Effect of Electrolyte on Phase Separation of Aqueous Organic System

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Abstract- The influence of salt on Liquid- Liquid Equilibrium cannot be ignored because it significantly changes the equilibrium composition. Liquid-Liquid Equilibrium is the result of intermolecular forces which can significantly change due to salt addition which introduces ionic forces , affecting the thermodynamic equilibrium . Aqueous electrolyte liquid-liquid equilibrium is often related to extraction processes. In the present work the salt effect on the system namely '2-Propanol+Water' has been studied with various salts under varied concentration. The salts used in the above system are $Na_2S_2O_3.5H_2O$ and Na_2CO_3. The effect of salt concentration on aqueous organic system has been studied using Cloud Point Method. The effect of different salt on phase separation of studied system is discussed on the base of intermolecular interactions. The free energy, enthalpy and entropy of clouding point is estimated using simple method, and the driving force for two phase formation process is discussed on the base of the estimated free energy values.

Index Terms- Alcohol, Cloud point data, Gibb's free energy, Enthalpy, Entropy Liquid - liquid equilibrium, Salt effect.

1. INTRODUCTION

Study of effect of salt on aqueous organic systems is very important for chemical industry due to its applications in separation and purification processes. Such as separation of solutropic mixtures, design of extractor, recycling of organic solvent in mixed solvent system. Salt effect also finds application in biological separation processes such as purification of proteins, enzymes, nucleic acids and others. Liquid-Liquid extraction technique utilizing Aqueous two Phase Systems (ATPSs) is clean alternative for traditional organic +water solvent extraction system due to its advantages such as easy processing on any scale, high capacity, easy and precise scale up, high product yields and low cost. Therefore many research groups have focused on theoretical and experimental study of phase equilibrium conditions in ternary aqueous two phase systems (ATPSs).

When one short-chain alcohol and one salt are dissolved in water above a critical concentration, two immiscible phases are usually formed which is referred to as aqueous two phase systems (ATPSs). These types of systems have shown great potential for efficient extraction and purification of biological products because of biocompatibility and low cost. Greve and Kula have described the use of some aqueous biphasic systems containing short-chain alcohols + water + inorganic salts for the extraction of salt from the primary bottom phase of protein extraction processes in polymer + salt systems. Liquid-liquid equilibria (LLE) in ATPSs are due to intermolecular forces, predominantly hydrogen bonding and ion-dipole interactions. Addition of a salt to such a system introduces ion-dipole interactions which alter the structure of the hydrophilic solvents such as alcohols in equilibrium. The molecules of water that surround the ions become unavailable for the hydrophilic solvents, and it becomes "salted out" from the aqueous phase. The opposite process can occur if a polar organic solvent is added to an aqueous salt solution. It captures part of the molecules of water that have been solvating the ions; hence, the salt crystallizes. This effect is used in a process called extractive crystallization in which salts can be recovered from concentrated aqueous solutions by the addition of a polar organic solvent, rather than by the more expensive evaporation process. On the other hand, the salting out effect is utilized for removing organic compounds from water.

2. MATERIALS

Table 1: Materials & Specifications

Chemical	Source	Purity (%)
2-Propanol	Rankem (India)	>99.7
Anhydrous Sodium carbonate	Lobachemie (India)	>99.5
H_2O	Milipore	>99.9
Sodium thiosulphate	Emparta Merck (Germany)	>99

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Double distilled deionizer water with specific conductance about < 0.2 µS/cm was used in all experiments.

