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Isobaric Vapour Liquid Equilibrium for Acetone + Methanol + Calcium bromide at different concentration

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***Abstract*—The vapour liquid equilibrium data at 760 mmHg (at atmospheric) pressure have been determined experimentally for the binary system, viz, acetone – methanol , at different concentration of calcium bromide .Smith and Bonner type still was used.. The present work involves the measurement of vapour liquid equilibrium of Acetone + methanol + calcium bromide at different concentrations of salt below saturation level. The addition of calcium bromide to this solvent mixture increases the acetone concentration in vapour phase at equilibrium. This indicates a preferential association of salt with less volatile component, methanol in the acetone – methanol solvent mixture.**

***Keywords*—vapour liquid equilibrium, Smith and Bonner type still, Azeotrope, Activity coefficient, solubility**

I. INTRODUCTION

The study of influence of salt on vapour liquid equilibrium of solvent mixture is of interest, because addition of salt to a mixed solvent will enhance the relative volatility and break azeotrope of the mixture. Extractive distillation with salt and salt containing distillation have been used in practice due to their low energy consumption high efficiency, reduced capital costs, higher yield of product, higher quality and less pollution.. Many commercial plants were given license to produce absolute ethanol using mixed acetate salts as the separating agents. concentration of aqueous nitric acid using magnesium nitrate, are some of the application of the salt effect on vapour liquid equilibrium.

The present work involves the measurement of vapour liquid equilibrium of Acetone + methanol + calcium bromide at different concentrations of salt below saturation level. The addition of calcium bromide to this solvent mixture increases the acetone concentration in vapour phase at equilibrium. This indicates a preferential association of salt with less volatile component, methanol in the acetone – methanol solvent mixture.

Most of the Salt effect studies were carried out at saturated level of salt. In this study the effort is made to study the salt effect below the saturation level of salt and to verify the furter model.

II. EXPERIMENTAL SECTION

2.1 Experimental set up:

Iso baric vapour liquid equilibrium was measured at atmospheric pressure using modified Smith and Bonner type still. The experimental technique and procedure were the same as explained in the paper except for the modification in the measurement of liquid composition. The liquid and vapour compositions were analysed by gas chromatography with the help of thermal conductivity detector and an integrator. A 1.2m column packed with porapak Q 80/100 was used for the separation. The calibration was carried out with gravimetrically prepared standard solutions. The accuracy of the measured vapour phase mole fraction was -+0.001.Before measuring the liquid composition the salt present has to be removed. This can be done by evaporating the known quantity of liquid to dryness and analyzing the evaporated liquid for its composition using gas chromatography. For comparison purpose all the composition were calculated on salt free basis. The boiling temperature was measured using a calibrated thermometer with an accuracy of 0.1 C

2.2 Chemicals :

Acetone (qualigen, Analar grade) with a stated purity of 99.8 mass percent, Methanol (qualigen,Analar grade) with a stated purity of 99.8 mass percent were used after redistillation. Calcium bromide (Qualigen Analar grade) was desiccated in a oven before use

III. RESULTS AND DISCUSSION

Iso baric vapour liquid equilibrium data for the system Acetone (1) – Methanol (2) – Calcium bromide (3) have been measured at different mole fraction of salts (0.0, 0.02, 0.03, 0.04,saturation) The experimental results are given in table 2.

***Table I:* Physical properties of chemicals used**

Solvent	Molecular weight	Boiling point K	Density kg/m/m^3	Refractive index at 293 k
Acetone	58.08	329.1 (329.29)	789 (790)	1.356 (1.3587)
Methanol	32.04	337.6 (337.7)	790 (792)	1.328 (1..3284)

Literature value in parantheses

Table 2. **Vapour – Liquid Equilibrium and Activity Coefficient Data for Acetone (1) – Methanol (2) – Calcium bromide (3)**

