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Isothermal Vapor−Liquid Equilibria for Nitromethane and Nitroethane + 1,3-Dichloropropane Binary Systems at Temperatures between (343.15 and 363.15) K

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ABSTRACT: Isothermal vapor−liquid equilibrium (VLE) data are reported at three temperatures, (343.15, 353.15, and 363.15) K, for the binary mixtures containing nitromethane or nitroethane with 1,3-dichloropropane. For the measurements an all-glass ebulliometer was used, which allows sampling from both phases in equilibrium. The experimental data were correlated using the nonrandom two-liquid (NRTL) and universal quasichemical activity coefficient (UNIQUAC) excess Gibbs energy models by means of maximum likelihood method, taking into account the vapor phase imperfection in terms of the second virial coefficients. Both systems are azeotropic and show positive deviations from ideal behavior. The experimental VLE data are analyzed in terms of the modified UNIFAC (Do) model.

INTRODUCTION

Nitroalkanes and chloroalkanes represent classes of technically important compounds used in industry as intermediates or as final products. The mixtures of these compounds are also interesting from a theoretical aspect because of their inter- and intramolecular interactions. The thermodynamic study of nitroalkane + chloroalkane mixtures is important for the determination of the type and magnitude of molecular interactions in these systems and for the further development of group contribution models frequently used in the prediction of thermodynamic properties.[1−4]

As part of an ongoing research project on vapor−liquid equilibria (VLE) in nitroalkane + chloroalkane mixtures, this paper presents the isothermal P, x, and y data for binary systems of nitromethane and nitroethane + 1,3-dichloropropane at temperatures of (343.15, 353.15, and 363.15) K. For these systems no VLE data are referenced,[5] and no experimental excess Gibbs energy values were found in the literature.[6] In a previous paper, Teodorescu et al. reported experimental VLE data for nitromethane and nitroethane + 1,2-dichloroethane[7] systems. In the open literature, only VLE data for nitromethane + 1-chlorobutane[8] or carbon tetrachloride[9] were found. Excess enthalpy and mixing volume data were reported for nitromethane and nitroethane + carbon tetrachloride binary mixtures.[10]

Our experimental VLE data were correlated using different models for G^E, namely, nonrandom two-liquid (NRTL)[11] and universal quasichemical activity coefficient (UNIQUAC)[12] equations. Afterward, they were compared with the predicted results obtained by means of the modified UNIFAC model (Dortmund, Do).[13]

EXPERIMENTAL SECTION

Materials. Nitromethane and nitroethane (purum ≥ 97 %) and 1,3-dichloropropane (purum ≥ 98 %) were purchased from Fluka. The liquids were dried and stored over 4A molecular sieves and used without further purification. The purity of substances checked by gas chromatograph was better than that stated (98.7 % for nitromethane, 98.9 % for nitroethane, and 99.6 % for 1,3-dichloropropane). An analysis was made using a Perkin-Elmer Clarus 600 gas chromatograph with a thermal conductivity detector (TCD) and an ELITE-PLOT Q capillary column (length 30 m, i.d. (inner diameter) 0.32 mm and d.f. 10 μm). The temperature of injector was settled at 523.15 K; the temperature of the oven was held at 433.15 K for 2 min, and then, after 283.15 $K \cdot min^{-1}$, it was held at 473.15 K. Hydrogen was used as a carrier gas, and the GC response peaks were integrated by using TotalChrom Workstation software. The purity test is also provided by a comparison of measured refractive indices, $n_D^{298.15K}$, and vapor pressures at three temperatures, with the literature values, as shown in Table 1, together with the calculated second virial coefficients, molar volumes, and UNIQUAC parameters (volumes and surfaces) for pure compounds.

During the measurements, no color changing was observed at the mixtures or at the pure components, and no decomposition or explosion took place.

Apparatus and Procedure. The vapor-pressure measurements of pure compounds and of the two binary mixtures were carried out by using an modified Swietoslawski ebulliometer.[27] The apparatus, which enables sampling of both phases in equilibrium, is described in detail elsewhere together with the working procedure.[28] For the testing and calibration of the ebulliometer we used the benzene + carbon tetrachloride system; a very good comparison of values of equimolar excess Gibbs energy with literature data was obtained (G^E $x = 0.5 < 2$ %).[28] This procedure is the one usually employed.[27,29,30] The apparatus and experimental procedure were successfully verified and used for the investigation of different systems.[31]

