Modeling Of Liquid-Liquid Equilibrium Data and Estimation of New Binary Interaction Parameters for NRTL Model for the Quaternary System Water/ Ethanol/1- Butanol / KCL at 298.15K

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ABSTRACT

The present study concerns experimental measurements of the salting-out effect on liquid-liquid phase equilibrium (LLE) of partially miscible systems such as water/ ethanol/1- butanol /Potassium chloride at 298.15K. The salt KCl was used at different mass percentages of 5, 10 and 15. The binodal and tie line data were determined by the cloud point method. The addition of the salt showed to be effective in altering the LLE of water/ ethanol/1- butanol system in favor of the solvent extraction of ethanol from the aqueous solution particularly at high salt concentrations. The experimental data were correlated considering the modified version of the NRTL model for the activity coefficient, with the estimation of new binary interaction parameters corresponding to salt-solvent and solvent-solvent pairs. The deviations between experimental and calculated compositions in both phases for the ternary system using these new interaction parameters showed the ability of NRTL to determine liquid-liquid equilibrium data of the studied systems in the presence of the salts.

Keywords: Salt Effect, Solubility, LLE, NRTL Model, Interaction Parameter.

1. INTRODUCTION

The presence of a salt or a non-volatile solute in a solvent mixture, is of increasing interest due to its influence on separation processes in chemical engineering. The effect of salts addition in distillation had been studied by several investigators. The results have shown that it is possible by the addition of a suitable salt to alter the relative volatility of the system and also avoid the formation of an azeotrope. Similarly, the separation by solvent extraction also becomes increasingly more difficult as the tie-line becomes parallel to the solvent axis leading to a solutropy which has also to be avoided [1-4].

The effect of the addition of a suitable salt or a non-volatile solute can be seen in two ways: graphically, by the variation in the size of the two-phases region as well as by significant changes in the tie-line slopes for a liquid-liquid equilibrium (LLE) mixture, to an extent which eliminates the solutropy, and induces quantitative changes of the solute distribution coefficient and the solvent selectivity. In recent years, liquid-liquid equilibria (LLE) have gained great interest in chemical technology. Due to the energy rising cost, new separation processes based on extraction are getting more attractive. Also it may be feasible to operate known processes at new conditions necessitating checks for liquid phase stability at various point of the process hence the need for calculating and predicting (LLE) compositions which may be calculated using any excess Gibbs energy model. Santos et al [4] estimated new interaction parameters between binary pairs of salt-solvent and solvent-solvent using NRTL model to correlate the ternary system of water-ethanol-1pentanol in the presence of Potassium bromide (KBr) at 298.15K and 313.15K, in agreement with Stragevitch and Avila [5]. These interactions parameters are functions of the temperature.

Tan's modified NRTL model [6] has shown its ability to predict fairly accurately the effect of salts on the activity coefficient of a solvent component in a solution using the solvent-salt interaction parameters obtained from appropriate boiling point data. A Tan's modified NRTL model has been used to predict the salt effect on (LLE) as in (VLE). The equation can be used to correlate the (LLE) data using the solvent-solvent interaction parameters of the same mixture without salt, at the same temperature. The salt-solvent interaction parameters can be assumed as a function of the salt concentration since the boiling point of a salt-solvent mixture varies with the concentration of the dissolved salt [7]. In this study, the experimental (LLE) of water, ethanol, 1-butanol and potassium chloride at various salt concentrations and at 298.15K were reported. The data were correlated by Tan's modified NRTL model [6], due to its simplicity and its proven quite good prediction of the LLE data

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2. EXPERIMENTAL

2.1 Materials

Ethanol and 1-butanol were supplied by Merck Eurolab with cerified purities higher than 99.5 % and 98.5 %, respectively. This was checked by refractive index measurements at T=293.15K with an accuracy of ±0.0004n_D. Densities were also measured using an Anton Paar (model DMA 5000) densimeter with a certified precision of (±10 -5 gcm^{-3}). The results were compared to literature data [8].

