

EFFECT OF CALCIUM CHLORIDE IN VAPOUR LIQUID EQUILIBRIA OF THE SYSTEM 1,4 DIOXANE-WATER

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A precise knowledge of vapour liquid equilibrium data is required in the design of distillation columns. In the present study an attempt is made to find out the effect of calcium chloride on the vapour liquid equilibrium of the system 1,4 dioxane-water at atmospheric pressure of 760 ± 1 mm Hg. It was observed that the calcium chloride is helpful in shifting the azeotropic concentration. Linear relationships were developed between the relative volatilities and concentrations of calcium chloride.

Key words: Salt effect, Vapour liquid, Equilibria, Extractive distillation.

Introduction

The vapour liquid equilibrium data is essential in the design of distillation columns. Special techniques such as extractive and azeotropic distillation are required for the separation of close boiling and azeotropic mixtures. In extractive and azeotropic distillation a third component is added to alter the relative volatilities. Generally liquids are used but the advantage of using solid rather than liquid as the third component is that the extracting agent would not be present in the overhead product since it is a non volatile. The presence of a salt reduces the volatility of liquid by lowering its vapour pressure.

The concept of adding a non volatile component to a liquid mixture to alter its properties is not new [1]. Wright [2] measured the vapour pressures under conditions of constant temperature in non boiling systems and predicted the salt effect. Cyparis [3] had compiled the vapour liquid equilibrium data for 188 systems containing salt. Samaddar *et al.* [4] also reported the work done on salt effect by first distilling the binary mixtures and then in the presence of salt by measuring the vapour enrichment or distillation rate. Tursi *et al.* [5] tried to correlate the vapour liquid equilibrium data of system involving a salt considering the molal solubility of salt in water at the boiling point. Johnson *et al.* [6] proposed a semi theoretical model to determine the salt effect in vapour liquid equilibrium. Sada *et al.* [7] predicted the data of vapour liquid equilibrium systems saturated in the salt from indirect measurements, salt free binary data and vapour pressure of saturated solutions. Isothermal vapour liquid equilibrium data for the pyrrole - pyridine system was studied by Liang Tiang Chu *et al.* [8]. Leu *et al.* [9] studied the vapour liquid equilibria in

selected binary systems. Recent investigators [10-27] had reported the vapour liquid equilibrium data for different systems.

The effect of a salt in a given system is a function of the degree of dissociation. The forces of causing the formation of association complexes within the liquid phase may also differ from system to system and from salt to salt. Even though a lot of work has been reported in the literature, the data on the vapour liquid equilibria for the system 1,4 dioxane-water-calcium chloride is scanty. The earlier investigators employed saturated salt concentrates rather than a constant salt concentration so as to measure the maximum effect of the added salt. But for the design of distillation columns, vapour liquid equilibria data is required at constant salt concentrations. In this study an attempt is made to find out the effect of different salt concentrations on the vapour liquid equilibria.

Experimental

Apparatus. The still used in the present system is shown in Fig. 1 and is similar to the still used by the earlier authors [24]. The still contains one litre flask made with pyrex glass. To prevent the entrainment, an internal vapour jacket is placed in the neck of the flask. A coil of nichrome wire is imbedded between the two layers of magnesia-asbestos lagging which is used to cover the pot from the top of the liquid level to the top of the neck. The wire is useful in superheating the vapour for 2-3°C and the superheating is controlled with the help of variac. The condenser is placed to eliminate air transport to the still. A large part on the side of the boiling still is useful to load the salt before the experimental work. The three way stop cock joining the condensate chamber is located at a higher level in order to prevent contamination of the condensate sample by back mixing of the salt saturated liquid from the

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pot. The three way stop cock is useful to vary the volume of the condensate chamber. The concentrated flame of one to two burners is found suitable for heating. The temperatures of superheated vapour and boiling liquid can be measured by the high quality of thermometers which will give accurate readings. After the steady state has been achieved, the stop cock is rotated to take the samples since the boiling is enough to give agitation, magnetic stirring has not been employed.