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Table 1. Refractive Indices, $n_D^{298.15K}$, Vapor Pressures, P, Calculated Second Virial Coefficients[a], B_{ii}, Molar Volumes[b], and V_0, Volume, r_i, and Surface, q_i, UNIQUAC Parameters for Pure Compounds

temperature	$n_D^{298.15K}$		P/kPa		B_{ii}	V_0		
K	this work	lit.	this work	lit.	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	r_i	q_i
Nitromethane								
298.15	1.3794	1.37941[14]					2.0086	1.8680
		1.3795[14]						
		1.37965[6]						
		1.3798[15]						
		1.37964[16]						
		1.38039[17]						
343.15			34.93	35.04[18] 34.46[19]	−2205.6	56.7		
353.15			50.14	50.42[18] 49.43[19]	−1902.5	57.4		
363.15			70.81	70.91[18] 69.28[19]	−1658.3	58.0		
Nitroethane								
298.15	1.3898	1.38960[20]					2.6829	2.4080
		1.3924[16]						
		1.390[21]	22.46	22.13[19]	−1749.3	75.5		
			32.84	32.47[19]	−1593.4	76.3		
343.15			47.13	46.52[19]	−1456.5	77.2		
353.15								
363.15								
1,3-Dichloropropane								
298.15	1.4462	1.4460[22,23]					3.6052	3.0680
		1.4459[24,25]						
343.15			18.31	18.39[26] 19.31[19]	−1954.5	100.3		
353.15			26.84	27.14[26] 28.10[19]	−1796.1	101.4		
363.15			38.65	38.77[26] 39.88[19]	−1657.8	102.5		

[a] Reference 33. [b] Reference 34.

The equilibrium temperatures in the ebulliometer were measured by means of mercury thermometers Laborterm-N. Eintauchtiefe 140 mm, previously calibrated at National Institute of Metrology, Bucharest, with an uncertainty of ± 0.05 K. The vapor pressure was measured by means of a mercury manometer. Manometric readings were performed with a Phylatex Physik-Gerate cathetometer to an uncertainty of ± 0.1 mm, and pressure reproducibility was estimated to be better than 50 Pa. The uncertainty of the pressure measurements is estimated to be 0.1 % of measured values. No pressure control (manometer) was used during the VLE measurements; the system was completely tied. During each measurement, the pressure was settled by using a system of vacuum and air valves, and at the same time an accurate heating of both liquid and vapors from equilibrium chamber up to the desired temperature was attended within ± 0.05 K. The temperature stays constant for at least 15 min which is the equilibration time of the ebulliometer. In this time, the drop counter of the condensate is kept constant at a number of drops established from calibration. No other equipment was used for temperature control.

The composition of the phases in equilibrium was analyzed by the refractometric method by means of the calibration curves obtained from measurements of the refractive index (at sodium D-line, $\lambda_D = 589.3$ nm) of weighed samples (A&D Company Ltd. Japan, GH-252 analytical balance with an uncertainty of ± 0.1 mg) at 298.15 K and the data correlation, within experimental uncertainties, with three-parameter Redlich−Kister polynomials. The refractive index was measured using an Abbe Carl Zeiss Jena refractometer, with an uncertainty of ± 0.0001. The samples were thermostatted with a Mechanik Prufgerate Medingen Thermostat U10 within the uncertainty of ± 0.1 °C. The error in the determination of the phase composition was 0.002 mole fraction.

RESULTS AND CORRELATION

The vapor pressures of pure compounds measured in the ebulliometer at the three temperatures are given in Table 1 together with literature values. The two sets of vapor pressure from the indicated references[18,26] taken as a comparison in Table 1 have been obtained by ebulliometry as well. The third data set from literature[19] is taken from a database in which the original source of measuring vapor pressure data is not given. A good agreement can be observed. The differences are acceptable since it is well-known that the vapor pressure is dependent on the purity of the chemical used.

The experimental isothermal P, x, and y data measured for the two binary systems at (343.15, 353.15, and 363.15) K are shown in Figures 1 and 2 and are summarized in Table 2, together with those calculated by NRTL model (γ_1, γ_2, G^E). The data for each binary system were correlated supplementary with the UNIQUAC model.

