JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Estimation of Activity Coefficients for the Pairs of the System 2-Ethoxyethanol + 2-Ethoxyethyl Acetate + 2-Butoxyethanol + 2-Butoxyethyl Acetate

Giorgia F. Cortinovis, Wilson M. Salvagnini, Denise T. Tavares, and Maria E. S. Taqueda*

Department of Chemical Engineering, Universidade de São Paulo, São Paulo−SP 05508-900, Brazil

ABSTRACT: The NRTL activity model parameters were determined for the following binary systems: 2-ethoxyethanol + 2-ethoxyethyl acetate, 2-ethoxyethanol + 2-butoxyethanol, 2-ethoxyethanol + 2-butoxyethyl acetate, 2-ethoxyethyl acetate + 2-butoxyethanol, 2-ethoxyethyl acetate + 2-butoxyethyl acetate, and 2-buthoxyethanol + 2-butoxyethyl acetate. For the estimate of NRTL activity model parameters, measurements of the bubble point of binary mixtures of a known composition were made at atmospheric pressure from (93 to 101.3) kPa. Ideal behavior was considered for the vapor phase. It was assumed that no reaction occurs between the acetates and alcohols of the binary mixtures.

1. INTRODUCTION

This work is part of an ongoing study to investigate a new industrial route to obtain 2-butoxyethyl acetate from the transesterification reaction between 2-ethoxyethyl acetate and 2-butoxyethanol in liquid phase. The main objective was to identify in a quick and preliminary way the potential nonidealities of the reaction system in the liquid phase, since it is a study for a new route of industrial production. For the same reason, the chemicals are used without any purification treatment. This work should provide allowance for obtaining both kinetic and equilibrium constants of the reaction studied, expressed by the activities of the components, as well as for studies related to the separation of the mixture by distillation. The activity coefficients of the tested binary systems cannot be accurately predicted from the activity models that are based on the concept of group contribution, e.g., ASOG (analytical solution of groups)[1] or UNIFAC (universal functional activity coefficient).[2] Nowadays, there are not groups representing glycol ethers ($-OCH_2CH_2OH$) or acetates of glycol ethers ($-OCH_2CH_2OR$); thus, the NRTL[3] model (nonrandom, two liquid) was employed for modeling possible nonidealities of the liquid phase. The NRTL model allows a good representation of systems data strongly nonideal, which is quite convenient, because it can be readily converted into the multicomponent system models and is easily used in of simulations of distillation. The behavior of the vapor phase is often assumed as ideal in systems at low pressures. The nonideality of the steam phase was not considered due to low pressure (atmospheric) in which the experiment was performed. For the same reason, the correction of the Poynting factor was ignored. As far as we are concerned, there are data in the open literature on activity coefficients for the system 2-butoxyethanol + 2-butoxyethyl acetate.[4] It is assumed that the reaction between acetates and alcohols do not occur during the tests, due to nonaddition of catalysts. The 2-butoxyethyl acetate is commercially known as butyl glycol acetate,[5] EGBEA, Butyl CELLOSOLVE[6] and is mainly used in formulations for cleaning products, coatings, coalescent, flexography inks, and printing inks for both textiles and leather. Butyl glycol acetate is a colorless liquid of mild odor. When compared with other solvents, it has a high boiling point, low solubility in water, and high solubility in alcohols, ketones, aldehydes, ethers, and glycol ethers.[7]

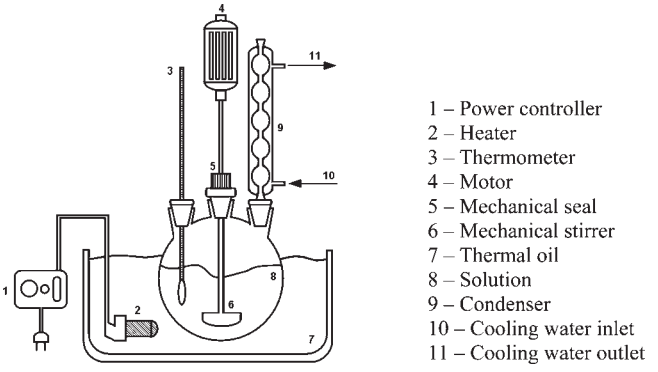

Figure 1. Schematic diagram of experimental apparatus.

2. EXPERIMENTAL SECTION

Chemicals. All chemicals were supplied by Oxiteno Indústria e Comércio S/A as products that meet commercial specifications. The products were used without further purification. The 2-butoxyethyl acetate has as a commercial specification with the minimum mass purity of 98%. Other products have a minimum purity of 99%.

Apparatus and Procedure. The apparatus used is illustrated in Figure 1 and consists of mechanical stirrer, condenser, thermometer, thermal oil, and heating power controller. A mechanical stirrer was used for obtaining uniform heating of the mixture. The bubble points of mixtures were measured with thermometers ASTM 102C and 103C, both with scale graduated in intervals of 0.2 °C.

