SALTING-OUT EFFECT OF SINGLE SALTS Na_2SO_4 AND $NaNO_3$ ON THE LLE OF THE SYSTEMS (WATER + TOLUENE + ACETONE), (WATER + CYCLOHEXANE + ETHANOL OR 2-PROPANOL) AND (WATER + XYLENE + METHANOL)

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ABSTRACT

The effect of sodium nitrate and sodium sulphate on the distribution of acetone, ethanol, methanol and 2-propanol between toluene, Cyclohexane, xylene and water at 25°C has been experimentally investigated. The McDevit and Long method has been employed to correlate the tie line data. Compared with previous work, the order of decreasing salting out, on a weight basis, is:

$Na_2SO_4 > NaCl > KCl > NaNO_3$ for water + toluene + acetone

$Na_2SO_4 > NaCl > NaNO_3 > KCl$ for water + cyclohexane or xylene+ alcohol

KEYWORDS: Phase equilibria model, salting effect, two-phase systems.

1 INTRODUCTION

Investigations of salt effects in liquids have dealt primarily with the solubilities of nonelectrolytes, such as toluene, xylene and benzene, in water. The effect of salts on the distribution of a solute between two immiscible solvents, a problem having engineering applications, has received very little attention.

The selection of the solvent extraction as a separation technique depends greatly upon how the solute distributes between the extract and the raffinate phases. Various means for altering this distribution in a desirable way exist, but one of the most commonly used nowadays is what is termed the salting effect. In fact, the presence of dissolved salt may influence the phase equilibrium behaviour of a mixture significantly. This phenomenon is often referred to as salting-in or salting-out effect (Eisen and Desai 1971, De Santis, Marrelli et al. 1976, Bourayou and Meniai 2005, Ghizellaoui and Meniai 2005, Hasseine, Meniai et al. 2009).

The major applications of the salt effect are in different separation processes as, for instance, in rectification, to shift favourably azeotropic conditions if they may occur, in extraction to alter miscibility gaps, in absorption and fractional crystallization to alter the distribution coefficients.

Consequently, many research programs have been developed to obtain reliable as well as reproducible experimental data for different systems, liquid–vapour or liquid–liquid, containing various salts. As examples, one can cite (Eisen and Desai 1971, De Santis, Marrelli et al. 1976, Govindarajan and Sabarathinam 1995, Govindarajan and Sabarathinam 1997, Sólimo, Bonatti et al. 1997, Zurita, Gramajo de Doz et al. 1998, Aznar, Araújo et al. 2000). However the present work is dealing with systems involving only liquid–liquid equilibria, as will be described further.

Generally, the addition of salt to a liquid–liquid system introduces ionic forces that inevitably affect the phase equilibrium, particularly for partially miscible liquids, inducing changes in the tie lines orientations. This can also be illustrated by certain systems which exhibit a particular behaviour where the slope of the tie line changes sign together with a corresponding change in the distribution ratio through a value of unity. Salting effect can be very useful for such systems which are termed solutropic by analogy to azeotropic systems in distillation and which may cause similar problems in the design of staged separations.

Salting out can also be explained by the fact that when the ions are solvated, some of the water becomes unavailable for the solute which is then salted out from the aqueous phase. This can be exploited to remove organic compounds from water.

Salting in occurs when, for instance, a polar solvent is added to an aqueous salt solution and it preferentially solvates the water and hence breaks the hydration cages previously formed around the salt ions. This may be used to recover salts from concentrated aqueous solutions, and it is also important in biological separation processes such as purification of proteins, enzymes, nucleic acids, and others.

In the present work, liquid–liquid equilibrium data have been obtained for four different systems, namely water-acetone-toluene, water-ethanol or 2-propanol-cyclohexane, and water-methanol-xylene in the presence of sodium nitrate or sodium sulphate at 298 K and at atmospheric pressure, at the three different mass percentages of 5, 10 and 20. The choice of these four systems has been mainly guided by the fact that the two solvents are totally immiscible (water and an aromatic compound) and the solutes (acetone, methanol, ethanol and 2-propanol) present very large solubilities in water. Therefore, it is worthwhile examining the effect of the two salts (Na2SO4 and NaNO3) on this great affinity of these solutes in water.

The tie line data obtained through experimental measurements have been correlated by making use of the expressions reported in (Eisen and Desai 1971, Ramasubramanian and Srinivasan 1983).