The activity coefficients, of each component i, γ_i, determined from experimental isothermal VLE and vapor pressure of pure

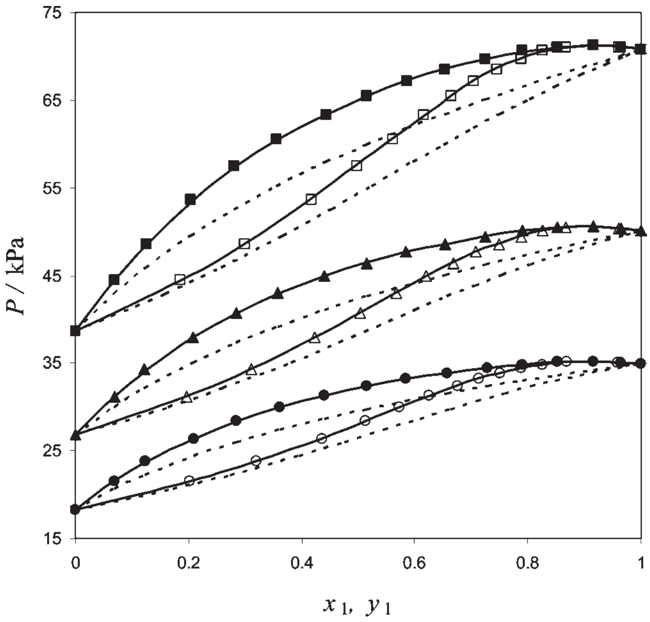

Figure 1. Isothermal (vapor−liquid) equilibrium data for the nitromethane (1) + 1,3-dichloropropane (2) system at: (●, ○), 343.15 K; (▲, △), 353.15 K; (■, □), 363.15 K; solid points, liquid phase; open points, vapor phase; solid line, NRTL correlation; dashed line, modified UNIFAC (Do) prediction.

component *i* at working temperature data, were calculated from the well-known Raoult equation:

$$\varphi_i y_i P = \gamma_i x_i P_i^0 \tag{1}$$

This was done in testing of thermodynamic consistency. For low and moderate pressures, the fugacity coefficient of component *i*, φ_i, was assumed to be 1.

In our correlation method of VLE experimental data with the two mentioned models, φ_i was considered to be different from 1.

The expressions for activity coefficients and excess Gibbs free energy in binary systems are:

For the NRTL equation:

$$\ln \gamma_1 = {x_2}^2 \left[\frac{\tau_{21} \exp(-2a_{12}\tau_{21})}{[x_1 + x_2 \exp(-2a_{12}\tau_{21})]^2} + \frac{\tau_{12} \exp(-2a_{12}\tau_{12})}{[x_2 + x_1 \exp(-2a_{12}\tau_{12})]^2} \right] \tag{2}$$

$$\ln \gamma_2 = {x_1}^2 \left[\frac{\tau_{12} \exp(-2a_{12}\tau_{12})}{[x_2 + x_1 \exp(-2a_{12}\tau_{12})]^2} + \frac{\tau_{21} \exp(-2a_{12}\tau_{21})}{[x_1 + x_2 \exp(-2a_{12}\tau_{21})]^2} \right] \tag{3}$$

$$\frac{G^E}{RT} = x_1 x_2 \left(\frac{\tau_{21}\Lambda'_{21}}{x_1 + x_2\Lambda'_{21}} + \frac{\tau_{12}\Lambda'_{12}}{x_2 + x_1\Lambda'_{12}} \right) \tag{4}$$

$$\text{in which}: \tau_{12} = (g_{12} - g_{22})/RT \quad \text{and} \quad \tau_{21} = (g_{21} - g_{11})/RT \tag{5}$$

$$\Lambda'_{12} = \exp(-a_{12}\tau_{12}) \quad \text{and} \quad \Lambda'_{21} = \exp(-a_{12}\tau_{21}) \tag{6}$$

The optimized model parameters were those energetic ($g_{12} - g_{22}$), ($g_{21} - g_{11}$), and that of the solution randomness a_{12}. Strict definitions of properties appearing in above equations are well-known and can be found elsewhere.[11]

For the UNIQUAC equation:

$$\ln \gamma_i = \ln \gamma_i^{\text{comb}} + \ln \gamma_i^{\text{res}} \tag{7}$$

$$\ln \gamma_1^{\text{comb}} = \ln \frac{\phi_1}{x_1} + \frac{z}{2} q_1 \ln \frac{\theta_1}{x_1} + \phi_2 \left(l_1 + \frac{r_1}{r_2} l_2 \right) - q_1 \ln(\theta_1 + \theta_2\tau_{21}) + \theta_2 q_1 \left(\frac{\tau_{21}}{\theta_1 + \theta_2\tau_{21}} - \frac{\tau_{12}}{\theta_2 + \theta_1\tau_{12}} \right) \tag{8}$$

$$l_1 = \frac{z}{2}(r_1 - q_1) - (r_1 - 1); \qquad l_2 = \frac{z}{2}(r_2 - q_2) - (r_2 - 1) \tag{9}$$