x1	y1	t1	Activity Coefficient	
			Gamma1	Gamma2
Without salt				
0.105	0.203	334.5	1.74	1
0.199	0.349	332.5	1.6	1
0.298	0.432	331.1	1.38	1.06
0.402	0.514	329.9	1.29	1.11
0.497	0.598	329.2	1.22	1.13
0.599	0.659	328.8	1.14	1.22
0.701	0.732	328.5	1.1	1.29
0.811	0.801	328.4	1.05	1.45
0.901	0.883	328.6	1.03	1.69
Salt 0.02 mole fraction				
0.105	0.215	335	2.46	1.79
0.199	0.367	333	2.32	1.63
0.298	0.469	331.2	2.06	1.48
0.402	0.549	330	1.83	1.35
0.497	0.635	329.4	1.74	1.27
0.599	0.691	329	1.49	1.17
0.701	0.769	328.7	1.43	1.13
0.811	0.828	328.5	1.2	1.07
0.901	0.957	328.6	2.47	1.1
Salt 0.03 mole fraction				
0.105	0.238	335.2	1.98	1.06
0.199	0.378	333.1	1.68	1.06
0.298	0.489	331.5	1.53	1.06
0.402	0.561	330.1	1.38	1.13
0.497	0.657	329.5	1.32	1.08
0.599	0.716	329.2	1.21	1.14
0.701	0.782	328.8	1.15	1.18
0.811	0.834	328.6	1.08	1.36
0.901	0.915	328.7	1.05	1.39
Salt 0.04 mole fraction				
0.105	0.238	335.3	1.97	1.06
0.199	0.386	333.2	1.71	1.04
0.298	0.513	331.6	1.6	1.01
0.402	0.587	330.3	1.43	1.05
0.497	0.671	329.5	1.35	1.04
0.599	0.731	329.3	1.23	1.07
0.701	0.791	328.9	1.16	1.13
0.811	0.849	328.7	1.09	1.23
0.901	0.928	328.8	1.06	1.17
Salt Saturation				
0.105	0.249	335.3	2.06	1.04
0.199	0.395	333.3	1.74	1.02
0.298	0.519	331.7	1.61	0.99
0.402	0.583	330.4	1.42	1.06
0.497	0.673	329.5	1.35	1.03
0.599	0.735	329.4	1.23	1.05
0.701	0.792	328.9	1.16	1.12
0.811	0.841	328.8	1.08	1.29
0.901	0.934	328.9	1.06	1.07

Experimental data are plotted in the form of x-y diagram.(Fig.1).From this figure it can be seen that the addition of calcium bromide to the system Acetone + Methanol increases the amount of acetone in the vapour phase and shifts the azeotrope to the acetone rich region and eliminates completely at saturation. As the concentration of the salt increases the relative volatility increases and azeotrope shifts from 0.8 to 1. This indicates the salting out effect of the salt. The liquid phase activity coefficients were calculated by applying a correction factor for the saturated vapour pressure of the components in presence of salts, as suggested by Jaques and Furter. The following relationship was used.

$$\gamma i = yi\ P/\ xi\ pi\ \varepsilon_i$$

where εi is the correction factor to account the changes in vapour pressure caused by the addition of salt. Azeotrope is completely shifted to 1 in the case of calcium bromide at 0.4 mole fraction and saturation level. At 0.03 mole fraction the azeotrope is shifted from 0.8 to 0.9. It is observed that for all concentration of salt the salting out effect is predominant in acetone lean region.

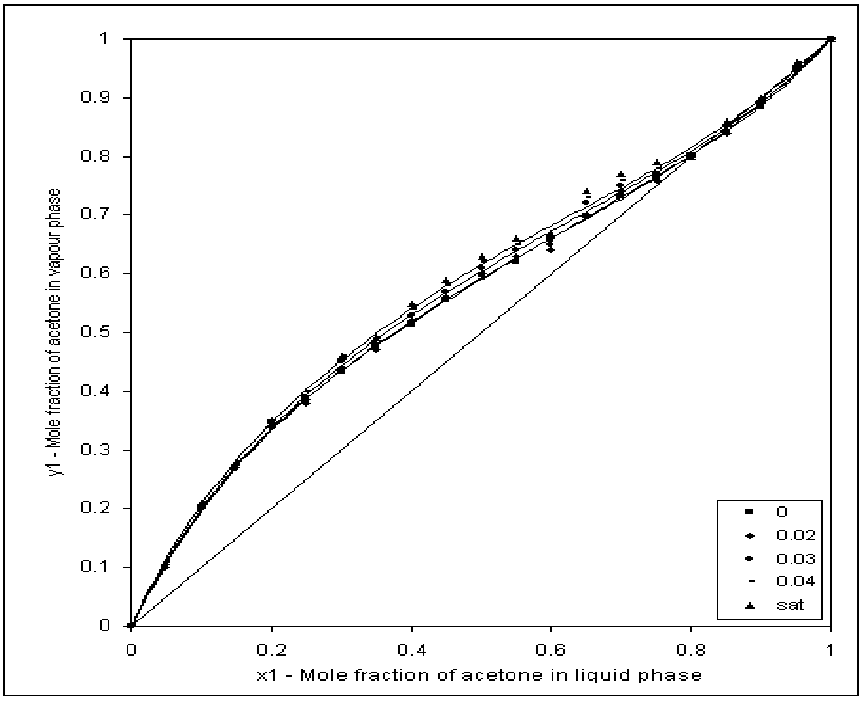

Figure 1 : x – y Vapour Liquid Equilibrium Diagram at 101.3 KPa for the system Acetone (1) – Methanol (2) – Calcium Bromide (3) at different concentration of salt

