

# Liquid–Liquid Equilibria of Nicotine + Water + Toluene at Various Temperatures

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The object of the present work is to evaluate the use of toluene as an alternative solvent for nicotine extraction from aqueous-leached solutions of tobacco wastes. The liquid–liquid equilibrium data of the ternary system water + toluene + nicotine has been determined at 295, 303, and 313 K. The results have been correlated using the UNIQUAC and NRTL equations with linear temperature-dependent parameters. It is concluded that toluene is an effective agent for nicotine extraction.

## Introduction

Tobacco dust is a waste byproduct of cigarette manufacture. A way to increase the value of this waste is the recovery of nicotine present in the dust for use as an insecticide. Nicotine, together with other water-soluble compounds present in the tobacco leaves can be easily extracted from tobacco dust using only pure water as solvent, with an acceptable yield. After that, nicotine must be recovered and concentrated from the leached solution in a second step.<sup>1</sup> Solvent extraction has been found to be an effective means of recovering nicotine from aqueous solution using kerosene and hexane as solvent.<sup>2</sup>

The object of the present work is the evaluation of toluene as an alternative solvent for nicotine extraction from aqueous-leached solutions in order to increase the efficiency of the extraction process. The availability of the relevant liquid–liquid equilibrium data is required for the design and simulation of extraction processes, and the data are of intrinsic thermodynamic interest.

In this paper, we report liquid–liquid extraction data for the ternary system water + toluene + nicotine, for which no such data have previously been published. Excess free energy equations, such as the nonrandom, two-liquid NRTL equation<sup>3</sup> and the universal quasi-chemical UNIQUAC equation,<sup>4</sup> have been applied for the correlation of this liquid–liquid system. The experimental data were regressed to obtain numerical values for the interaction parameters of these equations at different temperatures.

## Experimental Section

**Chemicals.** All chemicals used in this investigation were analytical grade and were used directly without any further purification (nicotine, Fluka 99% purity; toluene, Panreac 99.5% purity). Demineralized water was used throughout the experimental work.

**Procedure.** Samples were prepared in hermetically sealed vials. The vials were submerged in a temperature-controlled orbital agitated bath. The bath water temperature was controlled within  $\pm 0.1$  K. The mixtures were

Table 1.  $r$  and  $q$  Values for the Used Compound

compound	$r_i$	$q_i$
water	1.7334	2.4561
nicotine	6.4515	6.1232
toluene	2.7915	3.1095

prepared by mass, with an accuracy of  $\pm 0.0001$  g, placed in the orbital stirrer bath, and shaken for 2 h. After that, the agitation was stopped and the mixture was then left to settle for 5 h. Samples were taken using a syringe from the upper and the lower phases through a sampling stopcock. A series of liquid–liquid equilibrium measurements were made by changing the composition of the mixture in order to determine the solubility curve and the tie line.

The pH of the aqueous phase was measured after and before the experiments to ensure that the pH was  $> 9.5$  in all the cases.

The nicotine composition of the mixture was determined according to the method proposed by Willits and Swain,<sup>5</sup> using a Shimadzu UV-1603 model; the standard accuracy and reproducibility was found to be  $\pm 0.1\%$ . The water composition was determined by the Karl Fischer method by means of a Metrohm 701 KF Titrino model. Triplicate samples of each phase were taken, and the average value was used. Statistical measures of the repeatability and uncertainty of the final data were performed with a gravimetrically prepared standard mixture, giving an error of  $\pm 0.12\%$ .

## Model and Prediction

If a liquid mixture of a given composition and at a known temperature is separated into two phases, the compositions of the two phases can be calculated from the following equations:

$$\gamma^I x^I = \gamma^{II} x^{II} \quad (1)$$

$$z_i = z_i^I + z_i^{II} \quad (2)$$

where  $z_i$ ,  $z_i^I$ , and  $z_i^{II}$  are the numbers of moles of component  $i$  in the system and in phases I and II, respectively, and  $\gamma^I$  and  $\gamma^{II}$  are the corresponding activity coefficients of component  $i$  in phases I and II, as calculated from the NRTL

