 40°C$; n-heptane–dimethylformamide, $t = 40°C$; n-heptane–dimethyl sulfoxide, $t = 40°C$.

The data on the total vapour pressure as a function of liquid phase composition for the following systems were taken from the literature: n-Heptane–acetonitrile, $t = 45°C$ (ref.[7]); n-heptane–dimethylformamide, $t = 40°C$ (ref.[8]), and the following systems were measured n-heptane–acetonitrile, $t = 40°C$; n-heptane–aniline, $t = 40°C$; benzene–diethylene glycol, $t = 75°C$.

The solubility was determined by the turbidity method. 12 mm in diameter and 90 mm long ampules were filled to 3/4 of their volume. This method permits under the temperature used, the change of the composition due to evaporation to be neglected. Considering the error of weighing (including possible errors due to evaporation during weighing) the maximum error of the composition of the solution can be estimated to $\pm 0.1\%$ by mass. The temperature was held constant to within ± 0.05 deg. The solubility for the appropriate temperature was interpolated from the obtained concentration dependence of the temperature of the turbidity (Tables I–III).

The numbering of the components 1, 2 and 3 has been made with regard to their future presence in the calculation of the ternary equilibria in the hydrocarbon(1)–hydrocarbon(2)–solvent(3) type systems.

TABLE I

Solubility in the n-Heptane(1)–Dimethylformamide(3) System
  Interpolated for $t = 40°C$: $x_1^{(1)} = 0.923$, $x_1^{(2)} = 0.113$.

t, °C	26·7	31·4	32·4	36·3	41·5		49·5	46·1	41·2	39·4	35·9
x_1	0·938	0·930	0·928	0·925	0·920		0·144	0·134	0·117	0·112	0·102

TABLE II

Solubility in the n-Heptane(1)–Acetonitrile(3) System
  Interpolated for $t = 40°C$: $x_1^{(1)} = 0.902$, $x_1^{(2)} = 0.054$.

t, °C	36·6	39·1	41·5	43·4	46·5	47·4	47·0	45·3	44·2	42·0	41·6	38·8
x_1	0·912	0·905	0·897	0·891	0·880	0·877	0·064	0·062	0·060	0·057	0·056	0·053

TABLE III

Solubility in the n-Heptane(1)–Dimethyl Sulfoxide(3) System
  Interpolated for $t = 40°C$: $x_1^{(1)} = 0.9963$, $x_1^{(2)} = 0.014$.

t, °C	34·0	40·1	43·2	47·0		47·3	41·2	40·2	37·1	35·8
x_1	0·9975	0·9963	0·9956	0·9948		0·016	0·014	0·014	0·013	0·013

In systems with sufficient mutual solubility of the components at the given temperature were measured also the dependence of the total vapour pressure on the composition of the liquid phase. The experimental method used has been described in the preceding paper[9]. The results of measurement are summarized in Tables IV—VI. The same tables indicate also the limiting activity coefficients given in Eqs (5) through (8).

Vapour pressure of pure components used in data processing have been given previously[9].

Data Processing

The parameters of the NRTL equation can be computed from the experimental data by the approach described by Renon and coworkers[10] with the minimizing function

$$Q' = \varrho_{\gamma_{ij}}\left(\gamma_{ij}^{\infty C} - \gamma_{ij}^{\infty Ex}\right)^2 + \varrho_{\gamma_{ji}}\left(\gamma_{ji}^{\infty C} - \gamma_{ji}^{\infty Ex}\right)^2 +$$
$$+ \varrho_x^{(1)}\left(x_i^{(1)C} - x_i^{(1)Ex}\right)^2 + \varrho_x^{(2)}\left(x_i^{(2)C} - x_i^{(2)Ex}\right)^2 , \qquad (1)$$

TABLE IV

Total Vapour Pressure (Torr) as a Function of Liquid Phase Composition in the n-Heptane(1)–Acetonitrile(3) System at 40°C
$\gamma_{13}^{\infty} = 32\cdot6$, $\gamma_{31}^{\infty} = 24\cdot1$.

