

ACTIVITY COEFFICIENTS IN BINARY SYSTEMS OF PERFECTLY MISCIBLE COMPONENTS*

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The parameters are given of the NRTL equation for 5 hydrocarbon–hydrocarbon and 6 hydrocarbon–solvent systems. The parameters were evaluated from the isothermal dependence of total vapour pressure on liquid phase composition obtained partly from the literature, partly experimentally. The binary NRTL parameters are used to calculate the ternary liquid equilibria.

Renon and Prausnitz^{1,2} have derived the so called NRTL equation for the molar excess free enthalpy differing in principle from Wohl's expansion³ and related equations. The dependence of the activity coefficients on liquid phase composition following from the NRTL model takes for an n -component system the form

$$\ln \gamma_i = \frac{\sum_{j=1}^n x_j G_{ji} \tau_{ji}}{\sum_{k=1}^n x_k G_{ki}} + \sum_{j=1}^n \frac{x_j G_{ji}}{\sum_{k=1}^n x_k G_{ki}} \left[\tau_{ij} - \frac{\sum_{l=1}^n x_l G_{lj} \tau_{lj}}{\sum_{k=1}^n x_k G_{kj}} \right], \quad (1)$$

where

$$G_{ji} = \exp \left[-\alpha_{ji} \frac{C_{ji}}{RT} \right] = \exp \left[-\alpha_{ji} \frac{(g_{ji} - g_{ii})}{RT} \right] = \exp (-\alpha_{ji} \tau_{ji}).$$

The activity coefficients at constant temperature in an n -component system are thus given by a set of $3n$ binary parameters. Eq. (1) therefore allows predictions of the phase equilibria in multicomponent systems from the binary equilibrium data. This property of the NRTL equation has been tested by several authors attempting to predict the liquid–vapour^{4–9} or the liquid–liquid equilibria^{1,2,7,9–15,18}. Neither

* Part I in the series Application of the NRTL Equation to Hydrocarbon–Solvent Solutions.

* The numbering 1, 2 and 3 of the components have been made with respect to future presence of the components in ternary mixtures hydrocarbon–hydrocarbon–solvent.

TABLE I

Total Vapour Pressure (Torr) as a Function of Liquid Phase Composition in the Benzene(2)-
-n-Heptane(1) System at 40 and 75°C

x_2	P_{40}^{Ex}	P_{75}^{Ex}	P_{40}^C	P_{75}^C
			$\alpha_{21} = 0.2$	
0.099	109.6	407.2	109.18	409.57
0.171	119.3	440.9	120.19	441.78
0.253	131.0	476.6	131.39	475.39
0.324	140.2	503.5	139.99	501.83
0.409	149.9	531.4	149.03	530.36
0.497	156.8	555.4	157.07	556.47
0.583	164.1	580.5	163.82	579.06
0.663	168.5	596.6	169.19	597.33
0.753	174.2	614.2	174.34	615.16
0.839	177.9	628.4	178.34	629.41
0.925	181.4	639.7	181.34	640.63

TABLE II

Total Vapour Pressure (Torr) as a Function of Liquid Phase Composition in the Acetonitrile(3)-
-Toluene(2) System at 40°C

x_3	P^{Ex}	P^C
		$\alpha_{32} = 0.449$
0.063	90.4	88.85
0.113	105.9	105.78
0.176	121.3	121.42
0.257	133.5	135.46
0.334	143.6	144.70
0.405	150.8	151.01
0.492	156.9	156.93
0.588	162.4	162.06
0.654	165.6	165.02
0.739	169.2	168.27
0.819	172.1	170.59
0.837	173.4	171.00
0.912	172.9	171.68
0.959	172.3	171.07

of the papers accounted for the fact pointed to by Hála^{19,20} and partly by Nagata and Ohta²¹ that in multicomponent systems the coefficients C_{ij} are mutually de-