2.2. Experimental Procedure

Standard curves were determined by using the 'Cloud-Point' method which is described in detail by Letcher and Siswana [9]. The tie lines were determined by the method of the refractive index described in detail by Briggs and Coming [10]. The refractive index of the two phases at equilibrium, represented, respectively, by each extremity of the tie- lines was measured in order to determine their compositions, using the obtained calibration curve and then to draw point by point the equilibrium curves of the considered system. Binodal curves for each system were obtained by preparing binary mixtures of known volumes of the two partially miscible constituents and then by adding gradually the third constituent by means of a burette. The obtained ternary mixture was shaken at room temperature, by means of an agitator provided with a lamp to allow a good observation of the disappearance of the turbidity point, after which a small quantity of the solution was taken to measure the refractive index of each prepared sample by means of the refractometer (Type EUROMEX RD 645) with an accuracy of ±0.0004n_D.

After the turbidity disappearance the solution was sampled by means of a micropipette to measure the refractive index of each sample.

The binodal curves of the ternary systems were used for the determination of the composition of the phases at equilibrium for various tie-lines for the water/ethanol /1-butanol system at 298.15K. In order to determine experimental liquid-liquid equilibrium data ternary mixtures of solvent, solution and solute of volume equal to 10 ml but with different concentrations were prepared. The mixture was placed in an equilibrium cell, whereit was agitated in order to allow an intimate contact between the different phases, and the thermodynamic equilibrium was finally reached by letting the mixture at rest for 24 hours. The complete process was carried out at constant temperature, by using a thermostatic bath. After a necessary rest time, the mixture splitted into two clear and transparent liquid phases with a well defined interface, both phases were then separated by settling. Samples of the organic phase and the aqueous phase were subjected to the measure of the refractive index. The solubility of each constituent in each phase was determined by extrapolation from the binodal curves of the refractive index according to the fraction known for the constituent in the solution.

3. RESULTS AND DISCUSSION

3.1. Experimental Liquid-Liquid Equilibrium Data

The compositions of the different components of Water/ Ethanol/1-Butanol ternary system at 298.15K are presented in Table 2, where X_i denotes the mole fraction of the i^{th} component. Figures 1 to 4 show the corresponding binodal curves of the studied ternary mixtures.

The effect of the added salt amounts on the binodal curves are also shown in these figures where it can be seen that an increase in KCl amount led to an enlargement of the two phases region, inducing an increase of Ethanol and 1-Butanol miscibility.

Table 3 shows the experimental tie-line compositions of the equilibrium phases of the ternary system water/ ethanol/1-butanol at 298.15K. The superscripts I and II denote the organic and the aqueous phases, respectively.

The comparison between the equilibrium data obtained experimentally for the ternary system water/ ethanol/1-butanol at 298. 15K and those previously reported in the literature by Sorensen and Arlt [11] are presented in figure 5. An excellent concordance can be noticed between both results, confirming the reliability of the experimental procedure used in this work as well as the good accuracy.

Table 1. Pure components physical properties at 293.15K and 1 atm

Component	ρ/kgm^{-3}		Refractive index I_{nR}	
	This work	from Ref [8]	This work	from Ref[8]
Ethanol	0.7890	0.7894	1.3610	1.3605
1-Butanol	0.8100	0.8098	1.3982	1.3981