x_3	P
0·037	200·1
0·053	221·4
0·073	241·3
0·086	249·6
0·095	254·1
0·958	243·0
0·966	235·0
0·973	225·2
0·982	210·5
0·990	195·3

TABLE V

Total Vapour Pressure (Torr) as a Function of Liquid Phase Composition in the Benzene(2)–Diethylene Glycol(3) System at 75°C
$\gamma_{23}^{\infty} = 5\cdot97$, $\gamma_{32}^{\infty} = 129$.

x_2	P
0·027	100·1
0·033	119·9
0·047	166·2
0·064	217·9
0·082	268·6
0·914	629·6
0·926	629·9
0·948	632·8
0·961	634·9
0·967	636·3

TABLE VI

Total Vapour Pressure (Torr) as a Function of Liquid Phase Composition in the System n-Heptane (1)–Aniline(3) at 40°C
$\gamma_{13}^{\infty} = 24\cdot3$, $\gamma_{31}^{\infty} = 420$.

x_1	P	x_1	P
0·019	38·0	0·952	99·8
0·034	56·2	0·964	101·6
0·042	64·5	0·972	102·1
0·051	70·4	0·972	103·6
0·062	77·4	0·973	103·8
0·929	97·1		

where for mutual solubility we have that

$$\gamma_i^{(1)} x_i^{(1)} = \gamma_i^{(2)} x_i^{(2)} , \tag{2}$$

$$\gamma_j^{(1)}(1 - x_i^{(1)}) = \gamma_j^{(2)}(1 - x_i^{(2)}) , \tag{3}$$

while the activity coefficients are given by the NRTL equation, Eq. (1). For the limiting activity coefficients one can write from the same equation

$$\ln \gamma_{ij}^\infty = \tau_{ji} + \tau_{ij} \exp\left(-\alpha_{ij}\tau_{ij}\right) . \tag{4}$$

The subscripts i, j in Eqs (1) through (4) designate the components of the binary mixture i, j.

The limiting activity coefficients $\gamma_{ij}^{\infty \mathbf{Ex}}$ for Eq. (1) were evaluated from the above mentioned $P - x$ data from the so-called apparent activity coefficients of Carlson and Colburn

$$(\gamma_{ij})_{ap} = (P - P_i^0 x_j)/P_i^0 x_i \tag{5}$$

for which we have

$$\lim_{x_i \to 0} (\gamma_{ij})_{ap} = \lim_{x_i \to 0} \gamma_{ij} = \gamma_{ij}^\infty . \tag{6}$$

The value of $\log\left(\gamma_{ij}^\infty\right)$ was searched for by the least-square method as a constant A of the equation

$$\log\left(\gamma_{ij}\right)_{ap} = A + Bx_i , \tag{7}$$

assigning the following statistical weight[11]

$$\varrho_{(\log \gamma_{ij})_{ap}} = \left\{\left[\frac{\partial(\gamma_{ij})_{ap}}{\partial P}\right]^2 s_P^2 + \left[\frac{\partial(\gamma_{ij})_{ap}}{\partial P_i^0}\right]^2 s_{P_i^0}^2 + \left[\frac{\partial(\gamma_{ij})_{ap}}{\partial P_j^0}\right]^2 s_{P_j^0}^2 + \left[\frac{\partial(\gamma_{ij})_{ap}}{\partial x_i}\right]^2 s_{x_i}^2\right\}^{-1} . \tag{8}$$

The statistical weights $\varrho_{\gamma_{ij}}$ and ϱ_x in Eq. (1) were taken as recommended by Renon and coworkers[10], so as to express the equivalence of current errors of the solubility measurement and the limiting activity coefficients.

The value of the NRTL parameters as well as a comparison of the experimental and the computed limiting activity coefficients are given in Table VII.