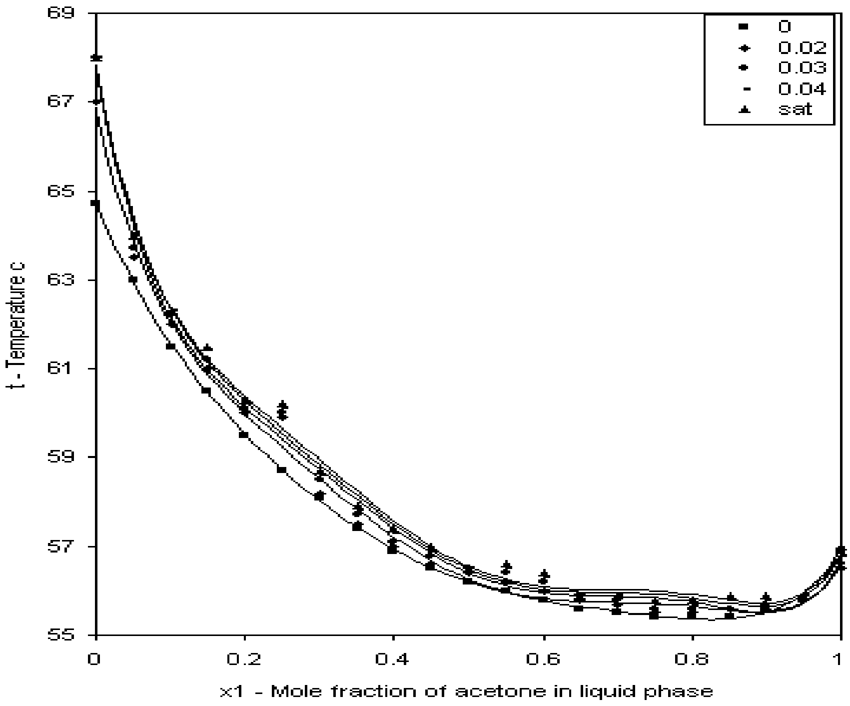

Figure 2 : x – t for the system Acetone (1) – Methanol (2) – Calcium Bromide (3) at different concentration of salt

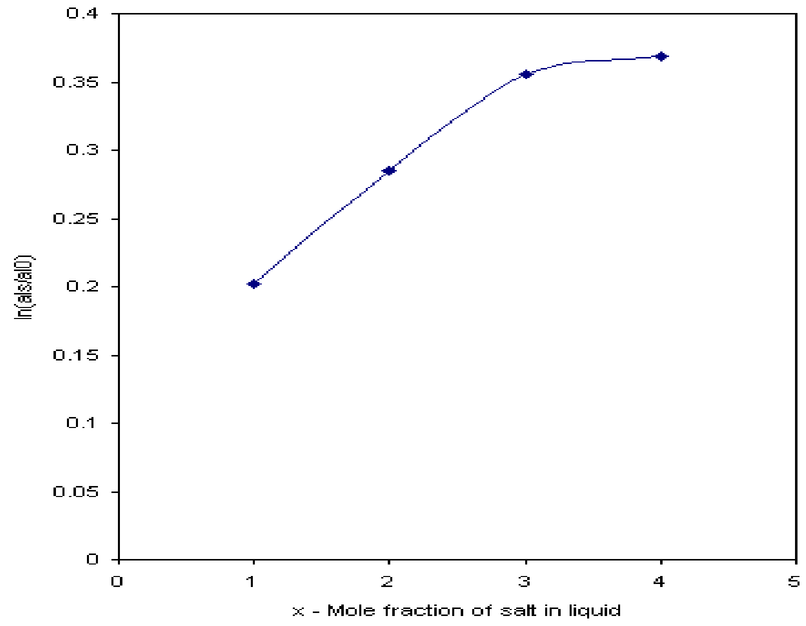

Figure 3 : x – ln(αs/αo) for the system Acetone (1) – Methanol (2) – Calcium Bromide (3) at different concentration of salt

Figure 2 x – t shows that as the concentration of salt increases in liquid phase the temperature increases. The General trend is noticed.
Figure 3, x-alpha indicates the relative volatility increases with increase in salt concentration which is the desired factor for increase in purity.

IV. CONCLUSION

Addition of salt in Acetone – Methanol mixture removes azeotrope completely in the concentration of 0.04 to saturation.. The experimental set up used was calibrated by conducting experiment for the known system. (acetone – water). The experimental data were checked for thermodynamic consistency.

Calcium bromide salt was added in the mixture 0,0.02,0.03,0.04, sat mole fraction. Azeotropic composition at 0 mole fraction is 0.8. At 0.02 mole fraction of salt the azeotropic composition is shifted to 1 mole fraction. At 0.03 mole fraction the azeotropic composition is shifted to 1. At 0.04 the azeotropic composition is shifted to 1. At saturation the azeotropic composition is shifted to 1. Salting out effect is noticed in all cases.

The solubility data reveals that calcium bromide is soluble in methanol and negligible solubility in acetone. The normal trend of salting out of acetone from the mixture is observed. The salting out may be due to the salts combining with the molecules of solvent in which the salt is more soluble. This is as a result of combining the probability that salt ions will tend to cluster preferentially with molecules of the more polar component and hence reduce its volatility in relation to that of the other.

List of symbols
γi - Activity coefficient
yi - Mole fraction of component in vapour phase
P – Total pressure
t – Temperature deg centigrade
xi - Mole fraction of component 1 in liquid phase
pi – Partial pressure of component 1
ε_i -correction factor

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