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Articles

Vapor−Liquid Equilibria of Binary Systems Comprising 1-Chloro-2-ethylhexane and 2-Ethyl-1-hexanol

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Vapor−liquid equilibria of four binary systems comprising *N*,*N*-dimethylformamide or toluene + 1-chloro-2-ethylhexane or + 2-ethyl-1-hexanol were measured at a pressure of 79.99 kPa. The corresponding sets of binary equilibrium data were fitted using the NRTL, Redlich−Kister, UNIQUAC, and Wilson models. Binary parameters of the chosen excess molar Gibbs energy models were calculated on the basis of the maximum likelihood procedure assuming ideal behavior of the vapor phase. Consistency of the measured data sets was tested showing good to excellent quality of experimental data.

Introduction

2-Ethyl-1-hexanol is a fatty alcohol used in the production of esters. Besides its principal use, production of bis(2-ethylhexyl) phthalate, other esters of this alcohol find application in the pharmaceutical industry and cosmetics, due to their emollient properties. Similarly, 1-chloro-2-ethylhexane is used in cosmetics as a UV-adsorbing component.

This study is intended to supply basic data necessary for simulation of separation of these compounds from mixtures containing industrial solvents. For this purpose, vapor−liquid (V−L) equilibria of *N*,*N*-dimethylformamide and toluene with 1-chloro-2-ethylhexane and 2-ethyl-1-hexanol were measured at a pressure of 79.99 kPa. To our knowledge, V−L equilibrium data of the chosen binary mixtures are absent in the literature.

Experimental

2-Ethyl-1-hexanol of chromatographic purity (99.6 %) was purchased from Aldrich. 1-Chloro-2-ethylhexane was supplied by CIBA Spezialitätenchemie AG. Its purity estimated by gas chromatography was 96.3 %. *N*,*N*-Dimethylformamide was obtained from Riedel de Haën and was guaranteed at 99.9 % purity. Toluene (analytical grade, Lachema Neratovice, Czech Republic) was redistilled at atmospheric pressure using a column with 20 theoretical plates. Its chromatographic purity was 99.6 %. All chemicals were stored over molecular sieves to avoid a possible contamination with atmospheric moisture. The properties of compounds are listed in Table 1.

Isobaric vapor−liquid equilibrium data sets for four binary systems, *N*,*N*-dimethylformamide + 1-chloro-2-ethylhexane, *N*,*N*-dimethylformamide + 2-ethyl-1-hexanol, toluene + 1-chloro-2-ethylhexane, and toluene + 2-ethyl-1-hexanol, were obtained by the circulation method in a modified Gillespie still described elsewhere.[5] Temperature was measured within an uncertainty of ± 0.05 K by a resistance thermometer. The pressure inside the measuring still was kept constant with an uncertainty of ± 13 Pa. The analyses of the liquid and vapor phase compositions were carried out chromatographically with an uncertainty of the component mole fractions ± 0.5 % and better.

The sets of *t*, *x*, *y* equilibrium data obtained for the four binary systems are given in Tables 2> and 3.

Results and Discussion

V−L equilibrium data of the studied binary systems were correlated using the NRTL, Redlich−Kister, UNIQUAC, and Wilson equations. In all cases, the model parameters were calculated using the maximum likelihood principle.[6] The objective function used adopted the form

$$F=\sum_{n}\left[(x_1-x_{\text{calc},1})^2+(y_1-y_{\text{calc},1})^2+\left(\frac{P-P_{\text{calc}}}{P}\right)^2\right]_n \quad (1)$$

where (y_1 and $y_{\text{calc},1}$) and (x_1 and $x_{\text{calc},1}$) represent measured and calculated mole fractions of component 1 in the vapor and liquid phase, respectively. The objective function (eq 1) was minimized in two independent iteration cycles.[7] By this procedure, the optimum parameters of the excess molar Gibbs energy equations and independent variables $x_{\text{cald},1}$ were obtained.

Mole fraction of component 1 in the vapor phase, $y_{\text{calc},1}$, and total pressure P_{calc} were calculated using the following relationships

$$y_{\text{calc},1}=\frac{x_{\text{calc},1}\gamma_1P_1^*}{(x_{\text{calc},1}\gamma_1P_1^*+x_{\text{calc},2}\gamma_2P_2^*)} \quad (2)$$

$$P_{\text{calc}}=\gamma_1x_1P_1^*+\gamma_2x_2P_2^* \quad (3)$$

where γ_i represents the value of the *i*th component activity coefficient. Saturated vapor pressures P^* of pure components at experimental temperatures were computed by the Antoine equation (Table 1).