3. EXPERIMENTAL PROCEDURE

To examine the effect of change in salt concentration on cloud point of aqueous 2-propanol solution, a measured (2-propanol+water) solution is taken inside the glass sample tube. Ratio of alcohol to water is maintained at constant value. A measured amount of salt is added into aqueous organic system. Sample tube is placed inside the glass water bath so that cloud point can be easily observed. The mixture inside the sample tube for uniform temperature distribution. Temperature is decreased at the rate of 0.1°C per minute with the help of ice, until solution become cloudy or turbid. Temperature of solution is measured using digital temperature indicator whose sensor is inserted inside the tube. The temperature at which first cloud appears is noted as cloud point temperature. Then solution again heated slowly at the rate of 0.1°C per minute till cloud gets disappeared. This process is repeated to get reproducibility in results. Similarly, at constant salt: water ratio, effect of change 2-propanol concentration on cloud point is measured.
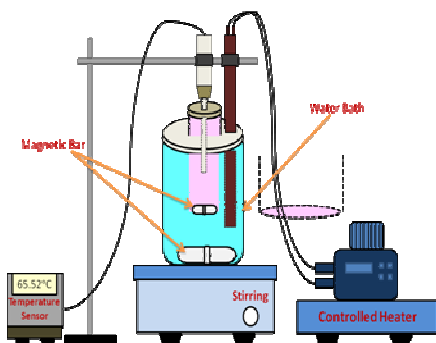

Figure 1: Experimental Setup to Study Effect of Salt on Aqueous organic System

4. RESULTS AND DISCUSSIONS

4.1 Effect of Change in Salt Concentration

To study the effect of salt (or electrolyte) on the investigated systems, the cloud point and cloud disappearance point temperatures were measured as functions of mole fraction of the salt at constant alcohol: water mole ratio. Figure 2 and figure 3 shows the salt concentration dependence of the cloud point and cloud disappearance point at constant concentration of aqueous 2-Propanol solution for each of the system studied. As shown in figure 2 in case of Aqueous Two Phase System (ATPS) composed of

sodium carbonate salt as electrolyte, cloud point temperature decreases with increase in concentration of electrolyte at constant 2-propanol:water mole ratio(0.0.247069). Same phenomenon is observed in case of sodium thiosulphate salt (figure 3) as electrolyte at constant 2-propanol to water mole ratio (0.0.2470). In other words, the salting out ability of salt increases with increase in concentration and decrease in temperature. The experimental result from figure 2 and figure 3 lead to conclusion that a salting out effect exists for both the salts under study and this effect increase with increase with concentration of salt.

This observation can be explained in terms of kosmotropicity of salts. Zafarani-moattor et.al researched on behavior of aqueous alcohol system in presence of kosmotropic salt. When such salt added into aqueous alcohol solution, the salt and alcohol compete with each other for water molecules. Salt have higher affinity towards water than alcohol. So intermolecular attraction between salt and water molecule increases and results into increased alcohol-alcohol self-intermolecular interactions of alcohol as they have weaker affinity towards water.
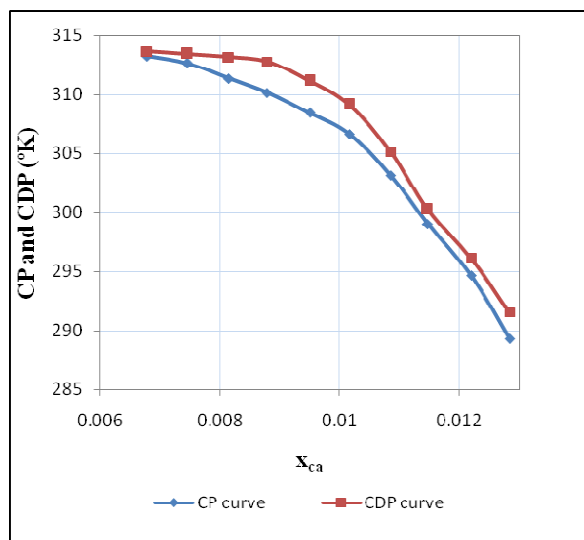

Figure 2 : Cloud Point (CP) and Cloud Disapperance Point (CDP) curve for 2-Propanol (m) + sodium carbonate (ca) + water (w) at constant 2-Propanol:water (mole ratio) = 0.247069