Received: July 6, 2011
Accepted: September 28, 2011
Published: October 20, 2011

Table 1. Correlations Used to Calculate the Vapor Pressure and Its Respective Constants

component	equation	constants	references
2-ethoxyethanol	$\log_{10} P^{V} = A + \frac{B}{T} + C\cdot\log_{10} T + DT + ET^2$	$A = 115.8686$; $B = -6.0128 \times 10^{3}$; $C = -4.0900 \times 10^{1}$;	
	$P = [\text{mmHg}]; T = [\text{K}]$	$D = -2.0888 \times 10^{-2}$; $E = 1.6481 \times 10^{-15}$	10
2-ethoxyethyl acetate	$\log_{10} P^{V} = A + \frac{B}{T} + C\cdot\log_{10} T + DT + ET^2$	$A = 1.9276$; $B = -3.1451 \times 10^{3}$; $C = 5.7407$;	
	$P = [\text{mmHg}]; T = [\text{K}]$	$D = -2.1017 \times 10^{-2}$; $E = 1.1834 \times 10^{-5}$	10
2-butoxyethanol	$\log_{10} P^{V} = A + \frac{B}{T} + C\cdot\log_{10} T + DT + ET^2$	$A = -39.3735$; $B = -3.0058 \times 10^{3}$; $C = 5.5696 \times 10^{1}$;	
	$P = [\text{mmHg}]; T = [\text{K}]$	$D = -5.7339 \times 10^{-2}$; $E = 3.2713 \times 10^{-5}$	10
2-butoxyethyl acetate	$\ln P^{V} = A - \frac{B}{(T + C)}, P = [\text{kPa}], T = [\text{K}]$	$A = 7.04027$; $B = 1856.286$; $C = -38.98$	12

Table 2. Experimental Boiling point T_e at pressure P and Calculated Boiling Point $T_{e,cal}$ Using the Correlations in Table 1

component	T_e/K	$T_{e,calc}$/K	P/kPa
2-ethoxyethanol	406.9	405.6	93.3
	407.8	405.7	93.6
	406.2	405.6	93.3
2-ethoxyethyl acetate	428.3	427.1	93.7
	428.6	426.9	93.3
	427.8	426.9	93.3
2-butoxyethanol	441.3	441.8	93.9
	442.1	441.9	94.1
	441.5	441.7	93.6
2-butoxyethyl acetate	463.3	461.4	93.6
	463.0	461.5	93.7
	464.2	461.5	93.9

The method used to estimate the activity model parameters consists of measuring the bubble point temperature of a binary mixture of a well-known composition. The atmospheric pressure was measured before starting the test, using a mercury barometer with a scale graduated in 0.5 mmHg (0.1 kPa). In a recipient, a desired amount of one component of the mixture was weighed and added to the flask in Figure 1. The amount added to the flask was calculated by the difference in the initial and final weight of the recipient. The same procedure was used for another component of the mixture. A digital balance with accuracy of 0.01 g was used for weighing the chemicals. Then, the heating and the stirring of the mixture were started, until the first bubbles appeared and the temperature of the mixture remains constant. The temperature at that time was measured as the bubble point of the sample. For each binary mixture, the bubble point was measured from 8 to 11 mixtures of different compositions. A small heating rate was used, and there was condensation of vapor only at the entrance of the condenser, avoiding appreciable change in the composition of the liquid phase.

Vapor Pressure. The vapor pressure data for 2-ethoxyethanol and 2-butoxyethanol were reported by Antosik et al.,[8] Chiavone-Filho et al.,[9] and Yaws.[10] The 2-butoxyethanol has vapor pressure data reported by Chiavone-Filho et al.[9] and Yaws.[10] For the 2-ethoxyethyl acetate, data were published by Steele et al.[11] and Yaws.[10] The only reference found containing vapor pressure data for the butoxyethyl acetate was published by Lee et al.[12] The references quoted above show equations that correlate temperature and vapor pressure of the substance. The boiling temperatures of pure substances were measured by using the apparatus illustrate by of Figure 1, and the results were compared to calculated temperatures, using the equations of the references. Among the references, the one which was closer to the boiling temperature measured was used, except for the 2-butoxyethyl acetate that has a single reference.

Table 3. Estimated Parameters for NRTL Model

component 1	component 2	Δg_{12}/J·mol^{-1}	Δg_{21}/J·mol^{-1}
2-ethoxyethanol	2-ethoxyethyl acetate	−2104.3	3301.5
2-ethoxyethanol	2-butoxyethanol	2335.6	−2445.9
2-ethoxyethanol	2-butoxyethyl acetate	1885.8	−1938.3
2-ethoxyethyl acetate	2-butoxyethanol	−2960.7	4579.9
2-ethoxyethyl acetate	2-butoxyethyl acetate	1548.0	−1693.3
2-butoxyethanol	2-butoxyethyl acetate	3871.5	−2525.3

Table 4. System 2-Ethoxyethanol (1) + 2-Ethoxyethyl Acetate (2): Measured and Calculated Variables from the NRTL Model[a]

	measured variables			calculated variables					
run	x_1	T/K	P/kPa	γ_1	γ_2	P_1/kPa	P_2/kPa	P_{cal}/kPa	T_{cal}/K
1	0.15	422.0	93.6	1.14	1.01	26.5	69.2	95.6	421.2
2	0.28	417.6	93.6	1.08	1.02	41.0	52.2	93.2	417.7
3	0.37	415.4	93.6	1.05	1.03	48.4	43.7	92.1	415.8
4	0.47	413.0	93.6	1.03	1.05	56.9	34.4	91.2	413.8
5	0.63	411.4	93.3	1.01	1.07	70.9	23.5	94.4	411.0
6	0.74	409.6	93.3	1.00	1.09	78.0	16.1	94.0	409.4
7	0.82	408.9	93.3	1.00	1.10	85.0	10.7	95.7	408.1
8	0.91	407.6	93.3	1.00	1.11	90.7	5.0	95.7	406.8

[a] $u(x) = 1.4 \times 10^{-4}$, $u(T) = 2.1$ K, and $u(p) = 0.4$ kPa.