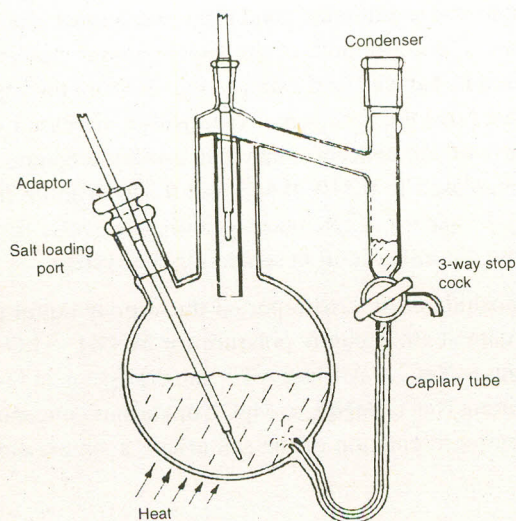


Fig. 1. Vapour liquid equilibrium still.

TABLE 1. VAPOUR LIQUID EQUILIBRIUM DATA FOR THE SYSTEM 1,4 DIOXANE-WATER WITH 0.02, 0.05 MOLE FRACTION OF THE SALT AT 760 mm Hg.

| No. | Mole fraction of dioxane in liquid phase | 0.02 Mole fraction of the salt | | 0.05 Mole fraction of the salt | |
|-----|--|------------------------------------|----------------------------|------------------------------------|----------------------------|
| | | Mole fraction of dioxane in vapour | Equilibrium temperature °C | Mole fraction of dioxane in vapour | Equilibrium temperature °C |
| 1. | 0.007 | 0.113 | 98.9 | 0.123 | 102.3 |
| 2. | 0.021 | 0.168 | 96.7 | 0.190 | 99.6 |
| 3. | 0.035 | 0.242 | 95.0 | 0.300 | 98.6 |
| 4. | 0.097 | 0.404 | 89.5 | 0.466 | 98.5 |
| 5. | 0.168 | 0.452 | 89.2 | 0.500 | 98.3 |
| 6. | 0.252 | 0.440 | 88.9 | 0.520 | 98.0 |
| 7. | 0.306 | 0.440 | 88.8 | 0.524 | 96.2 |
| 8. | 0.372 | 0.466 | 88.8 | 0.538 | 92.9 |
| 9. | 0.430 | 0.490 | 88.6 | 0.538 | 95.7 |
| 10. | 0.465 | 0.484 | 88.3 | 0.538 | 95.4 |
| 11. | 0.514 | 0.514 | 88.2 | 0.538 | 95.3 |
| 12. | 0.590 | 0.526 | 88.9 | 0.572 | 91.2 |
| 13. | 0.630 | 0.546 | 90.5 | 0.612 | 93.0 |
| 14. | 0.720 | 0.612 | 91.9 | 0.640 | 95.5 |
| 15. | 0.766 | 0.660 | 92.3 | 0.680 | 94.5 |
| 16. | 0.860 | 0.720 | 94.5 | 0.740 | 95.6 |
| 17. | 0.906 | 0.736 | 94.6 | 0.766 | 96.0 |

The Abbe refractometer whose accuracy is up to third decimal place and constant temperature bath are used to analyse the samples.

All the reagents used in the present study are of analytical reagent grade.

500 ml of the binary composition of the 1, 4 dioxane-water was prepared. The sample was withdrawn for analysis by using refractometer. The mixture was charged into the still

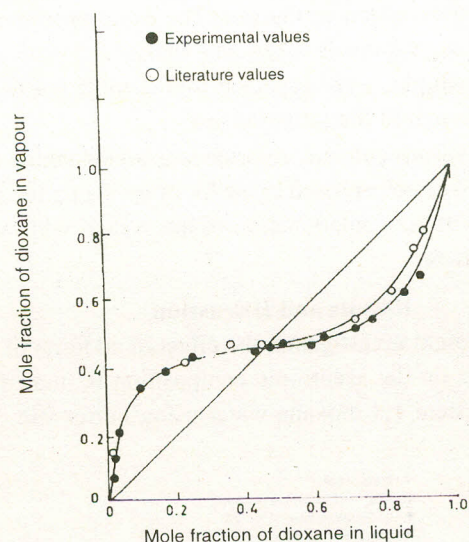


Fig. 2. Vapour liquid equilibrium curve for the system 1,4 dioxane-water.