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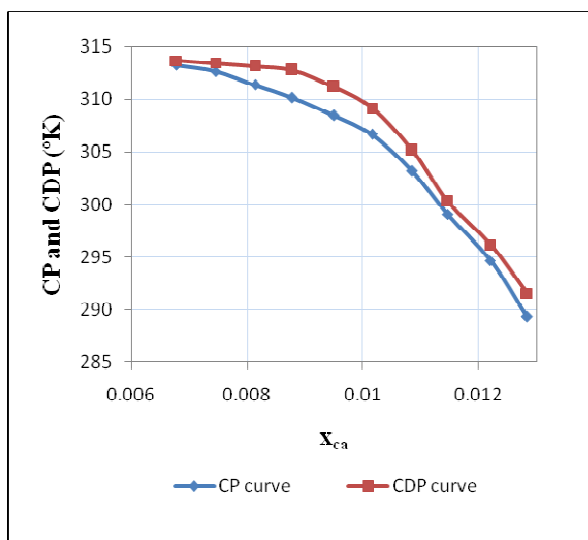*E-ISSN: 2321-9637*
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Figure 3 : Cloud Point (CP) and Cloud Disapperance Point (CDP) curve for 2-Propanol (m) + sodium thiosulphate (ca) + water (w) at constant 2-Propanol: water (mole ratio) = 0.2470
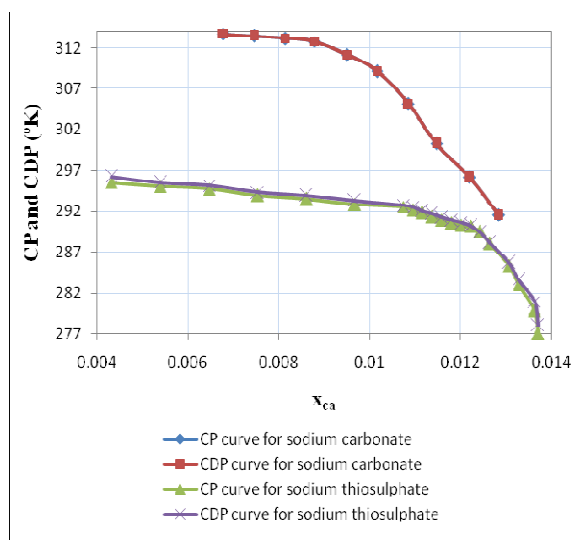

Figure 4 : Comparison between Cloud Point (CP) and Cloud Disappearance Point (CDP) curve for 2-Propanol (m) + sodium carbonate / sodium thiosulphate (ca) + water (w) at constant 2-Propanol : water (mole ratio) = 0.24707

4.2 Phase Separation Ability of Different Salt

In the present work, two sets of experiment with two different salts were carried out to study salting effect produced by addition of different salts to aqueous solution of alcohol.

As shown in figure 4, sodium thiosulphate is more effective than sodium carbonate at low concentration. For the same concentration of electrolyte sodium thiosulphate gives higher decrement in cloud point than sodium carbonate. For higher decrement in cloud point more concentration of sodium carbonate is required.

Phase separation ability of different salt can be explained in terms of solubility of salt in water. As the solubility of salt in water increases (i.e. salt- water interaction increases, alcohol get salted out more readily. Solubility of sodium thiosulphate in water (70.1 gm/100 gm of water at 20C) is higher than sodium carbonate (21.80gms/100gms of water) in water. As the solubility of salt in water increases the phase separation ability of increases. Sodium thiosulphate and sodium carbonate both are insoluble in alcohol and there is no data found on solubility of sodium thiosulphate and sodium carbonate in alcohol. Therefore salt-alcohol interactions are neglected in both the system studied and only salt-water and alcohol-water interactions are taken into consideration.

4.3 Effect of Change in Alcohol Concentration

As shown in figure 5 for the system (2-propanol- sodium carbonate-water), the experimental results are in good agreement with literature.

As shown in figure 6 and in case of ATPS composed of (2-propanol-sodium thiosulphate-water), as concentration of 2-propanol increases, cloud point temperature increases. On the other words, phase separation ability of system decreases with increase in temperature and the salting out ability of system decreases with increase in temperature. E. Nemati-Knade et.al studied (2-propanol- water- sodium thiosulphate) system and established cloud point data as function of mole fraction of alcohol for given temperature range (293.15-328.15). He reported that there is no effect of change in alcohol concentration on cloud point temperature in given temperature range (293.15°K-328.15°K). But experimental results are not in agreement with this statement. According to this result there is increase in concentration of 2-Propanol required as temperature increases. This means there is increase in cloud point temperature as concentration of 2-propanol increases. As shown in figure 5 for the system (2-propanol- sodium carbonate-water), the experimental results are in good agreement with literature.