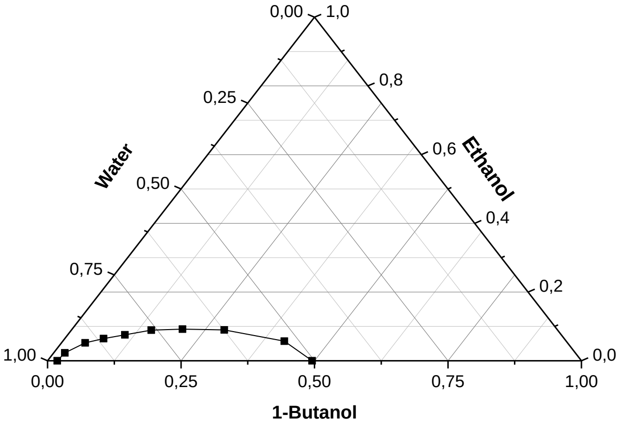

Fig. 1. Binodal curve of Water/Ethanol/1-Butanol system at 298.15K

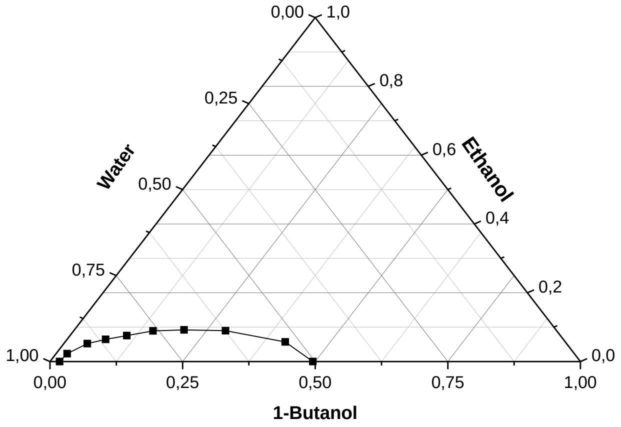

Fig. 2. Binodal curve of Water/Ethanol/1-Butanol/5% KCl system at 298.15K

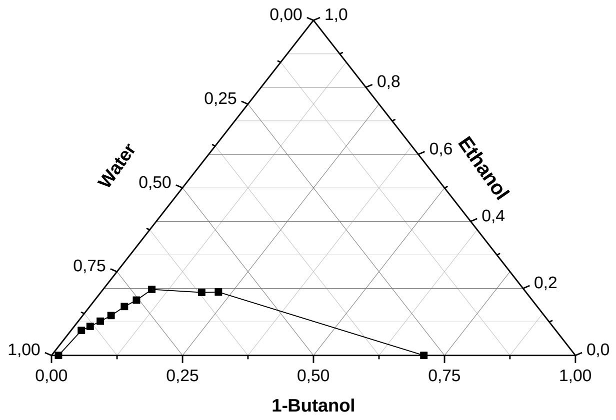

Fig. 4. Binodal curve of Water/Ethanol/1Butanol/15% KCl system at 298.15K

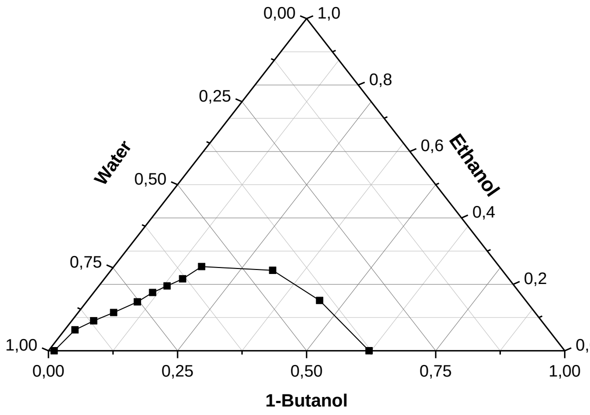

Fig. 3. Binodal curve of Water/Ethanol/1Butanol/10% KCl system at 298.15K

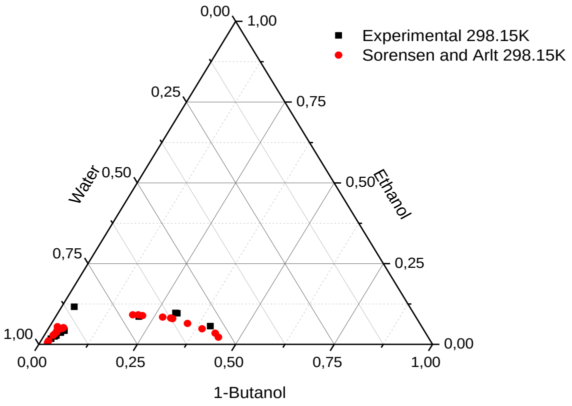

Fig. 5. Experimental LLE of the Water/ Ethanol/ 1-Butanol ternary system at 298.15K