Estimated NRTL Parameters. For each mixture of a known composition, the vapor pressure was calculated for the components in the bubble point of the mixture. Then, partial pressure for each component and total pressure were calculated (P_{cal}), considering vapor phase ideal and activity coefficients for the

dx.doi.org/10.1021/je200565u |J. Chem. Eng. Data 2011, 56, 4157–4163

Table 5. System 2-Ethoxyethanol (1) and 2-Butoxyethanol (2): Measured and Calculated Variables from the NRTL Model[a]

	measured variables			calculated variables					
run	x_1	T/K	P/kPa	γ_1	γ_2	P_1/kPa	P_2/kPa	P_{cal}/kPa	T_{cal}/K
1	0.11	437.3	93.8	0.89	1.00	22.3	73.5	95.8	436.1
2	0.21	432.4	93.8	0.90	0.99	38.1	56.5	94.5	431.7
3	0.25	428.9	93.8	0.91	0.99	42.7	47.7	90.5	429.7
4	0.34	426.4	93.5	0.93	0.98	54.7	38.7	93.4	426.1
5	0.35	424.7	92.1	0.93	0.98	53.2	36.4	89.5	425.8
6	0.41	422.8	92.1	0.94	0.98	59.4	31.0	90.4	423.6
7	0.48	420.6	92.1	0.95	0.97	67.4	24.9	92.2	420.7
8	0.59	417.9	92.1	0.97	0.95	77.0	17.8	94.8	417.1
9	0.74	412.9	92.1	0.98	0.91	84.7	9.3	94.0	412.4
10	0.83	411.2	92.1	0.99	0.88	90.8	5.7	96.5	409.9
11	0.88	409.8	93.3	1.00	0.86	93.5	3.5	97.0	408.3

[a] $u(x) = 1.5 \times 10^{-4}$, $u(T) = 2.0$ K, and $u(p) = 1.7$ kPa.

Table 6. System 2-Ethoxyethanol (1) and 2-Butoxyethyl Acetate (2): Measured and Calculated Variables from the NRTL Model[a]

	measured variables			calculated variables					
run	x_1	T/K	P/kPa	γ_1	γ_2	P_1/kPa	P_2/kPa	P_{cal}/kPa	T_{cal}/K
1	0.11	450.2	93.7	0.93	1.00	35.1	59.7	94.7	449.7
2	0.18	445.2	93.7	0.94	1.00	48.0	47.6	95.6	444.4
3	0.25	437.7	93.6	0.95	0.99	56.8	34.2	91.0	438.6
4	0.35	431.3	93.7	0.96	0.99	65.7	24.3	90.0	432.6
5	0.47	426.3	93.7	0.97	0.98	78.7	16.6	95.3	425.7
6	0.57	420.7	93.6	0.98	0.97	82.4	11.0	93.4	420.7
7	0.65	417.5	93.6	0.99	0.96	86.0	7.9	93.9	417.4
8	0.74	414.9	93.6	0.99	0.94	91.3	5.3	96.6	413.8
9	0.85	412.2	93.6	1.00	0.92	96.8	2.7	99.5	410.2
10	0.96	409.4	93.6	1.00	0.90	100.6	0.7	101.3	406.8

[a] $u(x) = 1.6 \times 10^{-4}$, $u(T) = 2.8$ K, and $u(p) = 0.1$ kPa.

components 1 and 2 (γ_1 and γ_2), which were calculated for Δg_{12} and Δg_{21} (eq 3), equals 1.0, according to eqs 1 to 5.[3]

$$P_1 = \gamma_1 x_1 P_1^V, \quad P_2 = \gamma_2 x_2 P_2^V \tag{1}$$

$$P_{cal} = P_1 + P_2 \tag{2}$$

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right],$$

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

$$\tau_{12} = \frac{\Delta g_{12}}{RT}, \quad \tau_{21} = \frac{\Delta g_{21}}{RT} \tag{4}$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}), \quad G_{21} = \exp(-\alpha_{12}\tau_{21}) \tag{5}$$

Table 7. System 2-Ethoxyethyl Acetate (1) and 2-Butoxyethanol (2): Measured and Calculated Variables from the NRTL Model[a]

	measured variables			calculated variables					
run	x_1	T/K	P/kPa	γ_1	γ_2	P_1/kPa	P_2/kPa	P_{cal}/kPa	T_{cal}/K
1	0.10	440.2	93.8	1.14	1.00	15.7	80.7	96.4	439.2
2	0.20	437.4	94.2	1.08	1.01	27.2	66.8	94.1	437.3
3	0.30	435.4	94.2	1.04	1.03	37.0	55.9	92.9	435.7
4	0.36	434.4	94.2	1.03	1.03	41.9	50.4	92.3	434.9
5	0.40	434.6	93.6	1.02	1.04	47.3	47.2	94.5	434.3
6	0.48	433.2	93.6	1.01	1.05	53.1	40.2	93.3	433.4
7	0.54	432.1	93.8	1.00	1.05	58.7	34.0	92.7	432.5
8	0.66	431.1	93.8	1.00	1.06	69.3	24.5	93.8	431.1
9	0.77	430.7	93.8	1.00	1.06	79.1	16.9	96.0	429.9
10	0.88	429.4	93.8	1.00	1.05	88.2	8.0	96.2	428.5

[a] $u(x) = 1.1 \times 10^{-4}$, $u(T) = 1.2$ K, and $u(p) = 0.4$ kPa.