$$\ln \gamma_1^{\text{res}} = q_1 \left[1 - \ln\left(\sum_j \theta_j \tau_{j1}\right) - \sum_j \left(\frac{\theta_j \tau_{1i}}{\sum_i \theta_i \tau_{ij}} \right) \right] \tag{10}$$

$$\theta_1 = \frac{q_1 x_1}{\sum_j q_j x_j}; \qquad \phi_1 = \frac{r_1 x_1}{\sum_j r_j x_j} \tag{11}$$

$$G^E = G^E_{(\text{comb})} + G^E_{(\text{res})} \tag{12}$$

$$\text{where}: G^E_{(\text{comb})} = RT \left(x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2} + \frac{z}{2} \left(q_1 x_1 \ln \frac{\theta_1}{x_1} + q_2 x_2 \ln \frac{\theta_2}{x_2} \right) \right) \tag{13}$$

$$G^E_{(\text{res})} = -RT[q_1 x_1 \ln(\theta_1 + \theta_2\tau_{21}) + q_2 x_2 \ln(\theta_2 + \theta_1\tau_{12})] \tag{14}$$

$$\text{and}: \phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2}; \qquad \phi_2 = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2} \tag{15}$$

$$\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2}; \qquad \theta_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2} \tag{16}$$

$$\tau_{21} = \exp[-(u_{21} - u_{11})/RT]; \quad \tau_{12} = \exp[-(u_{12} - u_{22})/RT] \tag{17}$$

In the combinatorial term appear only the *r* and *q* parameters from pure components, while in the residual term appear two adjustable parameters τ_{21} and τ_{12}. The pure component parameters are calculated as the sum of volumes and surfaces group contributions, R_k and Q_k:

$$r_i = \sum_k^p n_k^{(i)} R_k; \qquad q_i = \sum_k^p n_k^{(i)} Q_k \tag{18}$$

The adjustable energetic parameters are ($u_{21} - u_{11}$) and ($u_{12} - u_{22}$). Details of all other properties of the well-known UNIQUAC model can be found elsewhere.[12]

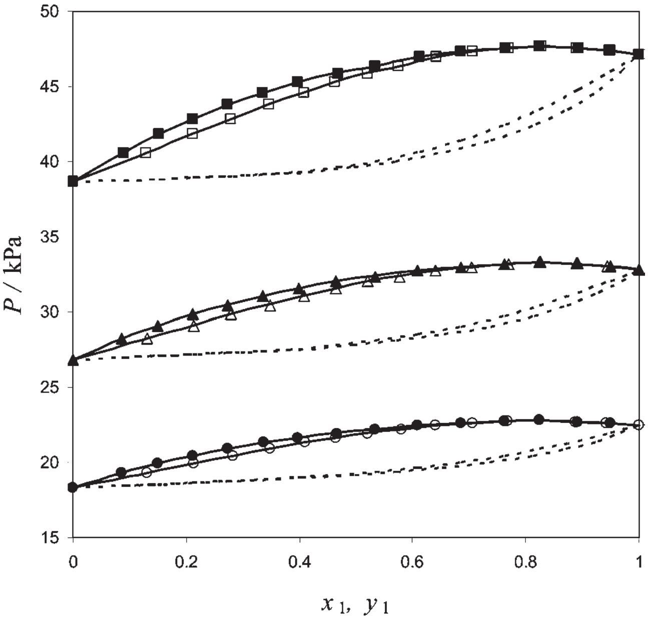

Figure 2. Isothermal (vapor−liquid) equilibrium data for the nitroethane (1) + 1,3-dichloropropane (2) system at: (●, ○), 343.15 K; (▲, △), 353.15 K; (■, □), 363.15 K; solid points, liquid phase; open points, vapor phase; solid line, NRTL correlation; dashed line, modified UNIFAC (Do) prediction.

The regression of the observed VLE data was performed by means of maximum likelihood method with a program described elsewhere.[32] In this program, the objective function is defined as follows:

$$S = \sum_{i=1}^{N} [(P_{ie} - P_{ic})^2/\sigma_P{}^2 + (T_{ie} - T_{ic})^2/\sigma_T{}^2 + (x_{ie} - x_{ic})^2/\sigma_x{}^2 + (y_{ie} - y_{ic})^2/\sigma_y{}^2] \tag{19}$$

where N is the number of experimental points and P_{ie}, T_{ie}, x_{ie}, and y_{ie} are the experimental data and P_{ic}, T_{ic}, x_{ic}, and y_{ic} are the corresponding calculated values for pressure, temperature, and the liquid and vapor composition, respectively. In this work, the standard deviations for pressure, temperature, and liquid and vapor compositions were set to $\sigma_P = 0.1$ % of measured value, $\sigma_T = 0.05$ K, and $\sigma_x = \sigma_y = 0.002$, respectively.