Table 3. Experimental tie-line data for Water/ Ethanol/ 1-Butanol at 298.15K

Organic phase I			**Aqueous phase II**		
X$_{\text{Water}}$	**X**$_{\text{Ethanol}}$	**X**$_{\text{1-Butanol}}$	**X**$_{\text{Water}}$	**X**$_{\text{Ethanol}}$	**X**$_{\text{1-Butanol}}$
0.5360	0.0560	0.4080	0.9600	0.0170	0.0230
0.6000	0.0960	0.3040	0.9480	0.0240	0.0280
0.6040	0.0970	0.2990	0.9420	0.0270	0.0310
0.6610	0.0900	0.2490	0.9260	0.0360	0.0380
0.7020	0.0860	0.2110	0.9140	0.0420	0.0440

Table 4. Experimental and prediction tie-line data for Water/ Ethanol/1-Butanol/KCl in a free-salt basis at 298.15K

Organic phase I			**Aqueous phase II**		
X_{Water}	$X_{Ethanol}$	$X_{1\text{-}Butanol}$	X_{Water}	$X_{Ethanol}$	$X_{1\text{-}Butanol}$
5% KCl (X_S=1.205%)					
Experimental data					
0.4646	0.1580	0.3774	0.9503	0.0313	0.0184
0.5219	0.2068	0.2713	0.9224	0.0506	0.027
0.5688	0.2020	0.2292	0.9070	0.0601	0.0329
0.5908	0.1937	0.2155	0.8904	0.0695	0.0401
0.6340	0.1732	0.1928	0.8878	0.0710	0.0412
Predicted using NRTL model					
0.4601	0.1519	0.3880	0.9004	0.0511	0.0485
0.5527	0.1905	0.2568	0.8994	0.0653	0.0352
0.5667	0.1989	0.2343	0.8985	0.0686	0.0329
0.5690	0.2007	0.2340	0.8983	0.0693	0.0324
0.5669	0.1990	0.2302	0.8985	0.0686	0.0328
10% KCl (X_S=2.410%)					
Experimental data					
0.4320	0.1730	0.3953	0.9567	0.0278	0.0154
0.4714	0.2316	0.2970	0.9374	0.0411	0.0214
0.5281	0.2569	0.2148	0.9131	0.0568	0.0301
0.5976	0.2420	0.1602	0.8771	0.0787	0.0441
0.6314	0.2260	0.1425	0.8452	0.0975	0.0571
Predicted using NRTL model					
0.4129	0.1714	0.4158	0.9606	0.034	0.0540
0.4731	0.2223	0.3045	0.9357	0.0513	0.0130
0.5413	0.2446	0.2141	0.8997	0.07	0.0303
0.5939	0.2517	0.1544	0.8506	0.0882	0.0612
0.5987	0.2529	0.1485	0.8478	0.0901	0.0621
15% KCl (X_S=3.620%)					
Experimental data					
0.4986	0.1397	0.3617	0.9702	0.0272	0.0260
0.6030	0.1117	0.2853	0.8809	0.0895	0.0296
0.6396	0.1015	0.2589	0.8371	0.1195	0.0434
0.6473	0.0994	0.2533	0.8256	0.1274	0.0470
0.6742	0.0918	0.2340	0.8141	0.1354	0.0505
Predicted using NRTL model					
0.5965	0.1077	0.3173	0.8618	0.0852	0.0530
0.5987	0.1203	0.2935	0.8521	0.0996	0.0483
0.5982	0.1239	0.2815	0.8453	0.1077	0.0470
0.5975	0.1248	0.2786	0.8430	0.1101	0.0469
0.5980	0.0862	0.2772	0.8430	0.1106	0.0464

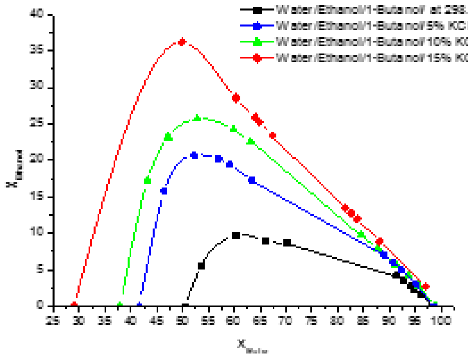

Fig. 6. Experimental LLE of the Water/Ethanol/1-Butanol/KCl system in a free-salt basis at 298.15K