Table 8. System 2-Ethoxyethyl Acetate (1) and 2-Butoxyethyl Acetate (2): Measured and Calculated Variables from the NRTL Model[a]

	measured variables			calculated variables					
run	x_1	T/K	P/kPa	γ_1	γ_2	P_1/kPa	P_2/kPa	P_{cal}/kPa	T_{cal}/K
1	0.12	457.0	93.9	0.93	1.00	21.9	72.8	94.7	456.5
2	0.23	453.0	93.9	0.95	1.00	39.8	56.3	96.1	452.0
3	0.26	451.2	93.6	0.95	0.99	43.6	51.1	94.7	450.7
4	0.33	448.2	93.6	0.96	0.99	51.0	42.4	93.5	448.2
5	0.37	445.8	93.6	0.96	0.99	54.7	36.8	91.5	446.5
6	0.45	442.6	93.3	0.97	0.98	61.4	29.1	90.6	443.7
7	0.51	440.4	93.3	0.97	0.98	66.7	23.9	90.7	441.5
8	0.58	439.0	93.3	0.98	0.97	73.2	19.6	92.8	439.2
9	0.66	437.3	93.3	0.99	0.96	81.0	14.7	95.6	436.4
10	0.75	435.0	93.3	0.99	0.94	87.0	9.8	96.9	433.7
11	0.88	431.6	93.3	1.00	0.92	93.6	4.0	97.7	430.0

[a] $u(x) = 1.2 \times 10^{-4}$, $u(T) = 2.1$ K, and $u(p) = 0.4$ kPa.

Table 9. System 2-Butoxyethanol (1) and 2-Butoxyethyl Acetate (2): Measured and Calculated Variables from the NRTL Model[a]

	measured variables			calculated variables					
run	x_1	T/K	P/kPa	γ_1	γ_2	P_1/kPa	P_2/kPa	P_{cal}/kPa	T_{cal}/K
1	0.12	458.9	93.9	1.09	1.00	18.9	76.9	95.8	458.1
2	0.23	455.4	93.9	1.08	1.00	33.9	60.5	94.4	455.1
3	0.36	452.2	93.9	1.07	1.01	47.8	46.1	93.9	452.1
4	0.44	450.1	93.9	1.06	1.01	54.5	38.3	92.7	450.5
5	0.52	448.0	93.9	1.05	1.02	60.9	30.8	91.6	448.8
6	0.53	448.8	93.9	1.05	1.02	63.0	31.1	94.1	448.7
7	0.58	448.0	93.9	1.04	1.03	66.6	27.5	94.2	447.8
8	0.62	447.5	93.9	1.03	1.04	70.6	24.4	95.0	447.0
9	0.69	446.6	93.9	1.02	1.06	75.9	19.7	95.6	445.9
10	0.79	445.0	93.9	1.01	1.09	82.4	12.9	95.4	444.4
11	0.89	443.4	93.9	1.00	1.14	87.8	6.8	94.6	443.1

[a] $u(x) = 1.1 \times 10^{-4}$, $u(T) = 1.1$ K, and $u(p) = 0.1$ kPa.

dx.doi.org/10.1021/je200565u |J. Chem. Eng. Data 2011, 56, 4157–4163

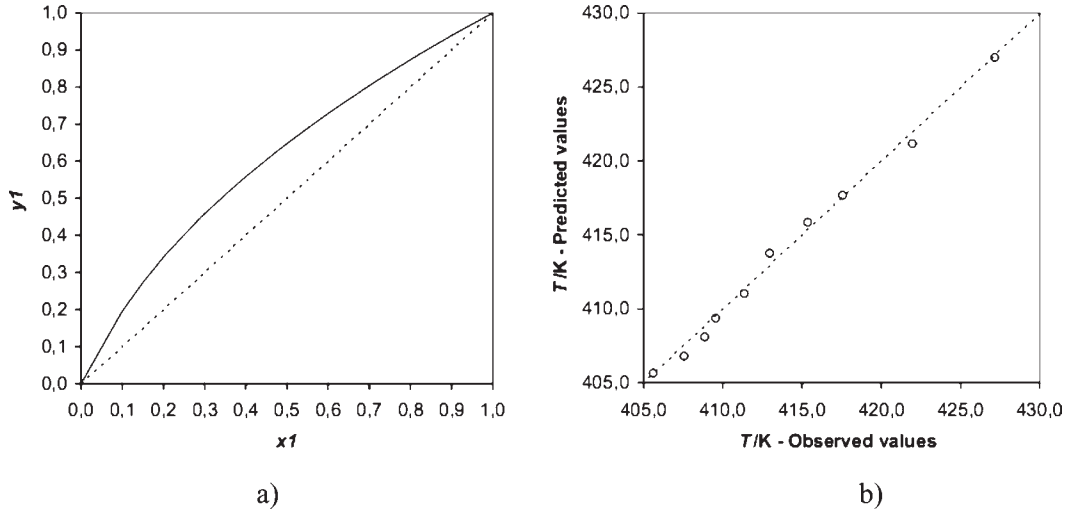

Figure 2. 2-Ethoxyethanol (1) + 2-ethoxyethyl acetate (2) system, for P_{ave} = 93.5 and s = 0.2 kPa. (a) xy diagram and (b) observed and predicted temperatures by NRTL model.