All standard deviations of correlation were calculated using the expression: $\sigma = [\Sigma(Z_{\text{exp}} - Z_{\text{calc}})^2/(N - m)]^{1/2}$, where Z is the value of the property P, T, x, y; N is the number of experimental points and m is the number of model parameters.

The real behavior of vapor phase was described with the virial equation of state. The second virial coefficients for all components and for all binary mixtures were evaluated by means of the Hayden and O'Connell method,[33] while the molar volumes were calculated by using a generalized Watson relation.[34] The Watson equation, $V = V_1\omega_1/\omega$, gives the liquid molar volume at saturation conditions as a function of the expansion factor, ω, which depends on the reduced pressure and reduced temperature, and it is based on properties of the substance in question at a reference state, designed by subscript 1. For its calculation, the following data are required: critical temperature, critical pressure, liquid molar volume at some temperature, and vapor pressure of the liquid.

Table 2. Vapor−Liquid Equilibrium Experimental Data (Pressure P, Temperature T, Liquid Mole Fraction x_1, Vapor Mole Fraction y_1) and Calculated (NRTL) Activity Coefficients (γ_1, γ_2) and Excess Gibbs Energy (G^E) in the Nitromethane (1) or Nitroethane (1) + 1,3-Dichloropropane (2) System[a]

		P			G^E
x_1	y_1	kPa	γ_1	γ_2	J·mol^{-1}
Nitromethane (1) + 1,3-Dichloropropane (2)					
T = 343.15 K					
0.0690	0.2018	21.46	1.737	1.002	122.6
0.1235	0.3198	23.81	1.644	1.009	214.0
0.2098	0.4359	26.37	1.526	1.024	323.8
0.2848	0.5128	28.36	1.429	1.046	405.4
0.3609	0.5732	30.00	1.346	1.077	464.5
0.4409	0.6264	31.32	1.262	1.124	507.4
0.5159	0.6758	32.33	1.199	1.178	522.2
0.5849	0.7127	33.17	1.146	1.245	515.3
0.6569	0.7509	33.85	1.103	1.325	488.3
0.7282	0.7889	34.38	1.065	1.434	435.3
0.7901	0.8255	34.84	1.039	1.552	367.8
0.8529	0.8686	35.12	1.019	1.693	282.4
0.9152	0.9152	35.17	1.007	1.865	178.1
0.9636	0.9586	35.00	1.001	2.029	81.2
T = 353.15 K					
0.0690	0.1958	31.18	1.821	1.003	128.7
0.1214	0.3107	34.34	1.702	1.010	224.0
0.2078	0.4226	38.00	1.560	1.028	336.9
0.2848	0.5034	40.74	1.448	1.054	420.1
0.3574	0.5673	43.06	1.356	1.087	479.4
0.4392	0.6194	44.94	1.274	1.134	518.5
0.5159	0.6677	46.44	1.206	1.192	533.0
0.5835	0.7088	47.68	1.154	1.258	525.4
0.6541	0.7484	48.60	1.108	1.344	496.6
0.7256	0.7889	49.46	1.070	1.454	444.0
0.7901	0.8255	50.10	1.042	1.578	376.5
0.8518	0.8675	50.46	1.022	1.731	290.7
0.9152	0.9152	50.57	1.008	1.928	182.7
0.9636	0.9606	50.36	1.001	2.121	83.0
T = 363.15 K					
0.0690	0.1857	44.48	1.737	1.002	122.6
0.1256	0.2996	48.61	1.644	1.009	214.0
0.2038	0.4176	53.68	1.526	1.024	323.8
0.2810	0.4988	57.50	1.429	1.046	405.4
0.3556	0.5614	60.53	1.346	1.077	464.5
0.4441	0.6165	63.25	1.262	1.124	507.4
0.5143	0.6650	65.46	1.199	1.178	522.2
0.5864	0.7049	67.21	1.146	1.245	515.3
0.6528	0.7446	68.54	1.103	1.325	488.3
0.7256	0.7877	69.66	1.065	1.434	435.3
0.7901	0.8255	70.59	1.039	1.552	367.8
0.8529	0.8675	71.07	1.019	1.693	282.4
0.9152	0.9152	71.21	1.007	1.865	178.1
0.9636	0.9606	71.07	1.001	2.029	81.2