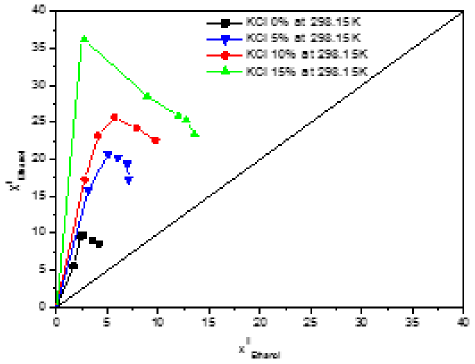

Fig. 7. Distribution curves of Ethanol obtained in different concentration of salt for the Water/Ethanol/1-Butanol/KCl system in a free-salt basis at 298.15K

Figure 6 shows the representation of the effect of the addition of the salt on the water/ethanol/1-butanol system in a free-salt basis at 298.15K, through a pseudoternary diagram. It can be seen from figure 6 that there is an increase in the area of immiscibility on addition of potassium bromide. The salt enlarged the area of the two-phase region; decreased the mutual solubility's of water marginally decreased the concentrations of ethanol and 1-butanol in the aqueous phase while significantly increased the concentrations of the same components in the organic phase. These effects essentially increased the heterogeneity of the system; which is an important consideration in designing a solvent extraction process. One way to analyze the salts effects is to compute the distribution curve of the organic, say ethanol in the present case, between the aqueous and organic phases. Also in order to assess the salt affinity for the aqueous and organic phase's affinity, its distribution curve has been computed. The distribution curves represented in Figure 7 confirm that the addition of potassium chloride actually disrupted the distribution of the ethanol between the 1-butanol and the water. We can see that the distribution curves for each percentage of salt added are always above the first bisector what indicates that the coefficient of distribution (the report enters the quantity of the Ethanol in the organic phase on that in the aqueous phase) is always upper to 1.

3.2. Parameters Estimation And Data Correlation

New binary interaction parameters for the modified version of NRTL model which takes into account the presence of the salt [7], were obtained from the experimentally measured data for the water/ethanol/1-butanol and potassium chloride system at various salt concentrations, by the minimization of the objective function of the squared activity differences for all components and over all the tie-lines, expressed as follows:

$$F = \sum_j \sum_i \left[(\gamma_i x_i)^I - (\gamma_i x_i)^{II} \right]^2$$

where x_i and γ_i represent the mole fraction and the activity coefficient of component, respectively for tie line i, I and II denote the first and second phases in equilibrium respectively. The minimization was performed according to the Simplex search technique modified by Nelder and Mead [12].The activity coefficient of component i in the absence of salt γ_{i0} is calculate from the following NRTL equation [13]

$$\ln \gamma_{i0} = \left[\frac{\sum_{j=1}^{j=3} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{k=3} G_{ki} x_k} + \sum_{j=1}^{j=3} \frac{x_j G_{ji}}{\sum_{k=1}^{k=3} G_{ki} x_K} \left(\tau_{ij} - \frac{\sum_{m=1}^{m=3} x_m \tau_{mi}}{\sum_{k=1}^{k=3} G_{kj} x_k} \right) \right]$$

Where: $\tau_{ji} = \left(g_{ji} - g_{ii} \right) / RT$ and $G_{ji} = \exp \left(-\alpha_{ji} \tau_{ji} \right)$

In which g_{ji} is the energy of interaction between components j and I and α_{ji} the non-randomness factor. All they α_{ji} were assumed to be 0.2 [11]. In a salts-solvents mixture, the activity coefficient γ_{iS} of the component i is given by according to [7] as follows:

$$\ln \gamma_{is} = \ln(\gamma_{i0}) + \tau_{is}$$

where τ_{is} is the salt-solvent interaction parameter

The experimental liquid-liquid equilibrium data were correlated, performing liquid-liquid flash calculation. For a ternary system, twelve interaction parameters are necessary and must be calculated. It is about parameters:

$\tau_{12}, \tau_{13}, \tau_{21}, \tau_{23}, \tau_{31}, \tau_{32}, (\tau_{1s})^I, (\tau_{2s})^I, (\tau_{3s})^I,$
$(\tau_{1s})^{II}, (\tau_{2s})^{II}$ et $(\tau_{3s})^{II}$.