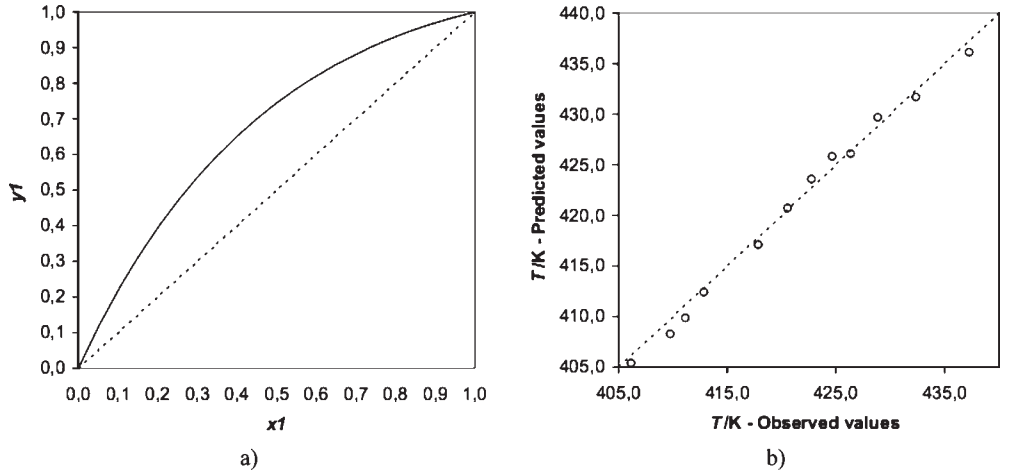

Figure 3. 2-Ethoxyethanol (1) and 2-butoxyethanol (2) system, for P_{ave} = 92.8 and s = 0.8 kPa. (a) xy diagram and (b) observed and predicted temperatures by NRTL model.

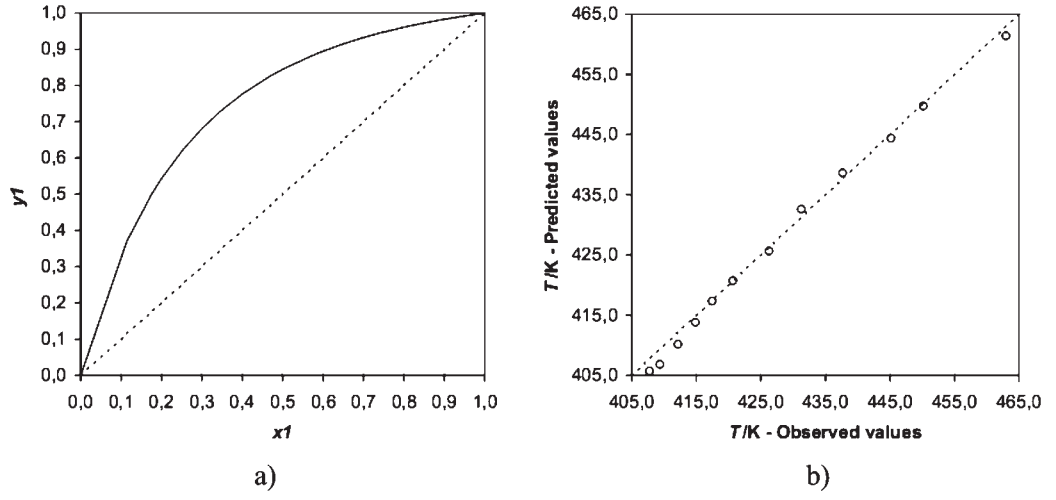

Figure 4. 2-Ethoxyethanol (1) and 2-butoxyethyl acetate (2) system, for P_{ave} = 93.7 and s = 0.1 kPa. (a) xy diagram and (b) observed and predicted temperatures by NRTL model.

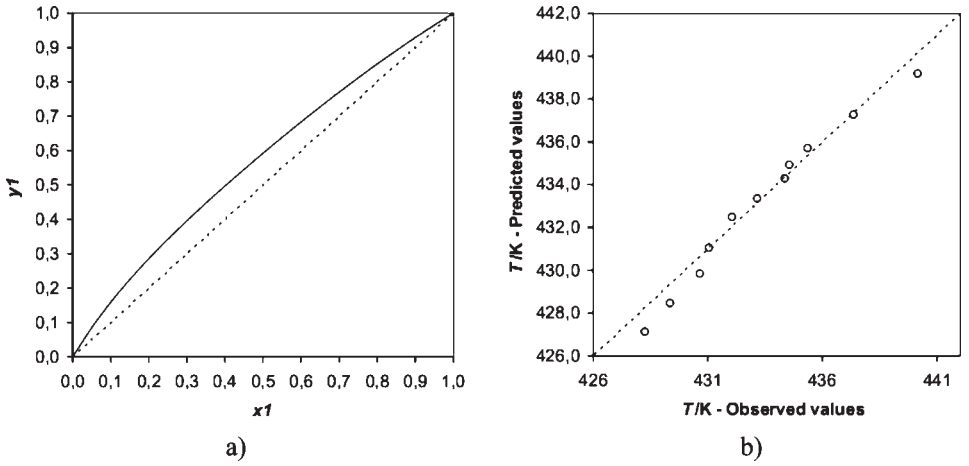

Figure 5. 2-Ethoxyethyl acetate (1) and 2-butoxyethanol (2) system, for P_{ave} = 93.9 and s = 0.2 kPa. (a) xy diagram and (b) observed and predicted temperatures by NRTL model.