Table 2. Continued

x_1	y_1	P kPa	γ_1	γ_2	G^E $J \cdot mol^{-1}$
Nitroethane (1) + 1,3-Dichloropropane (2)					
T = 343.15 K					
0.0869	0.1309	19.29	1.308	1.003	73.1
0.1496	0.2131	19.96	1.259	1.008	117.7
0.2111	0.2830	20.44	1.219	1.015	153.0
0.2732	0.3490	20.90	1.183	1.025	182.1
0.3375	0.4093	21.32	1.151	1.037	204.5
0.3963	0.4643	21.61	1.126	1.051	219.2
0.4661	0.5214	21.93	1.100	1.070	228.5
0.5337	0.5805	22.17	1.077	1.092	229.9
0.6077	0.6396	22.48	1.056	1.121	222.2
0.6859	0.7054	22.61	1.037	1.158	203.2
0.7616	0.7680	22.77	1.022	1.203	173.9
0.8246	0.8246	22.85	1.013	1.248	140.2
0.8909	0.8879	22.70	1.005	1.306	95.0
0.9488	0.9427	22.60	1.001	1.366	49.1
T = 353.15 K					
0.0869	0.1309	28.26	1.283	1.002	70.1
0.1496	0.2131	29.09	1.244	1.006	112.8
0.2111	0.2791	29.84	1.210	1.013	146.8
0.2732	0.3490	30.45	1.177	1.022	176.9
0.3356	0.4075	31.08	1.148	1.033	199.2
0.3982	0.4643	31.57	1.121	1.047	215.2
0.4643	0.5214	32.01	1.096	1.065	224.6
0.5337	0.5770	32.34	1.074	1.088	226.2
0.6094	0.6396	32.73	1.052	1.118	218.0
0.6859	0.7038	32.96	1.034	1.154	198.8
0.7616	0.7696	33.14	1.019	1.197	168.4
0.8246	0.8261	33.32	1.011	1.237	134.6
0.8909	0.8894	33.21	1.004	1.287	90.3
0.9488	0.9442	33.05	1.001	1.334	46.1
T = 363.15 K					
0.0890	0.1288	40.53	1.272	1.002	69.6
0.1517	0.2111	41.81	1.234	1.006	112.5
0.2111	0.2791	42.84	1.201	1.012	146.2
0.2732	0.3471	43.80	1.169	1.021	175.6
0.3356	0.4075	44.58	1.141	1.032	197.7
0.3963	0.4625	45.26	1.117	1.045	212.9
0.4679	0.5197	45.88	1.092	1.063	222.5
0.5337	0.5753	46.32	1.071	1.084	223.8
0.6128	0.6429	46.94	1.049	1.115	214.9
0.6859	0.7054	47.29	1.032	1.148	196.2
0.7632	0.7696	47.56	1.018	1.189	166.0
0.8246	0.8277	47.69	1.010	1.228	132.6
0.8925	0.8894	47.52	1.004	1.275	88.8
0.9488	0.9472	47.37	1.001	1.320	44.4

[a] σ_P = 0.1 % of the measured P value, σ_T = 0.05 K, and $\sigma_x = \sigma_y$ = 0.002.

The second virial coefficients and molar volumes are shown in Table 1. The experimentally determined vapor pressures of pure substances (as given in Tables 1) were used for all calculations.

Table 3. Parameters of Correlation Equations (Energetic Parameters Between Components A_{12}, A_{21}, and of Solution Randomness for NRTL, a_{12}) and Standard Deviations (for the Molar Fraction of Liquid, σ_{x1}, Molar Fraction of Vapor, σ_{y1}, Pressure, σ_P, Temperature, σ_T) of Nitromethane (1) or Nitroethane (1) + 1,3-Dichloropropane (2) Systems

T K	A_{12} $J \cdot mol^{-1}$	A_{21} $J \cdot mol^{-1}$	a_{12}	σ_{x1}	σ_{y1}	σ_P kPa	σ_T K
Nitromethane (1) + 1,3-Dichloropropane (2)							
NRTL Equation							
343.15	668.89	1190.7	−0.8550	0.0016	0.0018	0.013	0.04
353.15	684.30	1086.5	−1.2906	0.0020	0.0020	0.014	0.03
363.15	−1180.7	2974.8	−0.1711	0.0026	0.0025	0.021	0.03
UNIQUAC Equation							
343.15	−264.76	1498.4		0.0015	0.0018	0.011	0.03
353.15	−225.37	1443.1		0.0021	0.0021	0.014	0.03
363.15	−197.34	1381.8		0.0025	0.0024	0.020	0.03
Nitroethane (1) + 1,3-Dichloropropane (2)							
NRTL Equation							
343.15	670.11	545.19	2.2976	0.0008	0.0008	0.008	0.04
353.15	807.47	145.50	0.4117	0.0011	0.0012	0.013	0.04
363.15	813.50	125.19	0.3756	0.0014	0.0013	0.016	0.03
UNIQUAC Equation							
343.15	−227.88	633.09		0.0007	0.0007	0.009	0.04
353.15	−230.64	627.74		0.0011	0.0011	0.013	0.04
363.15	−259.61	657.21		0.0013	0.0013	0.015	0.03