Calculated values of the G^E parameters for the NRTL, Redlich−Kister, UNIQUAC, and Wilson equations are given in Table 4. For the NRTL model also the values of mean deviations in mole fractions of the liquid and vapor phases (d_x, d_y) and those of mean deviations in temperature (d_t) are

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Table 1. Properties of Pure Components

property		*N*,*N*-dimethylformamide	toluene	1-chloro-2-ethylhexane	2-ethyl-1-hexanol
M/(kg·kmol^{-1})		73.095	92.142	148.7	130.23
$t_{\mathrm{bp,calc}}$/°C (79.99 kPa)		142.77	102.51	163.02	176.08
Antoine equation[a]	A	5.37646	6.07954	6.09610[b]	6.01380
	B	1049.260	1344.800	1516.671[b]	1325.880
	C	159.310	219.482	198.685[b]	146.460
	reference	Dykyj and Repáš[1]	Riddick and Bunger[2]	Reid et al.[3]	Riddick and Bunger[2]
ρ^{20}/(kg·m^{-3})		948.7	867.0	791.8	833.2
n_D^{20}	Riddick and Bunger[2]	1.43047	1.49693	1.432−1.436[c]	1.42305
	experimental	1.4307	1.4961	1.4326	1.4310
UNIQUAC parameters	r	3.0855	3.9228	6.4121	6.6211
	q	2.7360	2.9679	5.3480	5.8240

[a] $\log(P^*/\mathrm{kPa}) = A - B/(C + t/°\mathrm{C})$. [b] Predicted from the pure component properties. [c] Ref 4.

Table 2. Vapor−Liquid Equilibrium Data of the Systems Containing *N*,*N*-Dimethylformamide at 79.99 kPa

x_1	y_1	t/°C	x_1	y_1	t/°C
N,*N*-Dimethylformamide (1) + 1-Chloro-2-ethylhexane (2)			*N*,*N*-Dimethylformamide (1) + 2-Ethyl-1-hexanol (2)		
0.0801	0.1173	159.10	0.1120	0.2004	171.60
0.1150	0.1963	156.40	0.2189	0.3363	168.95
0.1814	0.3474	150.85	0.3108	0.4480	165.90
0.2272	0.4175	147.90	0.3695	0.5259	163.60
0.2823	0.4774	145.85	0.4935	0.6988	157.70
0.4349	0.5908	142.40	0.6180	0.8186	153.00
0.5895	0.6761	140.75	0.7464	0.9016	148.80
0.6844	0.7173	140.25	0.8963	0.9610	145.05
0.9108	0.8807	140.80	-	-	-
0.9608	0.9308	141.70	-	-	-
0.9879	0.9754	142.40	-	-	-

Table 3. Vapor−Liquid Equilibrium Data of the Systems Containing Toluene at 79.99 kPa

x_1	y_1	t/°C	x_1	y_1	t/°C
Toluene (1) + 1-Chloro-2-ethylhexane (2)			Toluene (1) + 2-Ethyl-1-hexanol (2)		
0.0412	0.2162	154.50	0.0269	0.1436	169.45
0.1199	0.3836	148.10	0.0487	0.3021	164.00
0.1849	0.5040	143.25	0.1027	0.5236	154.00
0.2595	0.6388	136.55	0.1726	0.6847	144.25
0.2970	0.6869	133.55	0.2781	0.8116	133.05
0.4368	0.8046	125.20	0.3697	0.8721	125.75
0.4905	0.8453	121.25	0.5588	0.9350	115.05
0.6012	0.8865	115.20	0.6834	0.9601	111.50
0.7918	0.9629	107.90	0.8473	0.9827	105.75

presented. Similar values of these statistical parameters were obtained also for the fit of experimental data by the remaining G^E models. Table 5 summarizes the composition and temperature data of the azeotrope observed in the mixture of *N*,*N*-dimethylformamide + 1-chloro-2-ethylhexane calculated employing the above-mentioned model equations. The fit (by the NRTL equation) of experimental equilibrium data for the chosen systems at the pressure of 79.99 kPa is presented in Figures 1 to 4.

Table 5. Parameters of the *N*,*N*-Dimethylformamide (1) + 1-Chloro-2-ethylhexane (2) Azeotropic Point Calculated by the Chosen G^E Equations at 79.99 kPa

G^E equation	x_1	t/°C
NRTL	0.7799	140.42
Redlich−Kister	0.7900	140.31
UNIQUAC	0.7774	140.40
Wilson	0.7813	140.38

