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# Phase Equilibria of Binary Systems Comprising Formic Acid, *N*,*N*-Dimethylformamide, 1-Chloro-2-ethylhexane, and 2-Ethyl-1-hexanol

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Isobaric vapor−liquid equilibria of binary systems formed by formic acid + *N*,*N*-dimethylformamide or + 2-ethyl-1-hexanol as well as *N*,*N*-dimethylformamide + 1-chloro-2-ethylhexane were estimated at a pressure of 10.00 kPa. Mutual solubilities of formic acid + 1-chloro-2-ethylhexane were determined within the temperature range of (20 to 80) °C. The binary equilibrium data were fitted to the Redlich−Kister, Wilson, and NRTL equations employing the maximum likelihood procedure. Binary parameters of the chosen excess molar Gibbs energy models were calculated assuming ideal behavior of the vapor phase. A comparison of the goodness of fit of the selected $G^E$ models is presented.

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## Introduction

In the literature, relatively scarce information is presented about the phase equilibria of systems containing formic acid. Moreover, dimerization of formic acid could be a serious complication in assessing its binary equilibria with polar compounds.

In this study, VLE and also LLE of formic acid with selected compounds, namely, *N*,*N*-dimethylformamide, 1-chloro-2-ethylhexane, and 2-ethyl-1-hexanol, are presented. Isobaric vapor−liquid equilibria of the binaries formic acid + *N*,*N*-dimethylformamide, formic acid + 2-ethyl-1-hexanol, and *N*,*N*-dimethylformamide + 1-chloro-2-ethylhexane were measured at 10.00 kPa, while the LLE of the system formic acid + 1-chloro-2-ethylhexane was estimated on the basis of the components mutual miscibility at various temperatures.

## Experimental

Formic acid and 2-ethyl-1-hexanol were supplied by Aldrich with declared purity of (95 to 97) % and 99.6 %, respectively. *N*,*N*-Dimethylformamide was purchased from Riedel de Haën and was guaranteed at 99.9 % purity. 1-Chloro-2-ethylhexane was supplied by CIBA Spezialitätenchemie AG. Its purity was 96.3 %. Prior to their use, all chemicals were stored with added molecular sieves in order to avoid a possible contamination with atmospheric moisture. The properties of the compounds are listed in Table 1.

Isobaric (10.00 kPa) vapor−liquid equilibrium data of the binary systems formic acid + *N*,*N*-dimethylformamide and formic acid + 2-ethyl-1-hexanol were determined by a static method in a modified apparatus.[5,6] The liquid samples were weighted on an analytical balance with an uncertainty of ± $5 \cdot 10^{-4}$ g (which corresponds to a mass fraction of 0.0002). The pressure was measured by a precise U-manometer with an uncertainty of ± 13 Pa, and the temperature of the tempering jacket was maintained constant (± 0.05 K). During both the sample preparation by degassing and the measurement of saturated vapor pressure, molecular sieves were applied to remove traces of moisture. Each experimental point was estimated by interpolation from at least five experimental pressure−temperature points measured in a close vicinity to the required pressure.

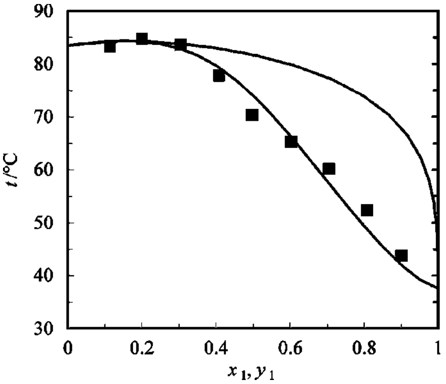

**Figure 1.** Experimental (squares) and calculated by the NRTL (solid line) vapor−liquid equilibrium data of the system formic acid (1) + *N*,*N*-dimethylformamide (2) at 10.00 kPa.