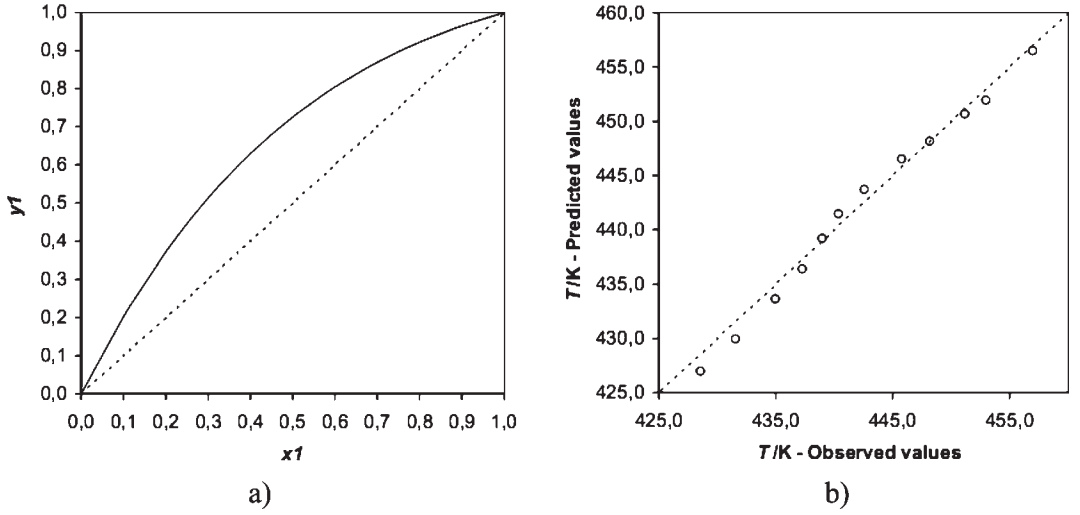

Figure 6. 2-Ethoxyethyl acetate (1) and 2-butoxyethyl acetate (2) system, for P_{ave} = 93.5 and s = 0.2 kPa. (a) xy diagram and (b) observed and predicted temperatures by NRTL model.

By using the method of least-squares, parameters Δg_{12} and Δg_{21} of NRTL model were adjusted to minimize the function (F), as recommended by Gmehling and Onken:[13]

$$F = \sum_{i=1}^{N} (P - P_{cal})^2 \qquad (6)$$

N is the total number of measurements for each binary mixture. The α parameter was equal to 0.3, as recommended by Prausnitz, Lichtentaler, and Azevedo for binary systems with scarce experimental data available.[4]

To minimize the function F, the SOLVER tool in Microsoft Excel 2003 was used. The 'Solver' routine uses the generalized reduced gradient (GRG) method.[15]

The uncertainty of temperature was evaluated using the predict temperature by NRTL model and measured temperatures. The NRTL model parameters (2, that are Δg_{12} and Δg_{21}) were estimated for each pair from n measured temperatures, and the uncertainty of temperature was evaluated from statistical methods for $(n - 2)$ degrees of freedom.

For the pressure (p), the standard uncertainty was evaluated as the standard deviation of the average from independent observations indicated in Tables 4 through 9. For the system 2-butoxyethanol + 2-butoxyethyl acetate, only one measured local atmospheric pressure has been done. In this case, the uncertainty was considered as the uncertainty of the mercury barometer. This pressure value (93.9 kPa) was used for all tests in this system.

For the molar fraction (x), the uncertainty was evaluated from the combined standard uncertainty of the measurement result using the law of propagation of uncertainty, assuming 0.01 g as the uncertainty from the digital balance.

All uncertainties were evaluated using 2 as the coverage factor.

3. RESULTS

Vapor Pressure. The equations, references and parameters used for calculating the steam pressure of each component are showed in Table 1. Table 2 shows the measured boiling temperatures at atmospheric pressure (T_e) and the calculated temperature ($T_{e,calc}$) using the equations in Table 1. The vapor