2 EXPERIMENTAL

2.1 Chemicals

Acetone, ethanol and methanol were supplied by J. Chemica (Belgium) whereas toluene, cyclohexane and xylene by Fluka Chemica (Swizerland). They are all 99.8 wt% pure. Na2SO4 and NaNO3 were purchased from Labosi (France). Bidistilled water was prepared using a GFL 2001/4 distillation unit.

2.2 Analytical methods

A weighted amount of an aqueous solution containing a known quantity of solute is mixed with a known quantity of solvent in a stoppered funnel. Quantities of salt are added to make corresponding mixtures of different salt mass percentages of 5, 10 and 20. These mixtures are maintained at constant temperature of 298 K ± 0.1 K in a thermostatic bath and agitated for an extended period of time until complete dissolution of the salt. The thermodynamic equilibrium is finally achieved by letting the mixture rest for 24 h.

After quantitative gravity separation, each phase is weighted. Since for each system, the two solvents are totally immiscible, the total amount of solute and salt having possibly migrated into the organic phase can be determined from an overall material balance. After evaporation of both phases, the salt solubility in the organic phase is found very negligibleand therefore it can be assumed that the compound which has migrated into the organic phase is the solute alone. The remaining amount of solute in the aqueous phase is also found from a material balance since the initial amount is known.

It should be noted that this procedure is simpler than the one consisting of analysing samples from both phases by measuring the respective refractive indexes by means of the digital refractometer Euromex RD 645. Prior to these refractometer measurements, calibration curves giving the change of the refractive index with the concentration of the solution have been plotted and used to read off the concentrations of the nonelectrolytes in the organic phase. The concentrations in the aqueous phase solution are obtained from material balance.

3 RESULTS AND DISCUSSION

The equilibrium concentrations of acetone, methanol, ethanol and 2-propanol, in the aqueous and organic phases are shown in Figures 1-4 as true mole fractions. The experimental results for various salt weight percentages of 5%, 10% and 20% of these four systems are plotted as X_C^E versus X_C^R, which are the solute C mass fractions on the salt free basis, in the Extract (E) and Raffinat (R) phases, respectively.

The distribution curves (on salt-free basis) corresponding the case of no salt, shown in Figures (1.a-b, 2.a-b, 3.a-b, 4.a-b), show the results from the system water (A)–toluene, xylene or Cyclohexane (B)–acetone, ethanol, 2-propanol or methanol (C) in the presence of sodium nitrate and sodium sulphate , respectively. It can be seen how the slopes of the distribution curves change with the addition of salt implying an increase of the activity coefficient of the solute, and hence causing salting-out of solute. From this one can see how, with the addition of the salt, the curves have moved above the bisector, eliminating the solutropy (Hasseine, Meniai et al. 2009).

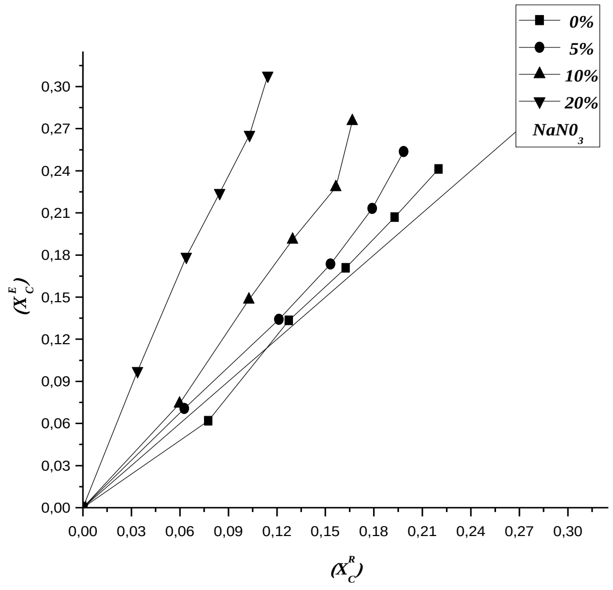

Figure 01: Effect of NaNO3 on the equilibrium distributions for different weight percentages for the system water (a)-toluene (b)-acetone(c) (Salt-free basis)