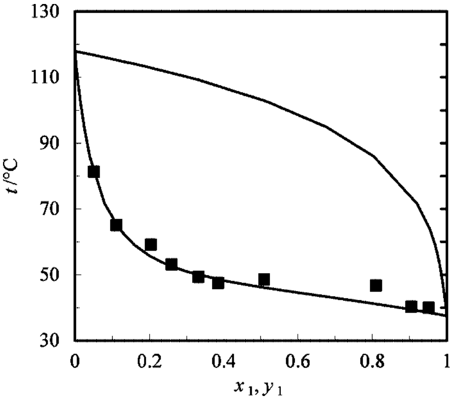

**Figure 2.** Experimental (squares) and calculated by the NRTL (solid line) vapor−liquid equilibrium data of the system formic acid (1) + 2-ethyl-1-hexanol (2) at 10.00 kPa.

The sets of *t*, *x* equilibrium data obtained for the binary systems formic acid + *N*,*N*-dimethylformamide and formic acid + 2-ethyl-1-hexanol are summarized in Table 2.

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**Table 1. Properties of Pure Components**

| properties | | formic acid | *N*,*N*-dimethylformamide | 1-chloro-2-ethylhexane | 2-ethyl-1-hexanol |
|---|---|---|---|---|---|
| $M$/(kg·kmol$^{-1}$) | | 46.026 | 73.095 | 148.7 | 130.23 |
| $t_{\mathrm{b,calcd}}$/°C (10.00 kPa) | | 37.50 | 83.45 | 98.93 | 117.98 |
| Antoine equation, $P^*$/kPa | $A$ | 6.06949 | 6.23340 | 6.09610[a] | 6.01380 |
| | $B$ | 1295.260 | 1537.780 | 1516.671[a] | 1325.880 |
| | $C$ | 218.000 | 210.390 | 198.685[a] | 146.460 |
| | | Gmehling and Onken[1] | Riddick and Bunger[2] | Reid et al.[3] | Riddick and Bunger[2] |
| $\rho^{20}$/(kg·m$^{-3}$) | reference | 1214.05[b] | 948.7 | 791.8 | 833.2 |
| $n_{\mathrm{D}}^{20}$ | ref 2 | 1.37140 | 1.43047 | 1.432−1.436[c] | 1.42305 |
| | experimental | 1.3720 | 1.4307 | 1.4326 | 1.4310 |

[a] Predicted from the pure component properties. [b] At 25 °C. [c] Ref 4.

**Table 2. Vapor−Liquid Equilibrium Data of the Systems Including Formic Acid at 10.00 kPa**

| $x_1$ | $t$/°C | $x_1$ | $t$/°C |
|---|---|---|---|
| formic acid (1) + *N*,*N*-dimethylformamide (2) | | formic acid (1) 2-ethyl-1-hexanol (2) | |
| 0.1136 | 83.35 | 0.0514 | 81.30 |
| 0.2005 | 84.75 | 0.1122 | 65.05 |
| 0.3028 | 83.65 | 0.2038 | 59.15 |
| 0.4069 | 77.85 | 0.2603 | 53.10 |
| 0.4973 | 70.40 | 0.3322 | 49.35 |
| 0.6022 | 65.35 | 0.3846 | 47.50 |
| 0.7038 | 60.20 | 0.5093 | 48.60 |
| 0.8071 | 52.40 | 0.8097 | 46.70 |
| 0.9001 | 43.80 | 0.9046 | 40.25 |
| – | – | 0.9512 | 40.00 |

**Table 3. Vapor−Liquid Equilibrium Data of the System *N*,*N*-Dimethylformamide (1) + 1-Chloro-2-ethylhexane (2) at 10.00 kPa**

| $x_1$ | $y_1$ | $t$/°C |
|---|---|---|
| *N*,*N*-dimethylformamide (1) + 1-chloro-2-ethylhexane (2) | | |
| 0.0914 | 0.3297 | 92.00 |
| 0.1686 | 0.4878 | 87.95 |
| 0.2721 | 0.5966 | 85.35 |
| 0.3813 | 0.6445 | 83.30 |
| 0.7758 | 0.7694 | 80.80 |
| 0.9039 | 0.8485 | 81.50 |
| 0.9445 | 0.8968 | 82.45 |