TABLE VII
NRTL Parameters in Binary Systems of Limited Miscibility

System i-j	Number of searched parameters	α_{ij}	C_{ij}	C_{ji}	Absolute deviation				Relative (%) deviation of lim. activity coeff.	
					solubility		lim. activity coeff.			
					$x_1^{(1)}$	$x_1^{(2)}$	γ_{ij}^∞	γ_{ji}^∞	γ_{ij}^∞	γ_{ji}^∞
n-Heptane(1)–acetonitrile(3)										
40°C	2	0·2	770·54	1 441·18	—	—	—	—	—	—
	3	0·3865	1 373·94	1 589·14	+0·002	+0·002	+0·41	−0·53	+1·26	−2·20
45°C	2	0·2	859·97	1 343·79	—	—	—	—	—	—
	3	0·3750	1 353·87	1 522·90	+0·002	+0·002	+0·16	+0·29	+0·55	+1·27
n-Heptane(1)–dimethylformamide(3)										
20°C	2	0·2	1 990·58	754·17	—	—	—	—	—	—
	2	0·2	1 990·58	754·17	—	—	—	—	—	—
	2	0·3	1 980·87	1 131·67	—	—	—	—	—	—
40°C	2	0·2	1 230·98	839·28	—	—	—	—	—	—
	3	0·3625	1 695·15	1 192·08	+0·015	+0·001	+0·26	−1·00	+1·41	−2·45
n-Heptane(1)–diethylene glycol(3)										
75°C	2	0·2	3 166·62	2 174·35	—	—	—	—	—	—
	3	0·3	3 523·15	2 744·38	—	—	—	—	—	—
	4	0·4	3 953·25	3 283·77	—	—	—	—	—	—

System											
Benzene(2)–diethylene glycol(3) 75°C	2	0·2	2 164·96	− 163·43	—	—	—	—	—	—	
	2	0·3	1 809·44	267·91	—	—	—	—	—	—	
	3	0·3875	2 888·47	701·15	+0·028	+0·004	+0·34	−0·10	+5·70	−0·08	
n-Heptane(1)–aniline(3) 40°C	2	0·2	831·13	1 169·68	—	—	—	—	—	—	
	2	0·3	1 022·21	1 241·63	—	—	—	—	—	—	
	3	0·3750	3 149·83	1 708·89	+0·022	+0·006	−9·00	+1·71	−37·0	+0·41	
n-Heptane(1)–dimethyl sulfoxide(3) 40°C	2	0·2	2 559·74	1 616·13	—	—	—	—	—	—	
	2	0·3	2 792·22	2 084·41	—	—	—	—	—	—	
	2	0·35	2 960·89	2 321·41	—	—	—	—	—	—	
1-Hexene(1)–dimethyl sulfoxide(3) 25°C	2	0·2	3 307·31	832·11	—	—	—	—	—	—	
	2	0·3	3 263·92	1 425·98	—	—	—	—	—	—	
	2	0·35	3 355·87	1 732·62	—	—	—	—	—	—	
Cyclohexane(2)–dimethylformamide(3) 20°C	2	0·2	1 461·62	455·95	—	—	—	—	—	—	
	2	0·3	1 394·98	738·80	—	—	—	—	—	—	

LIST OF SYMBOLS

s_P^2	variance of total vapour pressure
$s_{P_i0}^2$	variance of pure component i vapour pressure
$s_{x_i}^2$	variance of mole fraction for component i
x_i	mole fraction for component i
$x_i^{(k)}$	mole fraction of component i in phase k, solubility of component i
$x_i^{(k)C}$; $x_i^{(k)Ex}$	calculated and experimental solubility of component i
C_{ij}	NRTL parameter
P	total vapour pressure, Torr
P_i^0	pure component vapour pressure, Torr
Q'	minimizing function, Eq. (1)
α_{ij}	NRTL parameter^2
$\gamma_i^{(k)}$	activity coefficient of component i in phase k
γ_{ij}^∞	limiting activity coefficient of component i
$(\gamma_{ij})_{ap}$	apparent activity coefficient, Eq. (5)
ϱ_{x_i}	statistical weight of experimental solubility of component i
$\varrho_{\gamma_{ij}}$	statistical weight of experimental limiting activity coefficient of component i
$\varrho_{(\gamma_{ij})_{ap}}$	statistical weight of apparent activity coefficient
τ_{ij}	NRTL parameter^2

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