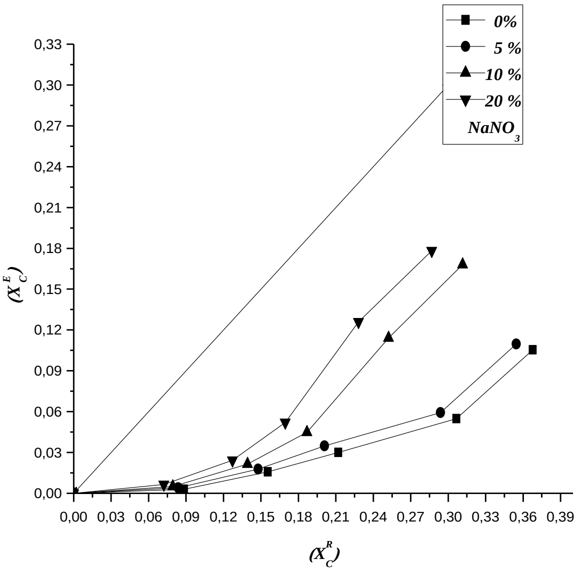

Figure 02a: Effect of NaNO3 on the equilibrium distributions for different weight percentages for the system water (a)-cyclohexane (b)-ethanol(c) (Salt-free basis)

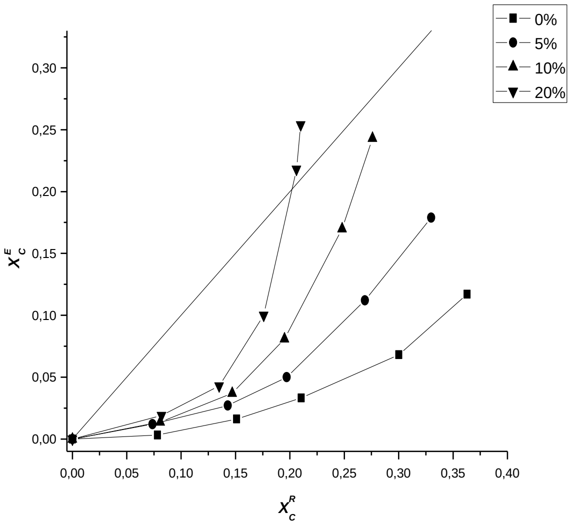

Figure 03a: Effect of Na2SO4 on the equilibrium distributions for different weight percentages for the system water (a)-cyclohexane (b)- 2-propanol (c) (Salt-free basis)

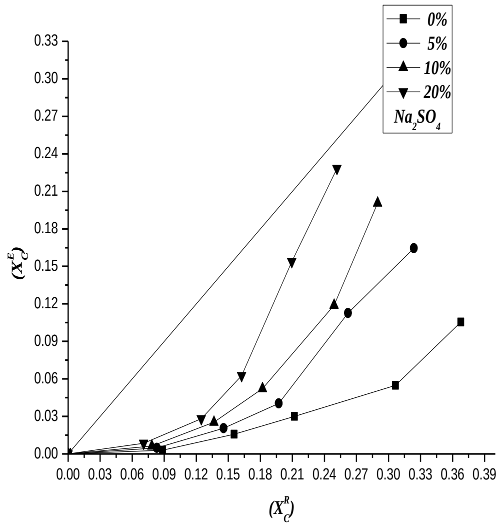

Figure 02b: Effect of Na2SO4 on the equilibrium distributions for different weight percentages for the system water (a)-cyclohexane (b)- ethanol (c) (Salt-free basis)

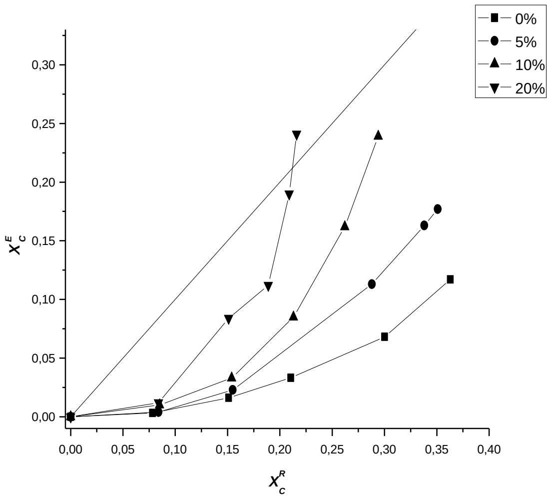

Figure 03b: Effect of NaNO3 on the equilibrium distributions for different weight percentages for the system water (a)-cyclohexane (b)- 2-propanol (c) (Salt-free basis)