**Table 4. Solubility Data for the System Formic Acid (1) + 1-Chloro-2-ethylhexane (2)**

| 1-chloro-2-ethylhexane-rich phase | | formic acid-rich phase | |
|---|---|---|---|
| $x_1$ | $t$/°C | $x_1$ | $t$/°C |
| formic acid (1) + 1-chloro-2-ethylhexane (2) | | | |
| 0.0184 | 39.65 | 0.9970 | 19.80 |
| 0.0251 | 55.05 | 0.9956 | 40.30 |
| 0.0388 | 64.70 | 0.9937 | 60.20 |
| 0.0557 | 77.10 | 0.9928 | 69.30 |
| 0.0622 | 68.20 | 0.9922 | 73.60 |
| – | – | 0.9915 | 78.55 |

**Table 5. Parameters of $G^{\mathrm{E}}$ Equations for the Binary Systems Containing Formic Acid (FA), *N*,*N*-Dimethylformamide (DMF), 1-Chloro-2-ethylhexane (EHCl), and 2-Ethyl-1-hexanol (EHOH) Evaluated from Isobaric Vapor−Liquid Equilibrium Data ($P$ = 10.00 kPa)**

| $G^{\mathrm{E}}$ equation | parameter | FA (1) + DMF (2) | FA (1) + EHOH (2) | DMF (1) + EHCl (2) |
|---|---|---|---|---|
| Redlich−Kister | $B_{ij}$ | −2.84831 | 1.13982 | 1.22771 |
| | $C_{ij}$ | −1.09859 | −0.28902 | 0.37273 |
| | $D_{ij}$ | −0.89495 | −0.80014 | −0.09434 |
| | $d_x$ | 0.0224 | 0.0160 | 0.0066 |
| | $d_y$ | – | – | 0.0063 |
| | $d_t$/°C | 0.40 | 0.27 | 0.17 |
| Wilson | $(\lambda_{12} - \lambda_{11})$/(J·mol$^{-1}$) | −3036.89 | 7240.66 | 3444.49 |
| | $(\lambda_{21} - \lambda_{22})$/(J·mol$^{-1}$) | −3356.69 | −2955.04 | 1719.45 |
| | $d_x$ | 0.0198 | 0.0251 | 0.0067 |
| | $d_y$ | – | – | 0.0125 |
| | $d_t$/°C | 0.34 | 0.52 | 0.21 |
| NRTL | $(g_{12} - g_{22})$/(J·mol$^{-1}$) | −776.60 | 1506.80 | 4464.45 |
| | $(g_{21} - g_{11})$/(J·mol$^{-1}$) | −5673.23 | 2518.23 | 478.45 |
| | $\alpha_{ij}$ | 0.400 | 0.500 | 0.400 |
| | $d_x$ | 0.0223 | 0.0222 | 0.0065 |
| | $d_y$ | – | – | 0.0110 |
| | $d_t$/°C | 0.35 | 0.47 | 0.19 |

VLE data at 10.00 kPa for the system *N*,*N*-dimethylformamide + 1-chloro-2-ethylhexane were obtained by a circulation method in a modified Gillespie still.[7] The uncertainties of temperature and pressure readings were ± 0.05 K and ± 13 Pa, respectively. For this purpose, a resistance thermometer and a precise U-manometer were used. The analyses of the liquid and vapor phases were carried out chromatographically after completing the measurement. The uncertainty of the mixture mole fraction determination was ± 0.1 %. Table 3 presents the corresponding equilibrium data.

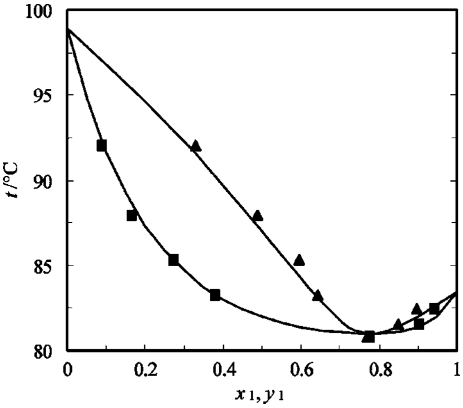

**Figure 3.** Experimental (symbols) and calculated by the NRTL (lines) vapor−liquid equilibrium data of the system *N*,*N*-dimethylformamide (1) + 1-chloro-2-ethylhexane (2) at 10.00 kPa.