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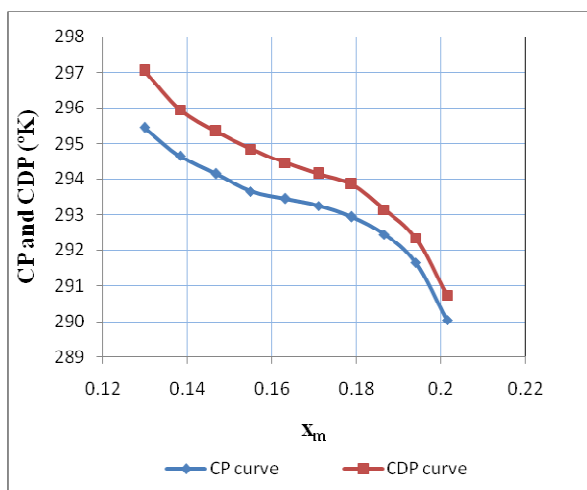*Available online at www.ijrat.org*

Figure 5 Cloud Point (CP) and Cloud Disappearance Point (CDP) curve for
2-Propanol (m) + sodium carbonate (ca) + water (w) at constant sodium carbonate: water (mole ratio) = 0.025835
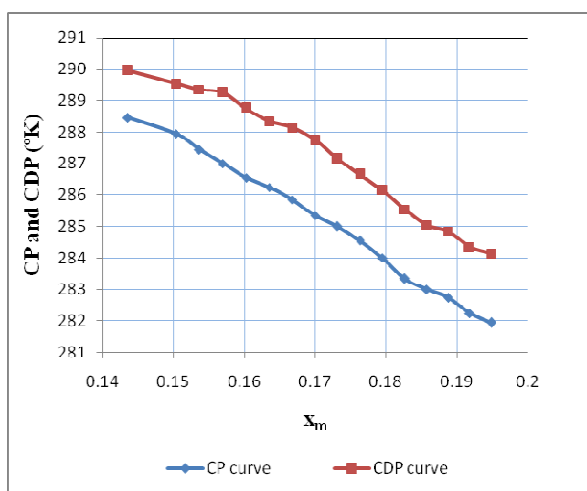

Figure 6 Cloud Point (CP) and Cloud Disappearance Point (CDP) curve for
2-Propanol (m) + sodium thiosulphate (ca) + water (w) at constant sodium thiosulphate: water (mole ratio) = 0.011033

4.4 EFFECT OF SALT AND ALCOHOL CONCENTRATION ON GIBB'S FREE ENERGY (ΔG_C), ENTHALPY (ΔH_C) AND ENTROPY (ΔS_C)

Recently, Dan et al., with consideration of clouding as the point of phase separation (or the solubility limit) estimated the free energy, ΔG_C, enthalpy, ΔH_C, and entropy, ΔS_C, of phase-separation to obtain some information about the driving force of the aqueous two-phase formation process. Following Dan et al., the free energy of phase separation or clouding (ΔG_C) can be calculated from the following relation:

$$\Delta G_C = R.T.\ln x \qquad \text{(Eq. 1)}$$

Where x is the mole fraction concentration of component at cloud point (CP or T). The values of ΔG_c, ΔH_c, ΔS_c are reported in Table 2, Table 3, with reference to the clouding point concentrations of T for the same concentration of the alcohol in the studied systems. The values of ΔG_c, ΔH_c, ΔS_c are reported in Table. 4, Table 5 with reference to the clouding point concentrations of T for the same concentration of the salt in the studied systems.