Consistency of the experimental data sets was tested according to Herington[8] (Redlich and Kister[9]). The results obtained employing the NRTL model equation are presented in Figure 5 and show that the sets of measured VLE data fulfill the requirements of the area test. Furthermore, the direct test of thermodynamic consistency[10] for the four studied binary systems was carried out. The proposed measure of the experimental data consistency corresponds to the residue mean square (rms) value of $\delta\ \ln(\gamma_1/\gamma_2)$, i.e., the differences between the logarithms of the activity coefficient ratio calculated by the model equation and directly from the experimental data. The worst consistency was observed in the case of the binary system *N*,*N*-dimethylformamide + 1-chloro-2-ethylhexane with the rms value of 0.137. According to Van Ness,[10] the respective consistency index (CI) of the experimental data set is equal to 6, i.e., medium

Table 4. Parameters of G^E Equations for the Binary Systems Containing *N*,*N*-Dimethylformamide (DMF), Toluene (T), 1-Chloro-2-ethylhexane (EHCl), and 2-Ethyl-1-hexanol (EHOH) Evaluated from Isobaric Vapor−Liquid Equilibrium Data (P = 79.99 kPa)

G^E equation	parameter	DMF (1) + EHCl (2)	DMF (1) + EHOH (2)	T (1) + EHCl (2)	T (1) + EHOH (2)
NRTL	$(g_{12} - g_{22})$/(J·mol^{-1})	2824.66	5415.43	−2242.13	5396.93
	$(g_{21} - g_{11})$/(J·mol^{-1})	1451.94	−3827.92	2959.05	−2507.30
	α_{ij}	0.45	0.30	0.20	0.20
	d_x	0.0172	0.0148	0.0124	0.0069
	d_y	0.0164	0.0133	0.0111	0.0141
	d_t/°C	0.24	0.26	0.35	0.37
Redlich−Kister	B_{ij}	1.03774	−0.10665	0.06504	0.54468
	C_{ij}	0.09935	0.01092	0.02251	0.13035
	D_{ij}	0.11103	0.46875	0.40497	0.25086
UNIQUAC	$(u_{12} - u_{22})$/(J·mol^{-1})	−712.19	2125.57	2137.22	−258.32
	$(u_{21} - u_{11})$/(J·mol^{-1})	2243.81	−1435.53	−1523.42	679.34
Wilson	$(\lambda_{12} - \lambda_{11})$/(J·mol^{-1})	4554.81	−817.64	−2362.23	641.10
	$(\lambda_{21} - \lambda_{22})$/(J·mol^{-1})	−178.54	3877.15	10227.90	2017.84

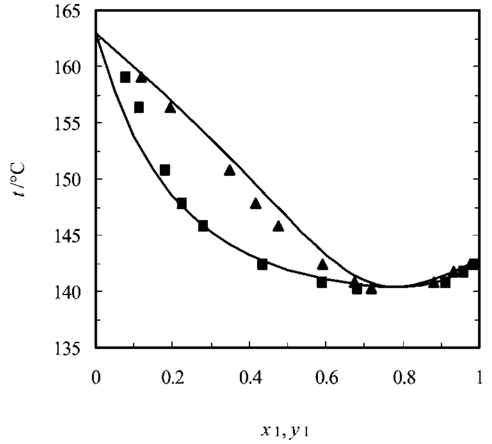

Figure 1. Experimental (■, x_1; ▲, y_1) and calculated by the NRTL (solid line) vapor−liquid equilibrium data of the *N*,*N*-dimethylformamide (1) + 1-chloro-2-ethylhexane (2) system at 79.99 kPa.

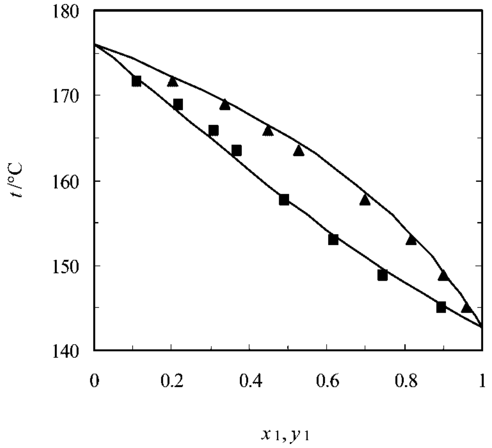

Figure 2. Experimental (■, x_1; ▲, y_1) and calculated by the NRTL (solid line) vapor−liquid equilibrium data of the *N*,*N*-dimethylformamide (1) + 2-ethyl-1-hexanol (2) system at 79.99 kPa.