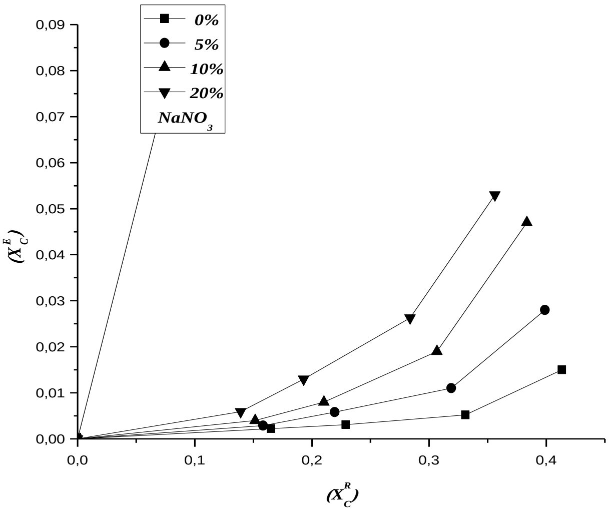

Figure 4a: Effect of NaNO3 on the equilibrium distributions for different weight percentages for the system water (a) - xylene (b) - methanol (c) (Salt-free basis)

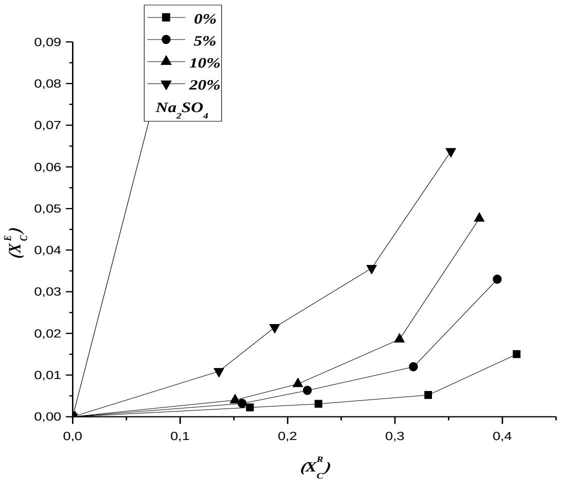

Figure 4b: Effect of Na2SO4 on the equilibrium distributions for different weight percentages for the system water (a) - xylene (b) - methanol (c) (Salt-free basis)

3.1 Equilibrium data for the salt containing water + toluene + acetone systems at 25°C

Figure 1c shows a very similar influence of NaNO3 and Na2SO4 on the distribution of the solute this effect is compared from the previous work (Hasseine, Meniai et al. 2009). Thus sodium sulphate is found to be the most effective salt in extracting out acetone from its aqueous solution for each salt and at the different concentrations used. The order of effectiveness is thus:

Na_2SO4 > NaCl >KCl > $NaNO_3$

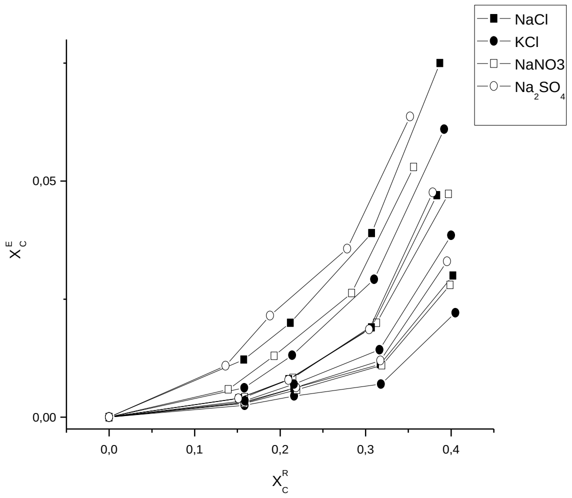

Figure 01c: Comparison of the salting out-out effect for the system water (a)-toluene (b)-acetone (c) (Salt-free basis)

3.2 Equilibrium data for the salt containing water + Cyclohexane or Xylene + Alcohol systems at 25°C

In the case of the system water + Cyclohexane or xylene + methanol, ethanol or 2-propanol, in the presence of sodium nitrate and sodium sulphate, the solute is a light alcohol which is soluble in the water. From the all results presented, for both, salts, in Figures 2. a-b, 4. a-b it can be seen that the curves of distribution are below the first bisector. This may be due to the large difference in solubility of the solute in the aqueous and organic phases. The distribution curves remain below the first bisector even with high salt mass percentages, indicating that the solute shows a certain "resistance" in order to remain in the aqueous phase, rather than to migrate into the organic one.