The solubilities of the partially miscible system formic acid + 1-chloro-2-ethylhexane were estimated using the cloud-point method. Binary heterogeneous samples of known composition were prepared by weighing the corresponding amounts of components into a glass ampoule accommodated with a magnetic blender. The ampoules were heat-sealed, immersed into a water bath, and heated to the temperature at which one homogeneous liquid phase was formed. Then, the sample was cooled down, and the temperature at which heterogeneous phases appeared was recorded. The samples were weighed on an analytical balance with an uncertainty of ± 5·10$^{-4}$ g, which corresponds to a mass fraction of 0.0002. The temperature of the water bath was determined with an uncertainty of ± 0.1 K.

The solubility of formic acid in 1-chloro-2-ethylhexane (1-chloro-2-ethylhexane-rich region) and the solubility of 1-chloro-2-ethylhexane in formic acid (formic acid-rich region) are shown in Table 4.

**Table 6. Parameters of Azeotropes in the Formic Acid (1) + *N*,*N*-Dimethylformamide (2) and *N*,*N*-Dimethylformamide (1) + 1-Chloro-2-ethylhexane (2) Systems and Heteroazeotrope in the Formic Acid (1) + 1-Chloro-2-ethylhexane (2) System at 10.00 kPa**

| | formic acid (1) + *N*,*N*-dimethylformamide (2) | | *N*,*N*-dimethylformamide (1) + 1-chloro-2-ethylhexane (2) | | formic acid (1) + 1-chloro-2-ethylhexane (2) | | | |
|---|---|---|---|---|---|---|---|---|
| $G^E$ equation | $x_1$ | $t$/°C | $x_1$ | $t$/°C | $x_{11}$ | $x_{21}$ | $y_1$ | $t$/°C |
| Redlich−Kister | 0.1403 | 84.82 | 0.7671 | 81.07 | 0.9959 | 0.0153 | 0.9959 | 36.60 |
| Wilson−Novák | 0.1572 | 84.39 | 0.7838 | 80.98 | 0.9958 | 0.0160 | 0.9559 | 36.61 |
| NRTL | 0.1572 | 84.39 | 0.7772 | 80.95 | 0.9957 | 0.0161 | 0.9560 | 36.61 |

**Table 7. Parameters for Recalculation of Mutual Solubility for the System Formic Acid (1) + 1-Chloro-2-ethylhexane (2) within the Temperature Range of (40 to 80) °C**

| parameter | $B_0$ | $B_1$/°C | $B_2$/°C$^2$ | $\sigma(x)$ |
|---|---|---|---|---|
| 1-chloro-2-ethylhexane-rich phase | $1.5416 \cdot 10^{-2}$ | $-5.09794 \cdot 10^{-4}$ | $1.39330 \cdot 10^{-5}$ | $9.3865 \cdot 10^{-3}$ |
| formic acid-rich phase | $9.9779 \cdot 10^{-1}$ | $-2.72125 \cdot 10^{-5}$ | $-6.64908 \cdot 10^{-7}$ | $6.4990 \cdot 10^{-5}$ |