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**Table 2. Comparing Experimental and Predicted LLE Data for the Ternary System Nicotine + Water + Toluene (in Molar Fractions of Component)<sup>a</sup>**

raffinate phase						extract phase					
nicotine (2)			water (1)			nicotine (2)			water (1)		
$x_{\text{exp}}$	$x_{\text{UNIQUAC}}$	$x_{\text{NRTL}}$	$x_{\text{exp}}$	$x_{\text{UNIQUAC}}$	$x_{\text{NRTL}}$	$x_{\text{exp}}$	$x_{\text{UNIQUAC}}$	$x_{\text{NRTL}}$	$x_{\text{exp}}$	$x_{\text{UNIQUAC}}$	$x_{\text{NRTL}}$
$T = 295 \text{ K}$											
0.0031	0.0045	0.0059	0.9966	0.9946	0.9930	0.1023	0.0703	0.0537	0.0197	0.0110	0.03335
0.0061	0.0074	0.0089	0.9932	0.9900	0.9900	0.1406	0.1160	0.0974	0.0273	0.0230	0.0447
0.0091	0.0107	0.0121	0.9898	0.9882	0.9867	0.1799	0.1521	0.1355	0.0404	0.0409	0.0603
0.0146	0.0150	0.0166	0.9838	0.9830	0.9820	0.2208	0.2054	0.1946	0.0610	0.0673	0.0822
0.0261	0.0233	0.0235	0.9717	0.9747	0.9747	0.2467	0.2768	0.2747	0.0915	0.0944	0.1050
0.0319	0.0305	0.0294	0.9653	0.9772	0.9686	0.2684	0.2803	0.2910	0.1019	0.1138	0.1199
0.0539	0.0524	0.0488	0.9415	0.9434	0.9480	0.2834	0.2926	0.3127	0.1267	0.1378	0.1395
0.0520	0.0541	0.0496	0.9423	0.9417	0.9473	0.2925	0.2808	0.3065	0.1284	0.1458	0.1454
0.0748	0.0763	0.0717	0.9183	0.9166	0.9237	0.3029	0.2971	0.3159	0.1711	0.1811	0.1754
0.1061	0.1106	0.1104	0.8844	0.8769	0.8824	0.3022	0.2901	0.2904	0.1877	0.1930	0.1869
0.1098	0.1154	0.1157	0.8795	0.8712	0.8766	0.3041	0.2893	0.2885	0.1970	0.2016	0.1942
0.1441	0.1500	0.1598	0.8393	0.8285	0.8285	0.3098	0.2978	0.2796	0.2518	0.2505	0.2383
0.1838	0.1559	0.1746	0.7817	0.8028	0.8016	0.2843	0.3353	0.2993	0.4264	0.3954	0.3755
*0.2932			0.4854			0.2929			0.4856		
$T = 303 \text{ K}$											
0.0004	0.0009	0.0039	0.9992	0.9989	0.9951	0.0504	0.0257	0.0058	0.0159	0.0022	0.0116
0.0020	0.0024	0.0074	0.9974	0.9973	0.9916	0.0925	0.07624	0.0254	0.0191	0.0082	0.0196
0.0059	0.0051	0.0118	0.9932	0.9946	0.9871	0.1416	0.1637	0.0710	0.0291	0.0213	0.0344