Figures 2c-4c shows the very similar influence of NaNO3 and Na2SO4 on the distribution of the solute this effect is compared from the previous work (Hasseine, Meniai et al. 2009) except the system water+ Cyclohexane + ethanol. Thus, sodium sulphate is found to be the most effective salt in extracting out methanol, ethanol and 2-propanol from its aqueous solution for each salt and at the different concentrations used. The order of effectiveness is thus:

Na_2SO_4 > NaCl > $NaNO_3$> KCl

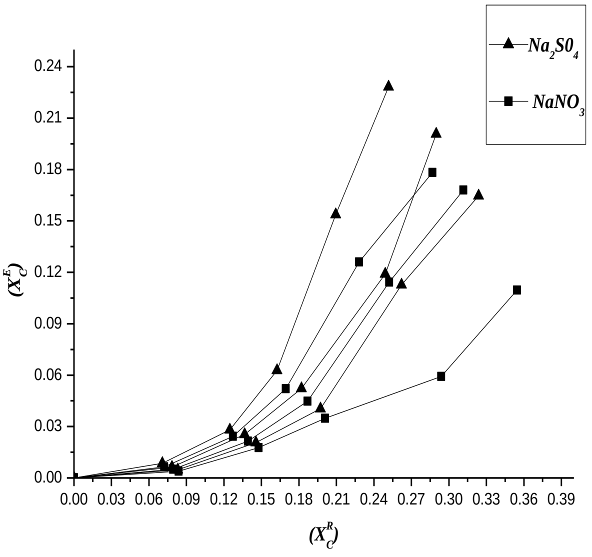

Figure 02c: Comparison of the salting out-out effect for the system water (a)- cyclohexane (b)- ethanol (c) (Salt-free basis)

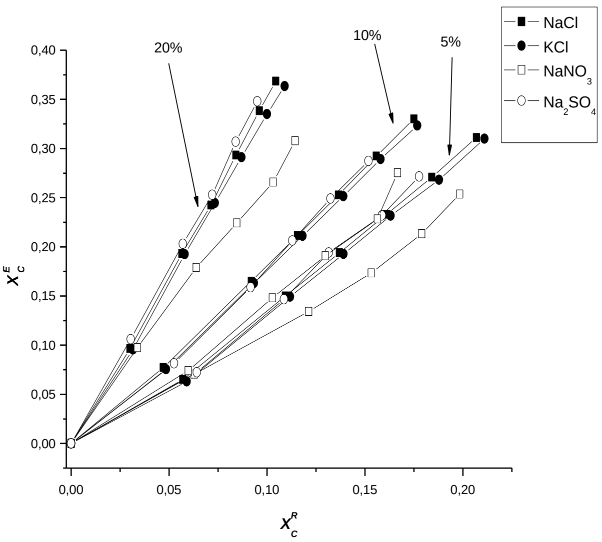

Figure 04c: Comparison of the salting out-out effect for the system water (a) – xylene (b) - methanol (c) (Salt-free basis)

Due to the complexity of experimental measurements, theoretical means to provide data are most welcome for the designer. Consequently, in this last section, correlations of the obtained experimental results for the three considered systems are presented, using the equation type reported in (Eisen and Desai 1971, Ramasubramanian and Srinivasan 1983). Rather than, the simpler Setschenow relation witch does apply more conveniently at very low concentrations. The general form of Mc Devit & Long correlation is expressed as follows:

$$\ln\left(X_{CA}^{0}/X_{CA}\right)=k_S X_{SA}+k_C\left(X_{CA}-X_{CA}^{0}\right) \qquad (1)$$

Where X_{CA} and X_{CA}^{0} are the mass fractions of solute C in the aqueous phase A on a salt free basis, in presence and in absence of the salt, respectively, in equilibrium with the same solute organic phase concentration, X_{SA} is the overall salt mass fraction in the aqueous phase, k_S and k_C are constants.