**Table 8. Temperature-Dependent Parameters of $G^E$ Equations for the Partially Miscible System Formic Acid (1) + 1-Chloro-2-ethylhexane (2) Evaluated from Mutual Solubility Data**

| $G^E$ equation | parameter | value | $\sigma$ |
|---|---|---|---|
| Redlich−Kister | $B_{ij}$ | $0.2383 + 1140.76/(T/\mathrm{K})$ | 0.0179 |
| | $C_{ij}$ | $2.6263 - 630.51/(T/\mathrm{K})$ | 0.0078 |
| | $D_{ij}$ | $-3.2465 + 1336.82/(T/\mathrm{K})$ | 0.0158 |
| Wilson-Novák | $(\lambda_{12} - \lambda_{11})/(\mathrm{J \cdot mol^{-1}})$ | $-3995.37 + 14.052/(T/\mathrm{K})$ | 68.35 |
| | $(\lambda_{21} - \lambda_{22})/(\mathrm{J \cdot mol^{-1}})$ | $21.69 + 0.219/(T/\mathrm{K})$ | 3.15 |
| | $D_{ij}$ | $4.3877 - 0.0094/(T/\mathrm{K})$ | 0.0437 |
| NRTL | $(g_{12} - g_{22})/(\mathrm{J \cdot mol^{-1}})$ | $10305.20 + 2.310/(T/\mathrm{K})$ | 12.04 |
| | $(g_{21} - g_{11})/(\mathrm{J \cdot mol^{-1}})$ | $25471.40 - 56.440/(T/\mathrm{K})$ | 14.97 |
| | $\alpha_{ij}$ | 0.2831 | − |

## Results and Discussion

VLE data of the binary systems were correlated using the Redlich−Kister, Wilson (Wilson−Novák), and NRTL equations. In all cases, the model parameters were calculated using the maximum likelihood principle.[8] Assuming the equilibrium data sets obtained either by the static ($t$, $x$) or circulation ($t$, $x$, $y$) methods, objective functions adopted the respective form (Graczová and Surový[9])

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

with $N$ being the number of experiments for the given binary and $x$ and $y$ being component mole fractions in the liquid and vapor phases, respectively, and $P$ being total pressure.

Temperature was optimized indirectly by optimizing the total pressure, which was computed according to the relation

$$P_{\mathrm{calcd}} = \gamma_1 x_1 P_1^* + \gamma_2 x_2 P_2^* \tag{2}$$

where $\gamma_i$ represents the component activity coefficient. Saturated vapor pressure of the mixture components, $P_i^*$, was calculated by the Antoine equation. With respect to the low saturated vapor pressure of components (1-chloro-2-ethylhexane and 2-ethyl-1-hexanol) and also due to the low total pressure, ideal behavior of the vapor phase was considered.

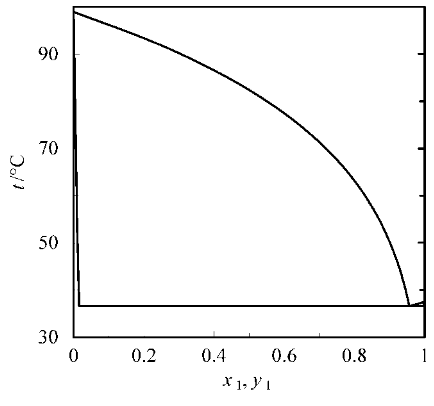

**Figure 4.** Vapor−liquid equilibrium data of the system formic acid (1) + 1-chloro-2-ethylhexane (2) at 10.00 kPa calculated by the NRTL equation.

The calculated values of the $G^E$ equation parameters with the corresponding values of statistical indices (mean deviations of the component mole fraction in the liquid and vapor phases, $d_x$ and $d_y$, and mean deviations in temperature, $d_t$) are given in Table 5. Goodness of fit is shown in Figures 1 to 3 considering the NRTL model equation. Parameters of the azeotropic point of the systems formic acid + *N*,*N*-dimethylformamide and *N*,*N*-dimethylformamide + 1-chloro-2-ethylhexane ($P$ = 10.00 kPa) calculated by $G^E$ equations are shown in Table 6.

Solubility data of the system formic acid (1) + 1-chloro-2-ethylhexane (2) were expressed using the second order polynomial

$$x_{1j} = B_0 + B_1 t/{}^\circ\mathrm{C} + B_2 (t/{}^\circ\mathrm{C})^2 \quad j = 1, 2 \tag{3}$$

where $j$ represents the formic acid- and 1-chloro-2-ethylhexane-rich phase, respectively.