0.0087	0.0074	0.0147	0.9902	0.9922	0.9841	0.1791	0.2104	0.1061	0.0453	0.0375	0.0525
0.0142	0.0123	0.0199	0.9843	0.9872	0.9788	0.2229	0.2577	0.1596	0.0622	0.0617	0.0786
0.0174	0.0185	0.0261	0.9808	0.9810	0.9725	0.2600	0.2446	0.1733	0.0590	0.0806	0.0977
0.0233	0.0241	0.0293	0.9739	0.9753	0.9690	0.2943	0.2852	0.2339	0.1094	0.1233	0.1449
0.0341	0.3301	0.0379	0.9639	0.9550	0.9601	0.3292	0.3134	0.2963	0.1423	0.1669	0.1902
0.0455	0.0452	0.0425	0.9499	0.9534	0.9546	0.3298	0.3325	0.3531	0.2157	0.2151	0.2377
0.0688	0.0812	0.0683	0.9226	0.9158	0.9268	0.3394	0.2880	0.3421	0.2207	0.2296	0.2501
0.0983	0.1046	0.0848	0.8940	0.8897	0.9070	0.3377	0.3175	0.3916	0.3212	0.3146	0.3268
0.1220	0.1184	0.0964	0.8668	0.8720	0.8908	0.3167	0.3262	0.4009	0.4194	0.3954	0.3974
*0.25891			0.6324			0.2589			0.6324		
$T = 313 \text{ K}$											
0.0006	0.0006	0.0005	0.9993	0.9993	0.9984	0.0526	0.0582	0.0632	0.0091	0.0021	0.0057
0.0017	0.0013	0.0012	0.9982	0.9986	0.9977	0.0901	0.1134	0.1249	0.0128	0.0069	0.0117
0.0026	0.0026	0.0027	0.9972	0.9972	0.9963	0.1525	0.1475	0.1446	0.0315	0.0241	0.0335
0.0041	0.0037	0.0039	0.9957	0.9962	0.9951	0.1892	0.2072	0.1953	0.0511	0.0412	0.0568
0.0055	0.0054	0.0061	0.9942	0.9945	0.9929	0.2338	0.2358	0.2090	0.0725	0.0676	0.0937
0.0071	0.0075	0.0088	0.9925	0.9924	0.9903	0.2694	0.2567	0.2194	0.0874	0.0925	0.1289
0.0100	0.0113	0.0138	0.9895	0.9886	0.9853	0.3170	0.2821	0.2310	0.1131	0.1345	0.1878
0.0138	0.0155	0.0195	0.9856	0.9843	0.9796	0.3546	0.3443	0.2504	0.1635	0.1909	0.2603
0.0181	0.0199	0.0234	0.9812	0.9800	0.9756	0.3675	0.3340	0.2836	0.1745	0.2087	0.2821
0.0211	0.0215	0.0251	0.9781	0.9784	0.9739	0.3691	0.3625	0.3105	0.2292	0.2483	0.3213
0.0356	0.0309	0.0313	0.9633	0.9688	0.9672	0.3536	0.4085	0.4022	0.3588	0.3454	0.4001
0.0777	0.0696	0.0539	0.9193	0.9286	0.9414	0.3172	0.3540	0.4571	0.4946	0.4632	0.4819
0.1079	0.1107	0.0836	0.8852	0.8854	0.9077	0.3099	0.3020	0.3998	0.5412	0.5250	0.5285
*0.19982			0.7597			0.1998		0.7597			