The ΔG_c values at different CP (or T) were processed according to the equation given below to get ΔH_c from the slope of the linear (least squares) plot of (ΔG_c /T) against (1/T) for each of the studied ATPSs.

$$\Delta H_c = d\ (\Delta G_c/T)\ /\ d(1/T) \qquad \text{(Eq. 2)}$$

Moreover, the following Gibbs–Helmholtz equation was used to calculate the entropy changes:

$$\Delta G_c = \Delta H_c - T.\Delta S_c \qquad \text{(Eq. 3)}$$

Table 2: Estimated ΔG_c (kJ.mol^{-1}), ΔH_c (kJ.mol^{-1}) ΔS_c (kJ.mol^{-1}) for the {2-Propanol (m) +salt (ca) +water (w)} as function of mole fraction of salt System 2-Propanol (m) +sodium carbonate (ca) +water (w)

T (°K)	ΔG_c (kJ.mol^{-1})	ΔH_c (kJ.mol^{-1})	T ΔS_c (kJ.mol^{-1})
313.65	-13.0223	18.132	31.15432
313.45	-12.7678	18.132	30.89975
313.15	-12.5252	18.132	30.65721
312.75	-12.3122	18.132	30.44425
311.15	-12.047	18.132	30.179
309.15	-11.7968	18.132	29.92879
305.15	-11.4773	18.132	29.60926
300.25	-11.1548	18.132	29.28676
296.15	-10.8504	18.132	28.98244
291.55	-10.5582	18.132	28.69022

The effect on change in salt concentration on free energy, enthalpy and entropy of studied aqueous two phase system is tabulated in Table 4.5 and Table 4.6. The values shows that the (ΔG_C) of ATPS composed of sodium thiosulphate is more (ΔG_C =-13.4095 kJ.mol^{-1}) than the ones of the sodium carbonate (ΔG_C = -13.0223 kJ.mol^{-1}). The salting out ability, kosmotropicity, of the salt can be related to the values of (ΔG_C) of salt. (ΔG_C) is the change in free

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energy from isolated naked ion in the gas phase to aqueous solvated ion in solution, and therefore the ions with the higher kosmotropicity have more negative value, due to resulting more structured water molecules 'lattice' the ion .In present cases, taking into account that both salt have same cation (Na+), the phase separation ability of different salt can be referred to the more negative values of (ΔG_C). Therefore, it can be concluded that the sodium thisulphate with negative (ΔG_C) values, results in more structured water 'lattice' around the anion of compared to sodium carbonate anion, with less negative (ΔG_C) value, and the more amount of the mobilized water molecules available to hydrated the alcohol molecules decreased, and subsequently the third component, alcohol, more effectively salted-out.

Table 3: System: 2-Propanol (m) +sodium thiosulphate (ca) +water (w)

T (°K)	ΔG_c (kJ.mol^{-1})	ΔH_c (kJ.mol^{-1})	$T\Delta S$ (kJ.mol^{-1})
296.25	-13.4095	21.8716	35.28109
295.55	-12.8321	21.8716	34.70371
295.15	-12.3701	21.8716	34.24172
294.35	-11.9618	21.8716	33.83344
293.95	-11.6219	21.8716	33.49353
293.35	-11.3135	21.8716	33.18506
292.75	-11.0365	21.8716	32.90814
292.55	-10.9813	21.8716	32.85294
292.05	-10.9159	21.8716	32.78752
291.75	-10.859	21.8716	32.73061
291.25	-10.7956	21.8716	32.66724
290.95	-10.7408	21.8716	32.61235
290.65	-10.6868	21.8716	32.55835
290.25	-10.6297	21.8716	32.50132
289.45	-10.5591	21.8716	32.43067
288.15	-10.4712	21.8716	32.34279
285.75	-10.3058	21.8716	32.17737
283.65	-10.1922	21.8716	32.06377
280.95	-10.035	21.8716	31.90664
278.05	-9.91862	21.8716	31.79022

The calculated ΔH_C and $T\Delta S_C$ values are presented in Table 3,Table 4,Table 5 and Table 6 which are all positive in the case of ATPSs composed of (2-propanol+sodium carbonate+water) and (2-propanol + sodium thiosulphate + water) and shows that the aqueous two phase formation processes are endothermic in these cases.

Also, the estimated $T\Delta S_C$ values are positive for the systems composed of (2-propanol+sodium carbonate+water) and (2-propanol+sodium thiosulphate+water). The positive entropy and enthalpy of the ATPSs suggest that the increase of

entropy is the driving force for the aqueous two-phase formation processes in these cases.