TABLE 2. VAPOUR LIQUID EQUILIBRIUM DATA FOR THE SYSTEM 1,4 DIONANE - WATER WITH 0.1 MOLE FRACTION OF THE SALT AND WITH SATURATED SALT CONDITION OF 760 mm Hg.

| No. | Mole fraction of dioxane in liquid phase | 0.02 Mole fraction of the salt | | 0.05 Mole fraction of the salt | |
|-----|--|------------------------------------|----------------------------|------------------------------------|----------------------------|
| | | Mole fraction of dioxane in vapour | Equilibrium temperature °C | Mole fraction of dioxane in vapour | Equilibrium temperature °C |
| 1. | 0.007 | 0.135 | 112.4 | 0.143 | 126.4 |
| 2. | 0.021 | 0.306 | 106.6 | 0.300 | 114.2 |
| 3. | 0.035 | 0.420 | 98.7 | 0.466 | 102.8 |
| 4. | 0.097 | 0.520 | 98.3 | 0.660 | 102.3 |
| 5. | 0.168 | 0.538 | 97.8 | 0.686 | 101.7 |
| 6. | 0.252 | 0.590 | 96.7 | 0.718 | 101.7 |
| 7. | 0.306 | 0.595 | 96.1 | 0.720 | 101.5 |
| 8. | 0.372 | 0.612 | 95.9 | 0.740 | 99.6 |
| 9. | 0.430 | 0.610 | 95.7 | 0.720 | 99.1 |
| 10. | 0.465 | 0.612 | 95.7 | 0.720 | 99.1 |
| 11. | 0.514 | 0.610 | 95.2 | 0.718 | 98.1 |
| 12. | 0.590 | 0.612 | 95.1 | 0.720 | 98.1 |
| 13. | 0.630 | 0.612 | 95.0 | 0.690 | 95.7 |
| 14. | 0.720 | 0.640 | 95.5 | 0.690 | 95.7 |
| 15. | 0.766 | 0.670 | 95.8 | 0.720 | 95.8 |
| 16. | 0.860 | -- | -- | 0.750 | 95.9 |

and calculated amount of 0.02 mole fraction of calcium chloride salt is added. The still was placed on a tripod and heating was adjusted for correct circulation rate. The still was given 15-20 min to get an equilibrium. The sample was quickly withdrawn in a small bottle and placed in a water bath to cool. After the vapour condensate sample is withdrawn, heating by variac and the flame is stopped. Then the extent of salt which is necessary for 0.05 mole fraction of calcium chloride is calculated and then added to the pot. The same procedure is adopted and the vapour is taken and analysed. In the same way vapour samples were collected for 0.1 mole fraction of the salt and to that of the saturated salt.

The anhydrous calcium chloride was added taking care to see that it was not exposed to air for more than a few seconds to prevent the contamination of the system with water from atmosphere.

Results and Discussion

In the present investigation the effect of addition of calcium chloride on the azeotropic composition is studied for the binary system 1,4 dioxane-water using Furter still. The

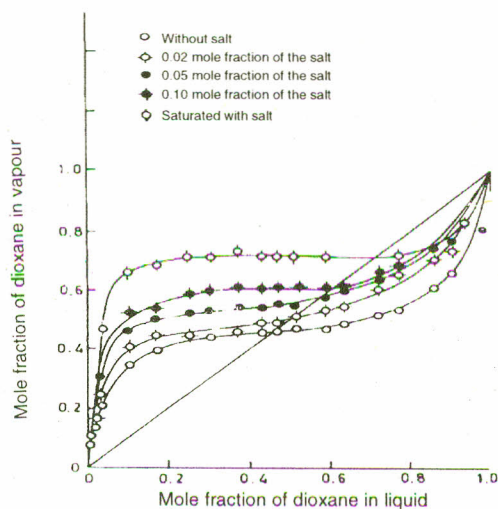


Fig. 3. Comparison of vapour liquid equilibrium curves for the system 1,4 dioxane-water-calcium chloride.

results are checked for consistency with the published data of salt free vapour liquid equilibrium data of 1,4 dioxane-water. The results are shown in Fig. 2. A close agreement between experimental and literature data [25] is noticed. From the figure it is observed that this system forms an azeotrope at $X_1 = 0.455$.

With a view to find out the effect of addition of salt on the system, salt concentrations of 0.02, 0.05 and 0.1 mole fractions and at saturation conditions of calcium chloride were studied. The entire data of the vapour liquid equilibrium is reported in Tables 1 and 2 and in Fig. 3. From the figure it is observed that the azeotropic composition increased with the increase of salt concentration. The azeotropic composition is also increased to 0.510, 0.565 and 0.620 at mole fractions 0.02, 0.05 and 0.1 of calcium chloride respectively. This shows calcium chloride useful in separating the system.