All results of fitting are summarized in Table 3. Here, the natural logarithms of activity coefficients in equations for their expression are used, and the parameters for NRTL and UNIQUAC equations are given in $J \cdot mol^{-1}$. Generally, the evaluated parameters should exhibit a smooth dependence on temperature. However, some discrepancies could be found here for the equation with more parameters, for example, for the exponential NRTL equation, which reflect the effect of more degrees of freedom during numerical processing. In the used program, there are no parameter constraints, and each isotherm is correlated independently resulting in different triads of parameters. The parameters describe, as best as possible, the particular isotherm, but no evident conclusion can be drawn for temperature dependence.

■ DISCUSSION AND CONCLUSIONS

The reliability of both the data and the correlation procedure is verified by the fact that the resulting standard deviations are approximately proportional to the magnitudes of input uncertainties. Generally, the inspection of deviation distribution from smoothed data confirms that there are only expectable, random, and nonsystematic errors. As can be seen in Table 3, either of the models can be used for correlation with almost the same accuracy. A thermodynamic test of consistency has been carried out with use of the procedure proposed by Van Ness.[35] According to this test, for the presented data, the "consistency index", in average, equals 1 for all six isothermal data sets within the 10 degree scale where 1 is excellent and 10 is unacceptable.

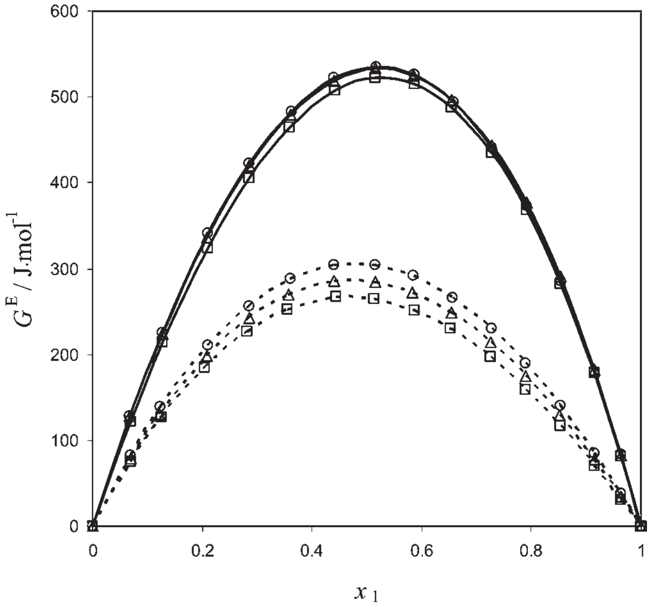

Figure 3. Calculated excess Gibbs molar energy versus liquid composition for the nitromethane (1) + 1,3-dichloropropane (2) system at: (—○—, ---○---), 343.15 K; (—△—, ---△---), 353.15 K; (—□—, ---□---), 363.15 K; solid line, NRTL correlation; dashed line, modified UNIFAC (Do) prediction.

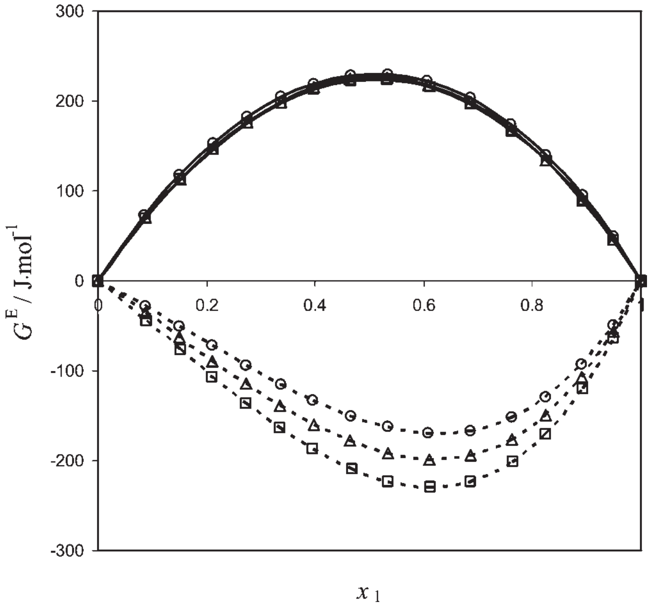

Figure 4. Calculated excess Gibbs molar energy versus liquid composition for the nitroethane (1) + 1,3-dichloropropane (2) system at: (—○—, ---○--), 343.15 K; (—△—, ---△---), 353.15 K; (—□—, ---□---), 363.15 K; solid line, NRTL correlation; dashed line, modified UNIFAC (Do) prediction.