<sup>a</sup> Values marked with an asterisk correspond to plait points.

and UNIQUAC equations. The measured ternary-component equilibrium data were used to determine the interaction parameters between nicotine/water/toluene; these in turn were used to estimate the activity coefficients from the NRTL and the UNIQUAC equations.

The  $r$  and  $q$  values for the UNIQUAC model, calculated using the UNIFAC<sup>6</sup> group contribution method, are shown in Table 1. The NRTL correlation was done with  $\alpha = 0.2$ , a value commonly used in the literature. Moreover, the NRTL-fit was improved by adjusting the  $\alpha_{\text{water-tol}}$  parameter simultaneously with the rest of the parameters. The best fitting was obtained with a  $\alpha$  value equal to 0.1917, not very different from the used value 0.2. From a statistical point of view, the deviation with  $\alpha_{\text{water-tol}} = 0.1917$  was 0.005 589, compared to the deviation with  $\alpha_{\text{water-tol}} = 0.2$ , that is 0.005 666 3; for that reason, 0.2 was chosen for practical purposes.

Equation 1 was solved to calculate the mole fraction ( $x$ ) of component  $i$  in each liquid phase. This method of calculation gives a single tie line.

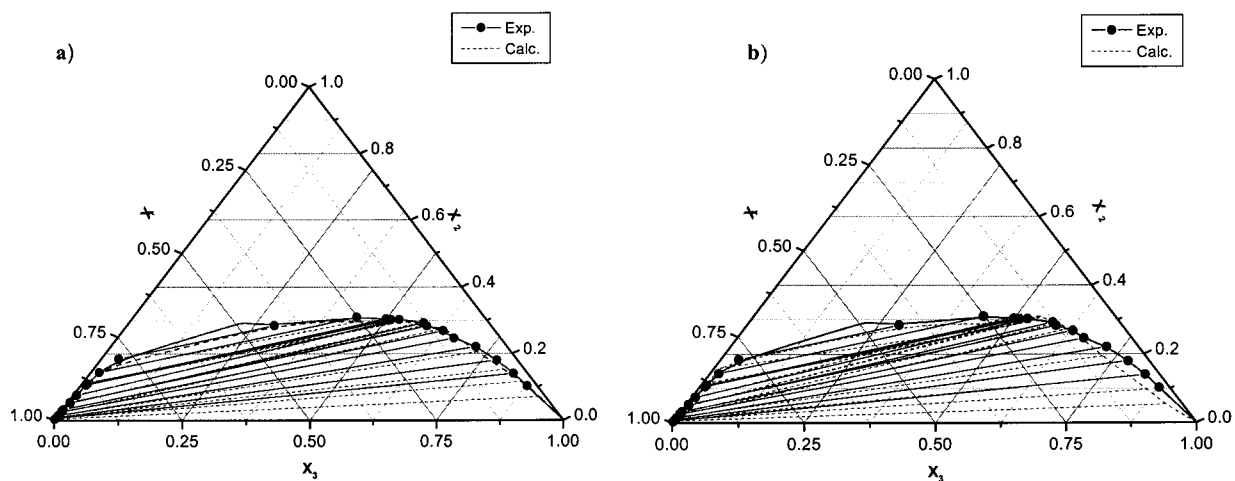
## Results and Discussion

The experimental data were used to calculate the optimum UNIQUAC and NRTL binary interaction parameters between the different constituents of the ternary system. The NRTL and UNIQUAC equations were fitted to experimental data using an interactive computer program based on Marquardt's algorithm developed by Valverde et al.<sup>7</sup> The measured equilibrium mole percentages are shown in Table 2, together with the results of the model fittings. These values were used to plot the solubility curves and the tie lines that are shown in Figures 1–3. As can be seen, the theoretical results are in good agreement with the experimental ones.

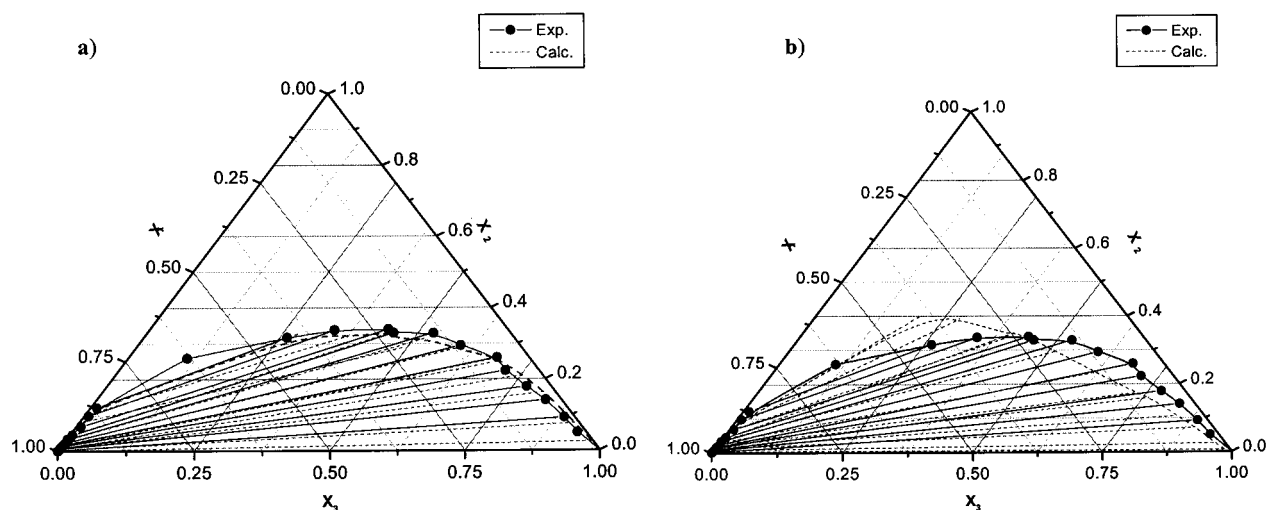
The values of the interaction parameters are shown in Table 3 and were fitted linearly with the temperature according to the equation