Table 4: Estimated ΔG_c (kJ.mol^{-1}), ΔH_c (kJ.mol^{-1}) ΔS_c (kJ.mol^{-1}) for the {2-Propanol (m) +salt (ca) +water (w)} as function of mole fraction of 2-Propanol. System: {2-Propanol (m) +sodium carbonate (ca) +water (w)}

T (°K)	ΔG_c (kJ.mol^{-1})	ΔH_c (kJ.mol^{-1})	$T\Delta S_c$ (kJ.mol^{-1})
297.05	-5.04373	56.3014	61.34513
295.95	-4.86714	56.3014	61.16854
295.35	-4.71199	56.3014	61.01339
294.85	-4.56967	56.3014	60.87107
294.45	-4.43866	56.3014	60.74006
294.15	-4.31771	56.3014	60.61911
293.85	-4.20432	56.3014	60.50572
293.15	-4.09213	56.3014	60.39353
292.35	-3.98494	56.3014	60.28634
290.75	-3.87291	56.3014	60.17431

Table 5: System: 2-Propanol (m) + sodium thiosulphate (ca) +water (w)

T (°K)	ΔG_c (kJ.mol^{-1})	ΔH_c (kJ.mol^{-1})	$T\Delta S_c$ (kJ.mol^{-1})
290.15	-4.61813	14.773	19.39113
289.95	-4.51215	14.773	19.28515
289.55	-4.4144	14.773	19.1874
289.35	-4.37088	14.773	19.14388
289.25	-4.32867	14.773	19.10167
288.75	-4.28619	14.773	19.05919
288.35	-4.25547	14.773	19.02847
288.15	-4.22122	14.773	18.99422
287.75	-4.18058	14.773	18.95358
287.15	-4.14687	14.773	18.91987
286.65	-4.12706	14.773	18.90006
286.15	-4.10786	14.773	18.88086
285.55	-4.09772	14.773	18.87072
285.05	-4.08938	14.773	18.86238
284.85	-4.07999	14.773	18.85299
284.35	-4.10115	14.773	18.87415
284.15	-4.19278	14.773	18.96578

5. CONCLUSION

The effect of Sodium Thiosulphate and Sodium Carbonate on aqueous 2-Propanol was studied using Cloud Point method. The obtained results show that the two phase formation ability of ATPSs composed of different salt is in the order of: Sodium Thiosulphate >Sodium Carbonate. Effect of salt on phase separation of aqueous 2-propanol was related to solubility of salt in water. As the solubility of salt in water increases the phase separacion ability of increases. On the base on obtained results, it can be concluded that two phase forming ability of the salt

with higher solubility is more than salt with lower solubility due to comparatively weaker salt to water intermolecular interaction.

Additionally, the result obtained for the effect of 2-Propanol concentration on electrolyte solutions show that the effect of alcohol concentration on Sodium Carbonate is higher than Sodium Thiosulphate.

Furthermore on the base of estimated free energy, enthalpy and entropy of clouding point as function of mole fraction of salt and mole fraction of 2-Propanol obtained in this work, it can be concluded that the increase of entropy is driving force for the aqueous two phase formation.

REFERENCES

[1] Nemati-Knade, E.; Shekaari, H.; Jafari, S. (2012): Thermodynamic study of aqueous two phase systems for some aliphatic alcohols + sodium thiosulfate + water, Fluid Phase Equilibria, **321**, pp. 64-72.

[2] Tzu-Jen Chou; Akihiko Tanioka (1998): Salting Effect on the Liquid-Liquid Equilibria for the Partially Miscible Systems of n-Propanol-Water and i-Propanol-Water, Ind. Eng. Chem. Res., **37**, pp. 2039-2044.

[3] Aznar, M.; Arau, R.; Romanato, J.; Santos, G.; D'Avila, S. (2000): Salt Effects on Liquid-Liquid Equilibrium in Water + Ethanol +Alcohol + Salt Systems, J. Chem. Eng. Data, **45**, pp. 1055-1059.

[4] Nemati-Kande, E.; Shekaari, H. (2013): Thermodynamic investigation of the ATPSs composed of some (aliphatic alcohol + sodium carbonate + water) ternary systems, J. Chem. Thermodynamic, **57**, pp. 541–549.