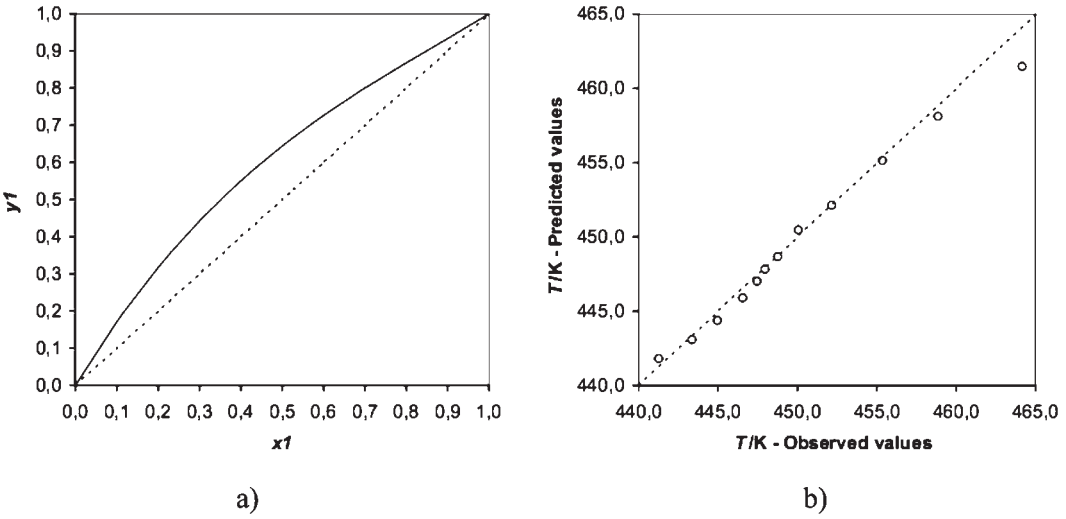

Figure 7. 2-Butoxyethanol (1) and 2-butoxyethyl acetate (2) system, for P = 93.9. (a) xy diagram and (b) observed and predicted temperatures by NRTL model.

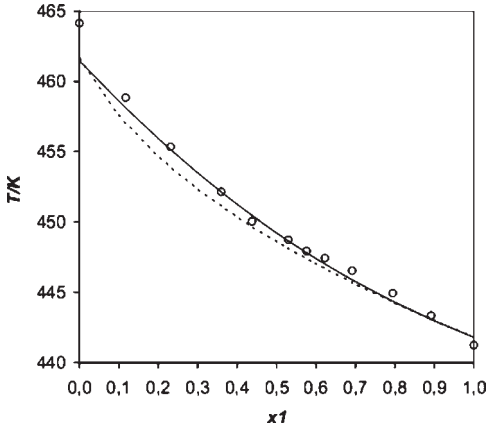

Figure 8. $T-x$ diagram for the system 2-butoxyethanol (1) and 2-butoxyethyl acetate: experimental data (this work); —, NRTL model with estimated parameters (this work); ---, Wilson model proposed by Wilding et al.[4]

pressure of the 2-butoxyethyl acetate is given by equation and Antoine; for the other chemicals, the vapor pressure is calculated from the equation DIPPR (Design Institute for Physical Properties).

Estimated NRTL Parameters. Table 3 shows the parameters of the NRTL model. Tables 4 to 9 show measured and calculated variables. The predicted temperatures (T_{cal}) were calculated by the NRTL model, assuming that F function is zero, using the parameters from Table 3.

Uncertainties (u) for measured variables (x, T, p) are reported in the data in Tables 4 to 9.

The main advantage of the employed methodology is its quickness in the estimation of parameters and in the obtaining of preliminary data from binary mixtures. Such methodology has also the advantage of not demanding physical and chemical analysis. The expectation was that the activity coefficients calculated did not show large deviations from ideality, and this result was confirmed. These results can be explained due to the similar polarities and chemical characteristics (same functional groups) of the components in the binary systems evaluated. The low deviations from ideality justify the application of the proposed experimental methodology. For systems whose components have large difference in polarity, this methodology is not recommended.

Figures 2 to 7 show the xy diagrams and the comparison between predicted and observed values for the six binary systems tested, whose bubble points were measured at local atmospheric pressure, as indicated in Tables 4 to 9. To estimate the predicted value, the average pressure of each binary system (P_{ave}) was considered, with standard deviation (s) are shown in Figures 2 to 7, except for the system 2-butoxyethanol +2-butoxyethyl acetate, in which one measured of the local atmospheric pressure has been done.

For the binary system 2-butoxyethanol +2-butoxyethyl acetate, the results obtained from this work were compared to those obtained by Wilding et al.,[4] by using the Wilson[16] model. The graph in Figure 8 shows the results from the NRTL model, by using the parameters estimated in this work, the results using the Wilson model with parameters estimated by Wilding et al. and the experimental results of this work. Wilding et al.[4] performed isothermal experiments to obtain the activity coefficients; for T = 443.2 K and 2-butoxyethanol mole fraction of liquid phase in (x_1) equal to 0.9085, they obtained results γ_1 = 1.001 and γ_2 = 1.117. In this study, for temperature of 443.4 K and liquid phase molar fraction x_1 = 0.89, results γ_1 = 1.00 and γ_2 = 1.14 were obtained, which are very close to the values obtained by Wilding, Giles and Wilson,[4] who used a more accurate methodology. The fugacity coefficients in the vapor phase obtained by Wilding et al.,[4] for this binary system, range from 0.95 to 0.98, showing that the behavior of the vapor phase is very close to ideality. This result enhances the adopted hypothesis of ideality of the vapor phase, not only for the binary system 2-butoxyethanol +2-butoxyethyl acetate, but also for other systems, due to the similarity of the functional groups of molecules.

4. CONCLUSIONS

In this work, pTx data for six binary mixtures of system 2-ethoxyethanol + 2-ethoxyethyl acetate + 2-butoxyethanol + 2-butoxyethyl acetate were correlated to the NRTL activity coefficient model. For the six pairs evaluated, small deviations

from ideality were found in the liquid phase. The constants Δg_{12} and Δg_{21} from NRTL model was obtained and it was α_{12} = 0.3 was adopted. The NRTL was well fitted to the experimental data.