$$a_{ij} = a^{\circ}_{ij} + b_{ij}(T/\text{K} - 273) \quad (3)$$

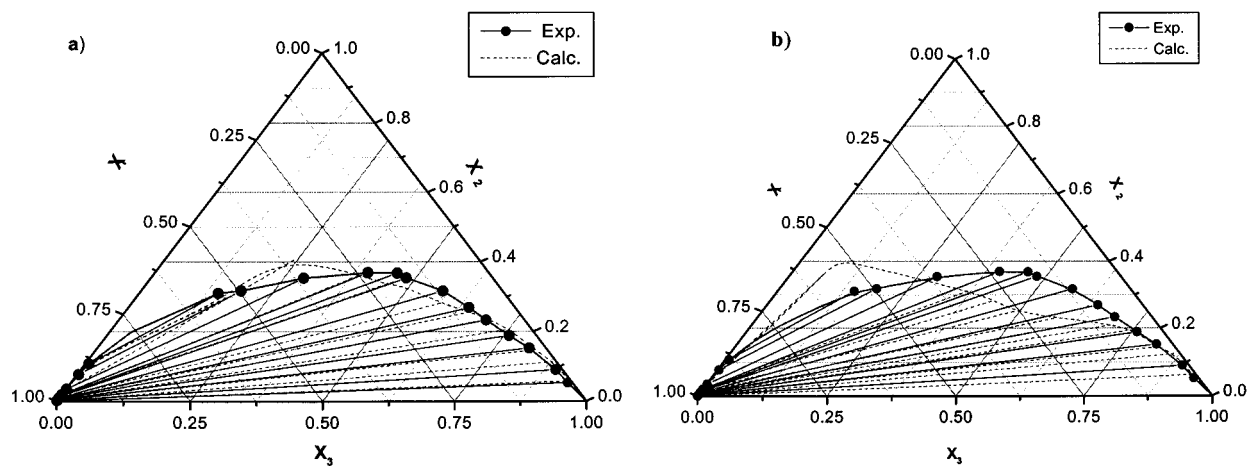
where  $T$  is the temperature in Kelvin and  $a^{\circ}_{ij}$  and  $b_{ij}$  are



**Figure 1.** Solubility curves for the system water (1) + nicotine (2) + toluene (3) at  $T = 295$  K: a, UNIQUAC model; b, NRTL model; —, experimental; ---, calculated (% mole).



**Figure 2.** Solubility curves for the system water (1) + nicotine (2) + toluene (3) at  $T = 303$  K: a, UNIQUAC model; b, NRTL model; —, experimental; ---, calculated (% mole).



**Figure 3.** Solubility curves for the system water (1) + nicotine (2) + toluene (3) at  $T = 313$  K: a, UNIQUAC model; b, NRTL model; —, experimental; ---, calculated (% mole).

the optimum interaction parameters between two groups or components in the system.

The percentage deviation from experimental basis DEB% was calculated from the difference, in absolute value (ABS), between the experimental concentrations of nicotine in

each phase and the predictions of the models at each temperature, according to the following formula:

$$\text{DEB\%} = \text{ABS} \left( \frac{\text{exp} - \text{cal}}{\text{exp}} \right) \times 100 \quad (4)$$

**Table 3. Optimum Interaction Parameters According to the UNIQUAC and NRTL Models**

<i>i</i>	<i>j</i>	$a_{ij}^{\circ}/K$	$b_{ij}$
UNIQUAC			
nicotine	H <sub>2</sub> O	-105	-2.775
nicotine	toluene	151.3	24.1
H <sub>2</sub> O	nicotine	198.00	6.022
H <sub>2</sub> O	toluene	9.322	15.56
toluene	nicotine	-119.7	-5.017
toluene	H <sub>2</sub> O	-46.89	127.00
NRTL			
nicotine	H <sub>2</sub> O	-253.32	-10.84
nicotine	toluene	3891.88	-110.41
H <sub>2</sub> O	nicotine	1823.6	-3.5
H <sub>2</sub> O	toluene	1557.63	2.43
toluene	nicotine	-561.01	10.66
toluene	H <sub>2</sub> O	-148.54	40.32

**Table 4. DEB% Average Values for the Nicotine Concentration Obtained for the Studied Models at Different Temperatures**

<i>T/K</i>	UNIQUAC		NRTL	
	aqueous phase	organic phase	aqueous phase	organic phase
295	10.6	9.8	18.6	13.7
303	16.6	12.8	28.0	19.4
313	8.5	8.42	21.5	21.4
avg	11.9	10.3	22.7	18.1

The comparisons between the two models are shown in Table 4. The UNIQUAC model gave the lowest average DEB%, with an average value of 11.4%. Greater deviations are obtained for the low concentration values. UNIQUAC

gives a better fit of these values, resulting in a better prediction of the equilibrium behavior of the system.

### Conclusions

The liquid-liquid equilibrium of the nicotine/water/toluene system has been measured at different temperatures. As was expected, toluene is an effective agent for nicotine extraction. The experimental equilibrium data can be satisfactorily correlated using the UNIQUAC model with an average DEB of about 11%, this model being quite superior to NRTL in the prediction of the nicotine + water + toluene equilibrium.

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