Yoshida *et al.* [26] reported the vapour liquid equilibrium data at atmospheric pressure for MeOH - H₂O system containing NaCl, CaCl₂ and AlCl₃ and the system H₂O-HOAC containing NaCl, NaNO₃ or MgCl₂ of various concentrations. For the representation of the salt effect, a simple empirical

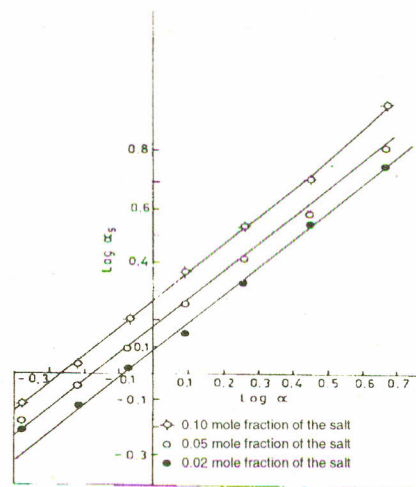


Fig. 4. Plot of $\log \alpha_s$ against $\log \alpha$ for the system 1,4 dioxane-water-calcium chloride.

TABLE 3. DATA OF RELATIVE VOLATILITIES FOR THE SYSTEM AT DIFFERENT SALT CONCENTRATIONS.

| S. No. | Mole fraction of the dioxane in liquid phase | Mole fraction of the dioxane in vapour phase | | | | Relative volatilities | | | |
|--------|--|--|---------------------------|----------------------------|---------------------------|-----------------------|----------------------------|---------------------------|---------------------------|
| | | Without salt | 0.2m fraction of the salt | 0.05m fraction of the salt | 0.1m fraction of the salt | without salt | 0.02m fraction of the salt | 0.05 fraction of the salt | 0.1m fraction of the salt |
| 1. | 0.1 | 0.340 | 0.390 | 0.425 | 0.505 | 4.6364 | 5.7541 | 6.6522 | 9.1818 |
| 2. | 0.2 | 0.415 | 0.470 | 0.490 | 0.565 | 2.8376 | 3.5472 | 3.8431 | 5.1954 |
| 3. | 0.3 | 0.440 | 0.480 | 0.525 | 0.595 | 1.7602 | 2.1538 | 2.5789 | 3.4280 |
| 4. | 0.4 | 0.450 | 0.485 | 0.545 | 0.610 | 1.2273 | 1.4126 | 1.7967 | 2.3462 |
| 5. | 0.5 | 0.460 | 0.510 | 0.555 | 0.615 | 0.8519 | 1.0408 | 1.2472 | 1.5974 |
| 6. | 0.6 | 0.475 | 0.530 | 0.570 | 0.615 | 0.6032 | 0.7518 | 0.8837 | 1.0649 |
| 7. | 0.7 | 0.495 | 0.590 | 0.600 | 0.640 | 0.4201 | 0.6167 | 0.6429 | 0.7619 |

equation is proposed.

$$\log (Y_s/Y) = K.M \dots\dots\dots (1)$$

The above equation fits the data for H₂O-HOAC system very well but does not fit for MeOH - H₂O system. The equation for constant salt concentrations conditions for unsaturated systems as follows:

$$\log \alpha_s = m \log \alpha + C \dots\dots\dots (2)$$

From the data obtained in the present study, relative volatilities in the absence and presence of the salt are calculated using the formula:

$$\text{Relative volatility, } \alpha = Y_1.X_2/Y_2.X_1 \dots\dots\dots (3)$$

The results are shown in Table 3. Relative volatilities increased with the increase of salt concentration and decreased with the increase of dioxane composition in the liquid phase. Fig. 4. shows the relative volatilities in the presence and absence of calcium chloride on a logarithmic scale at 0.02, 0.05 and 0.1 mole fractions of the salt concentrations. Parallel straight lines with a slope of 1.024 are obtained at a different salt concentrations. According to the published data [24] slope of the linear equations is having a value of 0.91-1.0. The linear equations developed from the present data are as follows:

$$\text{Log } \alpha_s = 1.024 \log \alpha + 0.08 \dots\dots (4) \text{ (0.02 mole fraction of the salt)}$$

$$\text{Log } \alpha_s = 1.024 \log \alpha + 0.17 \dots\dots (5) \text{ (0.05 mole fraction of the salt)}$$

$$\text{Log } \alpha_s = 1.024 \log \alpha + 0.26 \dots\dots (6) \text{ (0.10 mole fraction of the salt)}$$