AUTHOR INFORMATION

Corresponding Author

*Tel.: + 55 11 3091-2252. Fax.: + 55 11 3091-2238. E-mail address: mtaqueda@usp.br.

Funding Sources

The authors thank CAPES ("Coordenação de Aperfeiçoamento de Pessoal de Nível Superior") for financial support.

ACKNOWLEDGMENT

The authors thank Oxiteno Indústria e Comércio S/A for the supplied chemicals.

NOMENCLATURE

A	Antoine or DIPPR equation parameter
B	Antoine or DIPPR equation parameter
C	Antoine or DIPPR equation parameter
D	DIPPR equation parameter
E	DIPPR equation parameter
F	Function to be minimized
G_{12}	NRTL model parameter, dimensionless
G_{21}	NRTL model parameter, dimensionless
N	number of samples for each binary system
P	pressure, kPa
P_1	partial pressure of component 1, kPa
P_2	partial pressure of component 2, kPa
P_{ave}	average pressure, kPa
P_{cal}	calculated pressure, kPa
P^V	vapor pressure, kPa
R	gas constant, $J \cdot mol^{-1} \cdot K^{-1}$
s	standard deviation, kPa
T	measured temperature, K
T_{cal}	calculated temperature, K
T_e	boiling point temperature, K
$T_{e,cal}$	calculated boiling point temperature, K
u	uncertainty for measured variables
x_1	component 1 molar fraction (more volatile) in liquid phase, dimensionless
x_2	component 2 molar fraction (less volatile) in liquid phase, dimensionless
y_1	component 1 molar fraction (more volatile) in vapor phase, dimensionless
y_2	component 2 molar fraction (less volatile) in vapor phase, dimensionless
Δg_{12}	NRTL model parameter, J/mol
Δg_{21}	NRTL model parameter, J/mol

Greek Letters

α_{12}	NRTL model parameter, dimensionless
γ_1	activity coefficient for component 1 (more volatile), dimensionless
γ_2	activity coefficient for component 2 (less volatile), dimensionless
τ_{12}	NRTL model parameter, dimensionless
τ_{21}	NRTL model parameter, dimensionless

REFERENCES

(1) Kojima, K.; Tochigi, T. *Prediction of Vapor-Liquid Equilibria by the ASOG Method*; Elsevier: Amsterdam, 1979.

(2) Fredenslund, A.; Gmehling, J.; Rassmussen, P. *Vapour-Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977.

(3) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mistures. *AIChE J.* **1968**, *14*, 135–144.

(4) Wilding, W. V.; Giles, N. F.; Wilson, L. C. Phase Equilibrium Measurements on Nine Binary Mixtures. *J. Chem. Eng. Data* **1996**, *41*, 1239–1251.

(5) Oxiteno's Technical Bulletin. http://www.oxiteno.com.br/aplicacoes/mercados/doc/documento.asp?artigotecnico=29&segmento=0500&idioma=PO&r=.pdf. Accessed 05/19/2011.

(6) The Dow Chemical Company. Product Safety Assessment Ethylene Glycol Butyl Ether Acetate. 2007, acessed in 05/15/2011; http://www.dow.com/PublishedLiterature/dh_00c8/0901b803800c88fc.pdf?filepath=productsafety/pdfs/noreg/233-00340.pdf&fromPage=GetDoc.

(7) Stoye, D.; Freitag, W. *Paints, Coatings and Solvents*. Wiley-VCH Verlag GmbH: Weinheim, 1998.

(8) Antosik, M.; Fras, Z.; Malanowski, S. Vapor-Liquid Equilibrium in 2-Ethoxyethanol + Methanol at 313.15 to 333.15 K. *J. Chem. Eng. Data* **1999**, *44*, 368–372.

(9) Chiavone-Filho, O.; Proust, P.; Rasmussen, P. Vapor-liquid Equilibria for Glycol Ether + Water Systems. *J. Chem. Eng. Data* **1993**, *38*, 128–131.

(10) Yaws, C. *Chemical Properties Handbook: Physical, Thermodynamics, Environmental Transport, Safety & Health Related Properties for Organic & Inorganic Chemical*; McGraw-Hill: New York, 1999.

(11) Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A. Vapor Pressure of Acetophenone, (±)-1,2-Butanediol, (±)-1,3-Butanediol, Diethylene Glycol Monopropyl Ether, 1,3-Dimethyladamantane, 2-Ethoxyethyl Acetate, Ethyl Octyl Sulfide, and Pentyl Acetate. *J. Chem. Eng. Data* **1996**, *41*, 1255–1268.

(12) Lee, M.; Su, C.; Lin, H. Vapour Pressures of Morpholine, Diethyl Methylmalonate, and Five Glycol Ethers at Temperatures up to 473,15 K. *J. Chem. Eng. Data* **2005**, *50*, 1535–1538.

(13) Gmehling, J.; Onken, U. *Vapor-Liquid equilibrium data collection*; Frankfurt/Main Dechema; Port Washington, NY, 1991; Vol. 1.

(14) Prausnitz, J. M.; Lichtentaler, R. N.; Azevedo, E. G. *Molecular Thermodynamics of Fluid Phase Equilibria*. Prentice-Hall PTR: NJ, 1999.

(15) Microsoft Office Excel 2003, Help

(16) Wilson, G. M. Vapour-Liquid Equilibrium. XI. A New expression for the excess free energy of mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127–130.