TABLE III

Total Vapour Pressure (Torr) as a Function of Liquid Phase Composition in the Benzene(2)-Dimethyl Sulfoxide(3) System at 25 and 40°C

x_2	P_{25}^{Ex}	P_{40}^{Ex}	P_{25}^C $\alpha_{23} = 0.5726$	P_{40}^C $\alpha_{23} = 0.6418$
0.090	24.5	44.3	23.96	44.03
0.168	38.1	70.3	38.46	70.59
0.248	49.0	91.4	49.60	91.37
0.336	58.3	108.6	58.81	109.00
0.433	66.2	124.1	66.39	124.01
0.517	71.1	134.0	71.43	134.35
0.621	76.5	144.4	76.36	144.78
0.695	80.5	151.7	79.34	151.19
0.773	83.4	158.4	82.33	157.58
0.862	87.9	166.8	86.11	165.33
0.935	90.1	172.0	90.11	173.18

TABLE IV

Total Vapour Pressure (Torr) as a Function of Liquid Phase Composition in the Toluene(2)-Aniline(3) System at 40°C

x_2	P^{Ex}	P^C $\alpha_{23} = 0.7831$
0.083	14.0	13.91
0.169	22.3	22.48
0.245	28.5	28.19
0.326	33.3	33.06
0.413	37.2	37.36
0.501	40.6	41.04
0.516	44.3	44.53
0.684	47.1	47.47
0.764	50.9	50.06
0.842	53.5	52.76
0.920	57.0	55.57

pendent. Despite of this fact the agreement between the experimental and calculated multicomponent data was found good in a majority of the papers dealing with the subject.

The series of papers initiated by this paper will be devoted to the calculation of the ternary liquid equilibrium data from the binary data for some hydrocarbon-hydrocarbon-solvent systems. This paper presents the isothermal dependences of the total vapour pressure of the system on the liquid phase composition and the NRTL parameters computed from these data for systems of perfectly miscible components in the whole concentration range.

EXPERIMENTAL

The data on the following systems were taken over from the literature: Benzene-n-heptane^{22,23}, $t = 45^\circ\text{C}$; 1-hexene-benzene²⁴, $t = 25^\circ\text{C}$; benzene-acetonitrile^{22,23}, $t = 45^\circ\text{C}$; n-heptane-toluene, $t = 40^\circ\text{C}$, and toluene-dimethylformamide¹⁷, $t = 40^\circ\text{C}$.

The data on the following systems were obtained experimentally: Benzene-n-heptane, $t = 40^\circ\text{C}$ and 75°C ; acetonitrile-toluene, $t = 40^\circ\text{C}$; benzene-dimethyl sulfoxide, $t = 25$ and 40°C , and toluene-aniline, $t = 40^\circ\text{C}$. The isothermal $P - x$ diagrams of the last four systems were measured by the modified static method²⁸. The obtained results are summarized in Tables I through IV.

TABLE V
Pure Component Vapour Pressure

Component	Temperature $^\circ\text{C}$	Vapour pressure Torr	Ref.
Benzene	25	95.1	24
	40	182.8 ^a	16
	45	223.4	27
	75	647.3 ^a	16
n-Heptane	40	92.1	17
	45	114.2	27
	75	361.3 ^a	16
1-Hexene	25	185.0	24
Toluene	40	59.2	25
Acetonitrile	40	169.5	27
	45	208.85	
Aniline	40	2.1	this work
Dimethylformamide	40	9.75	17
Dimethyl sulfoxide	25	0.6	26
	40	1.7	26

^a Interpolated according to Antoine.