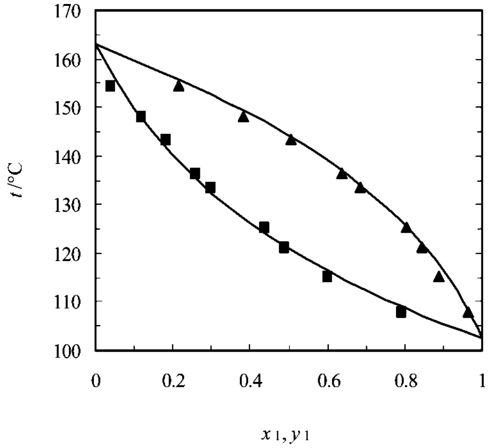

Figure 3. Experimental (■, x_1; ▲, y_1) and calculated by the NRTL (solid line) vapor−liquid equilibrium data of the toluene (1) + 1-chloro-2-ethylhexane (2) system at 79.99 kPa.

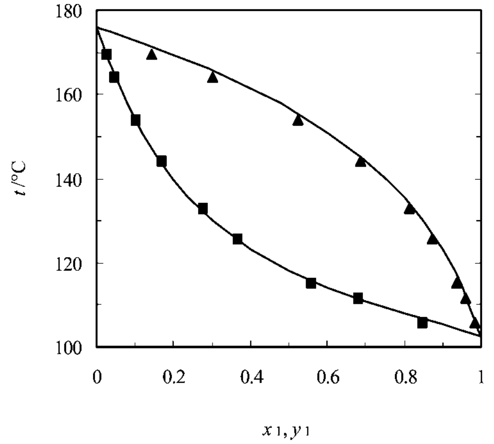

Figure 4. Experimental (■, x_1; ▲, y_1) and calculated by the NRTL (solid line) vapor−liquid equilibrium data of the toluene (1) + 2-ethyl-1-hexanol (2) system at 79.99 kPa.

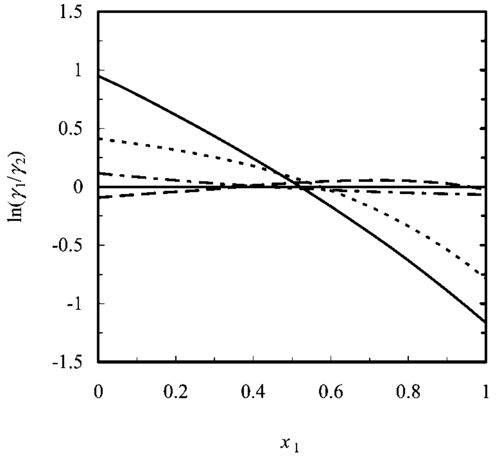

Figure 5. Area plot for the binary systems *N*,*N*-dimethylformamide (1) + 1-chloro-2-ethylhexane (2) (solid line), *N*,*N*-dimethylformamide (1) + 2-ethyl-1-hexanol (2) (dashed line), toluene (1) + 1-chloro-2-ethylhexane (2) (dotted line), and toluene (1) + 2-ethyl-1-hexanol (2) (dotted-dashed line) at 79.99 kPa.

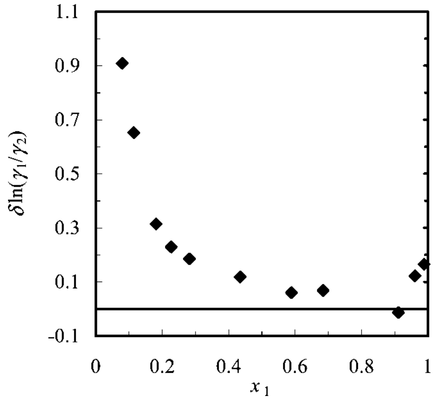

Figure 6. Direct test of thermodynamic consistency[10] of VLE data applied to the binary system *N*,*N*-dimethylformamide (1) + 1-chloro-2-ethylhexane (2) at 79.99 kPa Binary equilibria were modeled using the NRTL equation.

quality data. However, Figure 6 shows that the first two experimental points of this data set are seriously deviated. Omitting these two points, the consistency index would drop to CI = 2 (rms = 0.028), which is very good to excellent consistency. Relatively good consistency was attributed to the binary system toluene + 2-ethyl-1-hexanol (rms = 0.087, CI = 4), while for the systems *N*,*N*-dimethylformamide + 2-ethyl-1-hexanol and toluene + 1-chloro-2-ethylhexane, the consistency was excellent with rms values of 0.026 (CI = 2) and 0.019 (CI = 1), respectively.

Conclusions

Sets of experimental VLE data were obtained for the binary systems composed of *N*,*N*-dimethylformamide/toluene with

1-chloro-2-ethylhexane/2-ethyl-1-hexanol. Formation of a minimum boiling temperature azeotrope was observed in the case of the *N*,*N*-dimethylformamide + 1-chloro-2-ethylhexane binary system. Consistency of experimental data was proved on the basis of the area test as well as the direct test of thermodynamic consistency. According to the later test, while omitting the most deviated points, the quality of measured data was classified from good to excellent.

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