Table 4. Geometrical Parameters R_k and Q_k Corresponding to Constitutive Sub-Groups of Studied Compounds by Modified UNIFAC (Do)

main group	subgroup	R_k	Q_k
1 "CH_2"	1 "CH_3"	0.6325	1.0608
1 "CH_2"	2 "CH_2"	0.6325	0.7081
21 "CCl"	44 "CH_2Cl"	0.9919	1.3654
26 "CNO_2"	54 "CH_3NO_2"	2.6440	2.5000
26 "CNO_2"	55 "CH_2NO_2"	2.5000	2.3040

Table 5. Modified UNIFAC (Do) Interaction Parameters for the Studied Systems

	a_{nm}		c_{nm}	a_{mn}		c_{mn}
n m	K	b_{nm}	K^{-1}	K	b_{mn}	K^{-1}
1 21	401.00	−0.7277	0.0	−65.685	0.07409	0.0
1 26	2345.0	−13.200	0.02156	−396.50	3.0920	−0.006266
21 26	24.440	−0.4713	0.0	142.10	−0.1530	0.0

The two investigated systems are azeotropic, the location of the azeotropic points being determined by interpolation of the calculated NRTL phase diagrams at each isotherm. As can be observed, for the nitromethane +1,3-dichloropropane system, the azeotropic points have almost the same composition of $y_{1az} = 0.9150$ and $P_{az} = 35.18$ kPa at $T = 343.15$ K; $y_{1az} = 0.9147$ and $P_{az} = 50.57$ kPa at $T = 353.15$ K; and $y_{1az} = 0.9153$ and $P_{az} = 71.22$ kPa at $T = 363.15$ K. For the nitroethane + 1,3-dichloropropane system, the values obtained are: composition of $y_{1az} = 0.8242$ and $P_{az} = 22.83$ kPa at $T = 343.15$ K; $y_{1az} = 0.8252$ and $P_{az} = 33.29$ kPa at $T = 353.15$ K; and $y_{1az} = 0.8262$ and $P_{az} = 47.66$ kPa at $T = 363.15$ K. However, the temperature interval and pressure range are too short to make certain conclusions about the composition of the azeotrope behavior.

Both systems exhibit positive deviations from ideality, and this is obvious from the examination of Figures 3 and 4, the excess Gibbs energy for the nitromethane + 1,3-dichloropropane system being more positive at the same temperature. For the present measurements, from the variation of excess Gibbs energy with temperature (by the Gibbs−Helmholtz equation), the excess enthalpy at equimolar composition was calculated. The computed excess enthalpy, at equimolar composition and at the average temperature of 353.15 K, was 756 J·mol^{-1} for the nitromethane + 1,3-dichloropropane system and 333 J·mol^{-1} for the nitroethane + 1,3-dichloropropane system. No calorimetric data have been found in literature for comparison. The modified UNIFAC (Do) model gives about 972 J ·mol^{-1} for the system with nitromethane and 870 J·mol^{-1} for the system with nitroethane, to the same conditions (average temperature and equimolar composition).

From Figures 1 to 4 it can be observed that the modified UNIFAC (Do) model do not predict very well the VLE and G^E values, especially for the second system: the azeotrope behavior is not described, and a negative deviation from Raoult low is given. This is probable due to the fact that present VLE data are not included in the UNIFAC database and proper interaction parameters need to be readjusted. All UNIFAC calculations were made with parameters shown in Tables 4 and 5.

From the nitromethane with chloroalkanes in studied series so far, at about the same temperature, the excess Gibbs energy varies in the order: 1-chlorobutane > 1,3-dichloropropane > 1,2-dichloroethane > carbon tetrachloride. It is clear that it is a strong interaction of the dipole on the nitromethane with the polarizable clorine atoms and this effect increases with the number of chlorine atoms in the chloroalkane molecule. For the same chloroalkane (e.g., 1,2-dichloroethane or 1,3-dichloropropane), the G^E is smaller for nitroethane mixture than for nitromethane due to the higher polarizability of nitroethane. The same effect was detected by Marsh[10] when measured the heat and volume of mixing for nitromethane and nitroethane with carbon tetrachloride.

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