The inaccuracy of the prediction was estimated between the measured and calculated mole fractions using the root-mean square deviation (RMSD) defined as:

$$RMSD = \sqrt{\sum_{k=1}^{N} \left(\sum_{j=1}^{2} \sum_{i=1}^{3} \frac{\left(x_{ijk}^{Exp} - x_{ijk}^{Cal} \right)^2}{2 N_c N} \right)}$$

Where N and N_c are the numbers of tie-lines and components respectively, x^{Exp} and x^{Cal} are the experimental and calculated mole fraction, respectively, and i , j and k =1, 2…N (tie-lines) for components, phases and tie lines, respectively.

Group interaction parameters for pair solvent-solvent for the system water/ethanol/1-butanol in the presence of KCl appear in Table 5. Interaction parameters between pair solvent-salt are calculated in every phase organic and aqueous phases in the various concentrations of potassium chloride KCl, appear in Table 6. The interaction parameters between pairs salt-salt were not calculated because mixed-salt.

The correlated results are given in Table 4. In figures 8-10, comparative results between the calculated and experimental data are plotted together, for the quaternary system water/ethanol/1-butanol/KCl at 298.15K

There is a good agreement between the experimental and calculated values. As well as the root-mean square deviation (RMSD) for all components are (0.0411, 0.0208). These values show that the NRTL model was able to represent better the equilibrium in the presence of salt. This study confirmed the great performance of NRTL model.

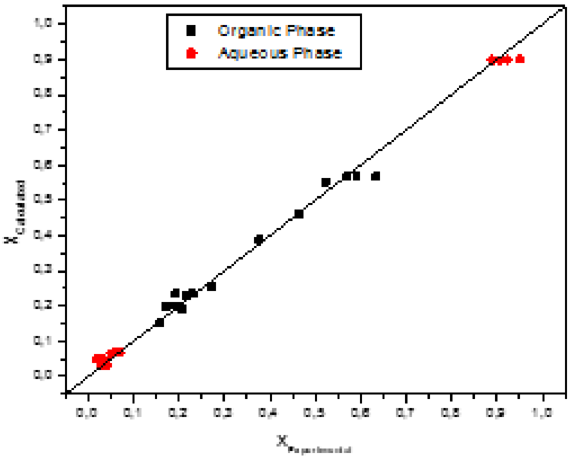

Fig. 8. Comparing the experimental LLE of Water/Ethanol/1-Butanol/ 5%KCl with the equilibria calculated from NRTL model at 298.15K

Table 5. NRTL binary interaction parameters τ_{ij} for the system Water/Ethanol/1-Butanol /KCl at 298.15K

Concentration (Salt-free basis)(g/100g)	**Component (ij)**	**NRTL parameters**		**RMSD**
		τ_{ij}	τ_{ji}	
5% KCl (X_S =1.205%)	Water-Ethanol	-1.503	-0.832	0.0208
	Water-1Butanol	3.327	4.649	
	Ethanol-1Butanol	17.48	-4.985	
10% KCl (X_S =2.410%)	Water-Ethanol	-0.783	3.285	0.013
	Water-1Butanol	7.835	0.675	
	Ethanol-1Butanol	-2.611	-2.717	
15% KCl (Xs =3.620%)	Water-Ethanol	-0.311	0.201	0.0411
	Water-1Butanol	4.514	0.158	
	Ethanol-1Butanol	4.043	5.743	

Table 6. NRTL binary interaction parameters τ_{is} for the system water/ethanol/1-butanol /KCl at 298.15K