For both conjugated phases, the values of polynomial parameters as well as the respective statistical parameters are given in Table 7. Then, within the chosen temperature range of (40 to 80) °C, the compositions of the 1-chloro-2-ethylhexane-rich and the formic acid-rich phases were recalculated by means of eq 3. These values were used for evaluation of the binary parameters of the corresponding $G^E$ equation parameters according to the isoactivity principle using the procedure described by Graczová et al.[10] The results of evaluation of Redlich−Kister,

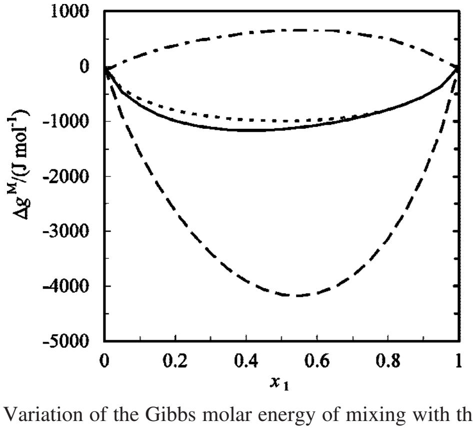

**Figure 5.** Variation of the Gibbs molar energy of mixing with the mixture composition calculated by the NRTL model equation for the systems formic acid (1) + *N*,*N*-dimethylformamide (2) (dashed line), formic acid (1) + 2-ethyl-1-hexanol (2) (dotted line), *N*,*N*-dimethylformamide (1) + 1-chloro-2-ethylhexane (2) (solid line), and formic acid (1) + 1-chloro-2-ethylhexane (2) (dotted-dashed line) at 10.00 kPa.

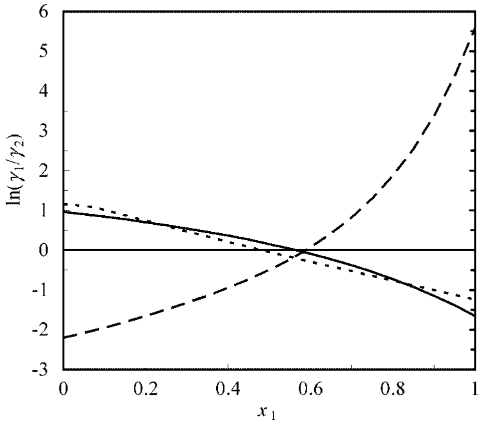

**Figure 6.** Area plot for the binary systems formic acid (1) + *N*,*N*-dimethylformamide (2) (dashed line), formic acid (1) + 2-ethyl-1-hexanol (2) (dotted line), and *N*,*N*-dimethylformamide (1) + 1-chloro-2-ethylhexane (2) (solid line).

Wilson−Novák, and NRTL equation parameters are presented with the respective statistical indices in Table 8. Isobaric VLE data of the system formic acid + 1-chloro-2-ethylhexane calculated by the NRTL equation are depicted in Figure 4. Composition of conjugated phases and the temperature at which the heteroazeotrope is predicted at 10.00 kPa by the chosen excess molar Gibbs energy equations are given in Table 6.

Variation of the Gibbs molar energy of mixing with the mixture composition calculated on the basis of the NRTL model parameters for the four measured binary systems is given in Figure 5. The Gibbs molar energy of mixing was calculated according to the following equation

$$\Delta g^{\mathrm{M}} = RT\sum_{i=1}^{2} x_i \ln(\gamma_i x_i) \qquad (4)$$

Consistency of the measured data was tested according to Herington[11] (Redlich and Kister[12]). Figure 6 presents the results obtained employing the NRTL model equation. It is obvious that the three sets of measured VLE data fulfill requirements of the area test. Moreover, the direct test of thermodynamic consistency proposed by Van Ness[13] was applied to check the consistency of the experimental data for the binary system *N*,*N*-dimethylformamide + 1-chloro-2-ethylhexane. The value of 0.0194 was found for the corresponding residue mean square (rms) of differences between the logarithms of the activity coefficient ratios calculated by the model equation and those obtained from a complete set of experimental data (*t*, *x*, *y*). The differences for rms calculation were obtained from the following equation

$$\delta \ln(\gamma_1/\gamma_2) = \ln(\gamma_1/\gamma_2) - \ln(\gamma_1^*/\gamma_2^*) \qquad (5)$$

where the asterisk denotes the values calculated directly from the measured data.