TABLE VI
The NRTL Parameters of the Systems Examined

System $i - j$	Number of searched parameters	α_{ij}	C_{ij}	C_{ji}	Mean absolute deviation of pressure Torr	Mean relative deviation of pressure %
Benzene(2)-n-heptane(1)						
40°C	2	0.2	773.39	-347.12	0.45	0.31
45°C	2	0.2	961.95	-471.24	0.57	0.29
75°C	2	0.2	812.90	-437.17	1.22	0.24
n-Heptane(1)-toluene(2)						
40°C	2	0.2	-491.20	937.89	0.67	0.86
1-Hexene(1)-benzene(2)						
25°C	2	0.2	-300.16	617.02	0.28	0.19
Acetonitrile(3)-toluene(2)						
40°C	2	0.2	442.36	403.58	1.19	0.84
	3	0.4490	447.31	472.73	0.96	0.66
Benzene(2)-acetonitrile(3)						
45°C	2	0.2	331.07	343.00	1.12	0.45
	3	0.8904	458.10	460.88	0.52	0.21
Toluene(2)-dimethylformamide(3)						
40°C	2	0.2	1 075.37	-385.24	0.27	0.86
	2	0.3	843.99	-184.29	0.35	1.00
	2	0.4	726.11	-75.86	0.27	0.86
Benzene(2)-dimethyl sulfoxide(3)						
25°C	2	0.2	962.95	-19.37	1.13	1.80
	2	0.3	829.92	135.58	1.06	1.70
	3	0.5726	792.11	340.27	0.61	0.99
40°C	2	0.2	970.21	-39.43	1.46	1.21
	2	0.3	827.88	118.99	1.37	1.14
	3	0.6418	787.56	360.32	0.53	0.40
Toluene(2)-aniline(3)						
40°C	2	0.2	592.18	144.48	0.58	1.37
	2	0.3	534.03	223.48	0.59	1.41
	3	0.7831	575.12	397.50	0.46	1.07
n-Heptane(1)-cyclohexane(2)						
	Parameters taken from Renon and coworkers ⁹					

The vapour pressures of pure components used in the processing of the experimental data are given in Table V. The critical properties of pure components were taken from Reid and Sherwood³⁰ and Renon and coworkers⁹ or calculated using the Lydersen's method.

Experimental Data Processing

Thermodynamic equilibrium was expressed by means of the following equation

$$P_i^0 x_i \gamma_i = P y_i \Phi_i, \quad i = 1, 2; \quad (3)$$

where the correction accounting for the real behaviour of the vapour phase, Φ_i , was computed, with regard to low pressures, according to Chidabaram and Narsimhan³¹. The parameters of Eqs (1) and (2) were evaluated from experimental data using the method published by Renon and coworkers⁹. The minimizing function of the least-square method takes the form

$$Q = \sum_{j=1}^N \varrho_j (P_j^C - P_j^{\text{Ex}})^2, \quad (4)$$

where J designates the J -th experimental point; N the number of experimental points; ϱ_j the statistical weight of the J -th experimental value of the total pressure P_j^{Ex} ; $\varrho_j = (100/P_j^{\text{Ex}})^2$, P_j^C stands for the total pressure computed from the condition (3) using Eqs (1) and (2). The above method was used to evaluate either all three NRTL parameters or only the parameters C_{ij} with α_{ij} selected in advance according to the recommendation of Renon¹⁴. Table VI, summarizing the calculated parameters, indicates the appropriate method in the column headed "Number of searched parameters". In addition, the table shows the average absolute and relative deviations of the measured pressure P^{Ex} from the value calculated using the NRTL parameters. Table I through IV indicate, in addition to the values of the total pressure, also the values calculated with those sets of the NRTL parameters representing best the experimental data.

LIST OF SYMBOLS

- g_{ji} free energy of interaction of molecules of the j -th and i -th component
- n number of components in the system
- x_i mole fraction of component i in liquid phase
- y_j mole fraction of component i in vapour phase
- $C_{ji} = (g_{ji} - g_{ii})$ parameter of NRTL equation (1), (2)
- N number of experiments
- P, P^{Ex}, P^C total vapour pressure, experimental, computed
- P_i^0 pure component vapour pressure
- R gas constant
- T absolute temperature

$\alpha_{ji} = \alpha_{ij}$ parameter of NRTL equation (1), (2) in system with components i and j

q_j statistical weight

$\tau_{ji} = C_{ji}/RT$ parameter in Eqs (1) and (2)

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