Concentration (Salt-free basis)(g/100g)	**Component (is)**	**NRTL parameters**		**RMSD**
		τ_{is}	τ_{is}	
5% KCl (X_S=1.205%)	Water-KCl	1.265	0.859	0.0208
	Ethanol -KCl	-0.069	1.017	
	1-Butanol-KCl	1.566	-2.576	
10% KCl(X_S =2.410%)	Water-KCl	0.847	0.236	0.013
	Ethanol -KCl	2.398	3.71	
	1-Butanol-KCl	1.467	-1.372	
15% KCl (Xs =3.620%)	Water-KCl	4.577	1.232	0.0411
	Ethanol -KCl	0.584	1.243	
	1-Butanol-KCl	1.545	1.89	

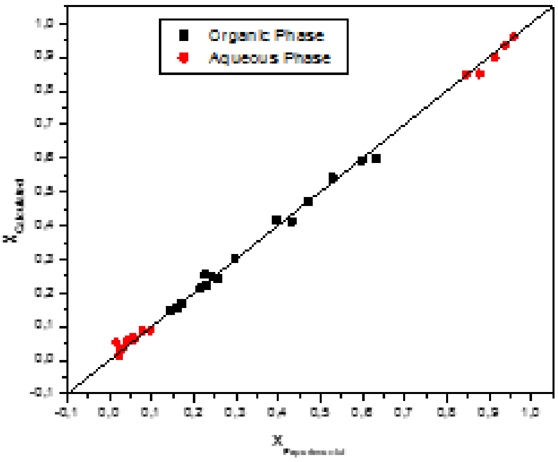

Fig. 9. Comparing the experimental LLE of Water/ Ethanol/ 1-Butanol/ 10%KCl with the equilibria calculated from NRTL model at 298.15K

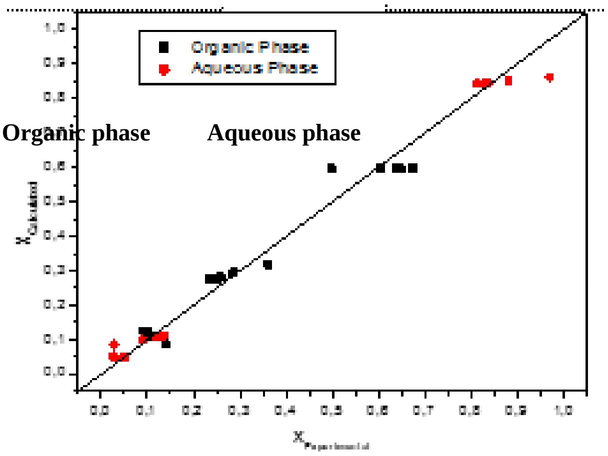

Fig. 10. Comparing the experimental LLE of Water/ Ethanol / 1-Butanol/ 15%KCl with the equilibria calculated from NRTL model at 298.15K

4. CONCLUSION

This study concerned the salting-out effect as applied to solvent extraction systems. Liquid-liquid equilibrium data for the partially systems of Water/ Ethanol/1-Butanol /Salts were experimentally measured at 298.15K and atmospheric pressure. The salt used was potassium chloride at different weight percentages of 10 and 15%.

The binodal and tie-line data results were determined by cloud point measurements method. The addition of salt showed to be effective in modifying the LLE of Water/ Ethanol/1- Butanol system in favor of the solvent extraction of ethanol from aqueous solution with 1-butanol, particularly at high salt concentrations. Potassium chloride increased the area of the two-phase region and decreased the mutual solubilities of 1-butanol and water and also decreased the concentration of 1-butanol and ethanol in the aqueous phase while significantly increased their concentrations in the organic phase.

The experimental data were correlated considering the modified version of the NRTL model for the activity coefficient, with the estimation of new binary interaction parameters solvent-solvent and solvent-salt.

The deviations between experimental and calculated compositions in both phases for the ternary system using this model were reasonable showing the ability of model NRTL for the determination of LLE of solvents-salt system using the solvent-solvent interaction parameters given on salt-free basis.

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