Johnson and Furter [6] proposed a semi theoretical model to determine the salt effect. They related the ratio of relative volatilities with and without salts to the salt concentrations in a given system in which the ratio of the volatile components present in liquid phase was held constant. The equation proposed by them is as follows:

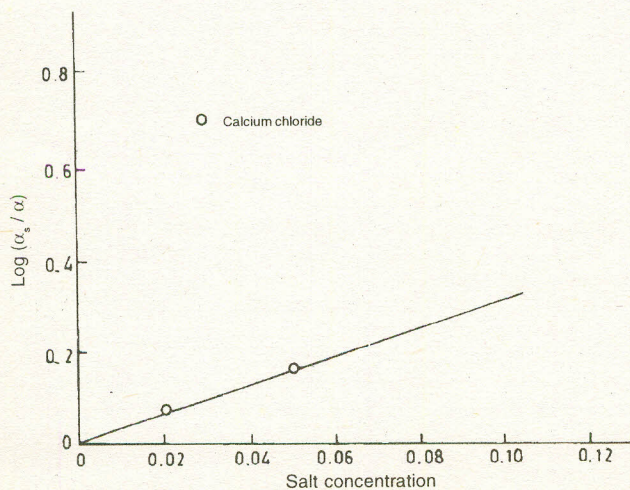


Fig. 5. Plot of $\log (\alpha_s/\alpha)$ against salt concentration in the system 1,4 dioxane water with salt calcium chloride at $x = 0.5$

$$\log \alpha_{s/\alpha} = K.N_3 \dots\dots\dots (7)$$

From the data of the present study, Fig. 5 shows:

$$\log \alpha_{s/\alpha} = 3.10 N_3 \dots\dots\dots (8)$$

The salt effect parameter K in the equation 7 represents the overall effect of a given salt on the vapour liquid equilibrium for the given system. The numerical value of K was used to assess the relative effectiveness of the salt in sorting out more volatile component of the mixture.

Variation of salt effect parameters with liquid phase composition (on salt free basis) for the present system is shown in Fig. 6. It was showed that the value of K would not be expected to remain constant even in a given system as X₂ is varied because not only the degree of salt dissociation but also all the interactions between the components of the liquid phase both volatile and non volatile are composition dependent.

Conclusions

1. The reproductibility of the data has been checked for the present system using Furter still.
2. The azeotropic composition increased with the increase of salt concentration.
3. The data has been fitted to the emperical equations developed earlier.
4. Salt effect parameter is not remained constant as expected by earlier investigations.

NOMENCLATURE

- Y_s Mole fraction of the organic solvent in the vapour phase in the presence of salt.
- Y Mole fraction of the organic solvent in the vapour phase in the absence of the salt.

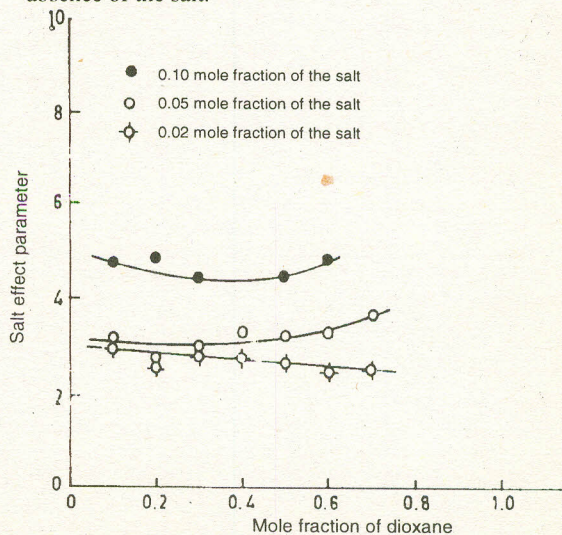


Fig. 6. Variation of salt effect parameter with liquid phase composition (on salt free basis) for the system 1,4 dioxane-water-calcium chloride.

- K Salt effect parameter.
 M Molal concentration of the salt, g. moles/kg of salt free liquid.
 α_s Relative volatility in the presence of salt
 α Relative volatility in the absence of salt
 m Empirical constant in Eqn. (2).
 C Constant for a silver constant salt in the equation (2)
 X_1 Mole fraction of dioxane in the liquid phase
 X_2 Mole fraction of water in the liquid phase
 Y_1 Mole fraction of dioxane in the vapour phase
 Y_2 Mole fraction of water in the vapour phase
 N_3 Salt concentration in the component basis, mole fraction

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