[5] Santos, F. M.; D'Ávila, S.; Aznar, M. (2001): Salt effect on liquid–liquid equilibrium of water + 1-butanol + acetone system: experimental determination and thermodynamic modeling, Fluid Phase Equilibria, **187–188**, pp. 265–274.

[6] Dagade, D.H.; Kumbhar, R. R.; Sabale, S. R.; Patil, K. J. (2007): Phase diagram of $Na_2S_2O_3$ + ethanol + water at ambient pressure and temperature, Fluid Phase Equilibria, **255**, pp. 110–114.

[7] Shekaari, H.; Sadeghi, R.; Jafari, S. A. (2010): Liquid-Liquid Equilibria for Aliphatic Alcohols + Dipotassium Oxalate + Water, J. Chem. Eng. Data, **55**, pp. 4586–4591.

[8] Furter, F. W.; Cook, A. R. (1967): Salt Effect In Distillation: A Literature Review, Int. J. Heat Mass Transfer, **10**, pp. 23-36.

[9] Mohsen-Nia, M.; Rasa, H.; Modarress, H.; (2006): Cloud-Point Measurements for (Water + Poly (ethylene glycol) + Salt) Ternary Mixtures by Refractometry Method, J. Chem. Eng. Data, **51**, pp. 1316-1320.

[10] Nozary, S.; Modarress, H.; Eliassi, A. (2003): Cloud-Point Measurements for Salt Poly(ethylene glycol)Water Systems by Viscometry and Laser Beam Scattering Methods, Journal of Applied Polymer Science, **89**, pp. 1983–1990.

[11] Boutris, C.; Chatzi, E. G.; Kiparissides, C. (1997): Characterization of the LCST behavior of aqueous Poly (N-isopropyl acrylamide) solutions by thermal and cloud point techniques, Polymer, 38(10), pp. 2567 -2570.

[12] Gomis, V.; Ruiz, F.; Boluda, N.; Saquete, M. D. (1997): The influence of temperature on the liquid-liquid-solid equilibrium of the ternary system water-potassium chloride-2-propanol, Fluid Phase Equilibria, **130**, pp. 223-229.

[13] Wang, Y.; Hu, S.; Yan, Y.; Guan, W. (2009): Liquid–liquid equilibrium of potassium/sodium carbonate + 2-propanol/ethanol + water aqueous two-phase systems and correlation at 298.15 K, CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry, **33**, pp. 726–731.

[14] Nemati-Kande, E.; Shekaari, H.; Jafari, S. A. (2012): Liquid–liquid equilibrium of 1-propanol, 2-propanol, 2-methyl-2-propanol or 2-butanol + sodium sulfite + water aqueous two phase systems, Fluid Phase Equilibria, **329**, pp. 42–54.

[15] Zafarani-Moattar, M. T.; Hosseinpour-Hashemi, V.; Banisaeid, S.; Shamsi Beirami M. A. (2013): The study of phase behavior of aqueous 1-propanol/2-propanol/2-butanol/2-methyl-2-propanol systems in the presence of disodium tartrate or disodium succinate at T = 298.15 K, Fluid Phase Equilibria, **338**, pp. 37–45.

[16] Zafarani-Moattar, M. T.; Banisaeid, S.; Shamsi Beirami M. A. (2005): Phase Diagrams of Some Aliphatic Alcohols + Potassium or Sodium Citrate + Water at 25 °C, J. Chem. Eng. Data, **50**, pp. 1409-1413.

[17] Salabat, A.; Hashemi, M. (2006): Temperature Effect on the Liquid-Liquid Equilibria for Some Aliphatic Alcohols + Water + K2CO3 Systems, J. Chem. Eng. Data, **51**, pp. 1194-1197

[18] Shekaari, H.; Sadeghi, R.; Jafari, S. A. (2010): Liquid-Liquid Equilibria for Aliphatic Alcohols + Dipotassium Oxalate + Water, J. Chem. Eng. Data, **55**, pp. 4586–4591.

[19] Nemati-Kande, E.; Shekaari, H. (2013): Thermodynamic investigation of the ATPSs composed of some (aliphatic alcohol + sodium carbonate + water) ternary systems, J. Chem. Thermodynamics, **57**, pp. 541–549.