In this work, it is proposed to express k_S and $k_C\left(X_{CA}-X_{CA}^{0}\right)$ as simple polynomial functions and the relations obtained in this work for both salts are as follows:

3.2.1 Water (A) – Toluene (B) – Acetone (C) system

-For NaNO3:

$$\ln\left(X_{CA}^{0}/X_{CA}\right)=\left(1.75+3.0947X_{CA}^{0}\right)X_{SA}+\left(0.00344+0.0379X_{CA}^{0}\right) \qquad (2)$$

For Na2SO4:

$$\ln\left(X_{CA}^{0}/X_{CA}\right)=\left(4.6494-6.4801X_{CA}^{0}\right)X_{SA}+\left(-0.0339+0.286X_{CA}^{0}\right) \qquad (3)$$

3.2.2 Water (A)-Cyclohexane (B) -ethanol(C) system

Similarlyto the above system, the relations which have been obtained for the two salts are as follows:

-For NaNO3 :

$$\ln\left(X_{CA}^{0} / X_{CA}\right) = \left(0.8445 + 1.0322X_{CA}^{0}\right)X_{SA} + \left(0.00377 - 0.0086X_{CA}^{0}\right) \tag{4}$$

-For Na2SO4:

$$\ln\left(X_{CA}^{0} / X_{CA}\right) = \left(0.5478 + 3.5264X_{CA}^{0}\right)X_{SA} + \left(0.0035 + 0.0.0303X_{CA}^{0}\right) \tag{5}$$

The above expressions for the two systems have been obtained with correlation factors very close to unity, and hence a very negligible deviation between the experimental values and the corresponding ones which would be obtained by the use of the above developed correlations. Their main advantage is that they provide a mean to influence, particularly, the slopes of the distribution curves by just manipulating X_{CA}^{0} , to promote or not the salting-out.

3.3 Water (A) - Xylene (B) - Methanol (C) system

For this system, the experimental data could not be correlated by means of the Long and Mc Devit correlation since the correlation factors are very low. This can be explained by the negligible salting out of the methanol solute, for the reasons outlined in the preceding sections.

4 CONCLUSION

Liquid–liquid equilibrium data for this systems, water–acetone–toluene, water–cyclohexane-ethanol or 2-propanol, and water– xylene-methanol, in the presence of Na2SO4 or NaNO3 were measured at 298 K and atmospheric pressure.

The effect of the salt addition to the original ternary systems was observed by the increase in the two-phase region in a general form, both, salts have caused a salting-out effect; however, it appears that the effect of sodium nitrate is less important than that of the sodium sulphate. The importance of this salting effect has also been demonstrated through this study, particularly when a solutropy case has been eliminated, by acting on the salt mass percentage.

Finally, empirical correlations have been developed using the obtained experimental data, for the first two systems (water–acetone–toluene and water–2-propanol or ethanol–cyclohexane) and not the third one (water–methanol–xylene), due to very similar behaviour and hence affinity, of water and methanol molecules in the aqueous phase.

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[12] Figures captions

[13] Figure 1a: Effect of NaNO3 on the equilibrium distributions for different weight percentages for the system water (a)-toluene (b)-acetone(c) (Salt-free basis).

[14] Figure 1b: Effect of Na2SO4 on the equilibrium distributions for different weight percentages for the system water (a)-toluene (b)-acetone(c) (Salt-free

basis).

[15] Figure 1c: Comparison of the salting out-out effect for the system water (a)-toluene (b)-acetone (c) (Salt-free basis).

[16] Figure 2a: Effect of NaNO3 on the equilibrium distributions for different weight percentages for the system water (a)-cyclohexane (b)-ethanol(c) (Salt-free basis).

[17] Figure 2b: Effect of Na2SO4 on the equilibrium distributions for different weight percentages for the system water (a)- cyclohexane (b)- ethanol (c) (Salt-free basis).

[18] Figure 2c: Comparison of the salting out-out effect for the system water (a)- cyclohexane (b)- ethanol (c) (Salt-free basis).

[19] Figure 3a: Effect of Na2SO4 on the equilibrium distributions for different weight percentages for the system water (a)- cyclohexane (b)- 2-propanol (c) (Salt-free basis).

[20] Figure 3b: Effect of NaNO3 on the equilibrium distributions for different weight percentages for the system water (a)- cyclohexane (b)- 2-propanol (c) (Salt-free basis).

[21] Figure 3c: Comparison of the salting out-out effect for the system water (a)- cyclohexane (b)- 2-propanol (c) (Salt-free basis).

[22] Figure 4a: Effect of NaNO3 on the equilibrium distributions for different weight percentages for the system water (a) - xylene (b) - methanol (c) (Salt-free basis).

[23] Figure 4b: Effect of Na2SO4 on the equilibrium distributions for different weight percentages for the system water (a) - xylene (b) - methanol (c) (Salt-free basis).

[24] Figure 4c: Comparison of the salting out-out effect for the system water (a) – xylene (b) - methanol (c) (Salt-free basis).