For all binary systems containing formic acid, an anomalous behavior was observed. In the case of miscible binary systems, i.e., formic acid + *N*,*N*-dimethylformamide and formic acid + 2-ethyl-1-hexanol, hysteresis was observed during the measurement of *t*, *x* equilibrium data. This behavior was complicating the setting up of the experimental conditions (required pressure) inside the measuring still. Looking at the system composed of partially miscible liquids, formic acid + 1-chloro-2-ethylhexane, almost instantaneous phase segregation was observed without turbidity occurrence even if the system was cooled very slowly.

## Conclusions

Sets of experimental VLE and LLE data were obtained for the binary systems containing formic acid, *N*,*N*-dimethylformamide, 1-chloro-2-ethylhexane, and 2-ethyl-1-hexanol. The presence of formic acid caused a complex behavior of the respective binary mixtures. Therefore, it is to be expected that similar problems would arise when working with multicomponent mixtures containing this component.

Area tests showed that the measured data are thermodynamically consistent. Moreover, the direct test of thermodynamic consistency was applied to the complete (*t*, *x*, *y*) set of experimental VLE data obtained by the circulation method for the system *N*,*N*-dimethylformamide + 1-chloro-2-ethylhexane. The results of this test correspond to the consistency index CI = 1 (rms < 0.025), i.e., a very good consistency.

## Literature Cited

(1) Gmehling, J.; Onken, U. *Vapor−Liquid Equilibrium Data Collection*, Part 1; DECHEMA: Frankfurt/Main, Germany, 1977; Vol. I.

(2) Riddick, J. A.; Bunger, W. B. *Organic Solvents. Physical Properties and Methods of Purification*; Wiley: New York, 1970.

(3) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*; McGraw-Hill: New York, 1988.

(4) ChemBlink. Online database of chemicals from China and around the World. Retrieved on April 11, 2008 from http://www.chemblink.com/products/123-04-6.htm.

(5) Surový, J.; Graczová, E.; Bafrncová, S. Modified apparatus for measuring V-L equilibria by static method. *Collect. Czech. Chem. Commun.* **1994**, *59*, 1729–1737.

(6) Surový, J.; Dojčanský, J. Dependence of the vapour pressure and activity coefficients on the composition of some two-component polar solvents. *Chem. Pap.* **1974**, *28*, 313–323.

(7) Graczová, E.; Huňarová, T.; Surový, J. A modified Gillespie still for measuring vapor-liquid equilibria. *Collect. Czech. Chem. Commun.* **1987**, *52*, 258–263.

(8) Rod, V.; Hančil, V. Iterative estimation of model parameters when measurements of all variables are subject to error. *Comput. Chem. Eng.* **1980**, *4*, 33–38.

(9) Graczová, E.; Surový, J. Isothermal vapour-liquid equilibrium data for the system toluene-*N*-methylpyrrolidone at 40 °C, 50 °C, and 60 °C. *Chem. Pap.* **1999**, *53*, 428–430.

(10) Graczová, E.; Surový, J.; Kozma, J.; Ovečková, J. Isobaric binary equilibrium data for the system water-benzthiazole at 101.3 kPa. *Chem. Pap.* **1993**, *47*, 75–78.

(11) Herington, E. F. G. A thermodynamic test for the internal consistency of experimental data of volatility ratios. *Nature* **1947**, *160*, 610–611.

(12) Redlich, O.; Kister, A. T. Algebraic representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.* **1948**, *40*, 345–348.

(13) Van Ness, H. C. Thermodynamics in the treatment of vapor/liquid equilibrium (VLE) data. *Pure Appl. Chem.* **1995**, *67*, 859–872.

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