Prediction of Salt Effect in Vapour-liquid Equilibria of System Ethyl Acetate-ethanol at Atmospheric Pressure

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Experimental determination of vapour-liquid equilibrium (VLE) data of the azeotropic system ethyl acetate-ethanol in presence of three inorganic salts, namely, lithium chloride, lithium bromide and lithium iodide has been studied at atmospheric pressure (98.6 ± 0.03 kPa). The concentration of salts in the system are varied in the range of 5%-20% (weight %). It is noticed that all the three salts have pronounced effect of the VLE of the system, even to the extent that the azeotrope is completely eliminated at higher concentration of both lithium bromide and lithium iodide. A semi-empirical model similar to that of Furter model is suggested which can predict the vapour composition and boiling temperature of the system in presence of the salts with a fair degree of accuracy. The system in absence of the salt is found to be thermodynamically consistent according to the Herington criteria.

Keywords: Salt effect; Vapour-liquid equilibrium; Thermodynamic consistency

NOTATION

D, J	:	Heringcon constants
K	:	Furter constant
K_s	:	salt effect parameter
p_i	:	vapour pressure of pure component i in the mixture in presence of salt, kPa
p_i'	:	corrected vapour pressure of component i in the mixture in presence of salt
P_T	:	total pressure of the system, kPa
P_i^o	:	vapour pressure of pure component i in presence of salt, kPa
T	:	system temperature, K
X_i	:	mole fraction of component i in the liquid phase
X_{sa}	:	mole fraction of the salt in the liquid phase
Y_i	:	mole fraction of the component i in the vapour phase

Greek Letters

α	:	relative volatility
γ_i	:	liquid phase activity coefficient of component i
ε	:	correction factor for vapour pressure calculation

θ	:	difference between maximum and minimum boiling temperature in the system, K
Σ	:	total area under the curve of the plot $\left[\log \dfrac{\gamma_1}{\gamma_2} \text{ against } X_1 \right]$

Subscript

i	:	component i
s	:	in the presence of salt
cal	:	calculated
expt	:	experimental
sa,3	:	salt
1	:	more volatile component
2	:	less volatile component

Superscript

a, b, c	:	constants of the proposed model
o	:	pure component in the absence of salt
s	:	pure component in the presence of salt

INTRODUCTION

Azeotropic system/systems having low relative volatility is/are either difficult or uneconomical to separate by conventional method of fractional distillation. For such systems, addition of a third liquid component to alter the system properties to effect easier separation is a common industrial practice. The choice of the liquid component is based on the selectivity of its molecules for associating

preferentially, usually through a formation of association complexes or 'clusters' with the molecules of the less volatile feed component over that of the more. It results in lowering of its volatility to a greater extent than that of the other, thus increasing the value of the relative volatility. If the system happens to be an azeotropic one and the selectivity as well as the concentration of the agents are sufficiently high, the complete elimination of the azeotrope is possible. But it needs an extra column to recover the separating agent from the product stream for recycling.

To overcome this difficulty, the use of solid salts instead of liquid separating agents is gaining more attention during the last few decades. It has the advantages of producing a solvent-free extract at the top of the column and requires no additional separating column and this consumes much less energy as compared to the conventional method of extractive distillation. Extensive research in this field has established the fact that the presence of a dissolved salt in a mixture of solvents can often change the VLE of the system considerably. Actually when a salt is added to a system consisting of two liquid components, it has either both salting-in or/and salting-out effect on the components. The salting-out effect increases the volatility of that component with which the salt is less soluble and *vice-versa*. Therefore, the overall effect is a net change in relative volatility or shifting of the azeotropic point or complete elimination of the azeotrope, if the selection of the salt is proper.

It is known that when a salt is dissolved in a solution, it dissociates into ions. It may also happen that only a part of it dissociates leaving some un-dissociated molecules in the solution. Consequently the interaction forces between un-dissociated salt molecules, ion-molecules and ion-ion can coexist. The strength of interaction forces depends on the configuration of ions and molecules, polarities of molecules, ionic strength and composition of the mixture. Due to the above reasons, a sound theoretical basis of the salt effect is yet to be developed. As a result, most investigations concerned with the study of salt addition on the vapour-liquid equilibrium of binary systems are limited to only presentation of experimental data with no attempt to develop correlations. At the same time attempt to correlate experimental data by Van Laar[1], Redlich, *et al*[2], Wilson[3] and Renon and Prausnitz[4] have gained some success. However, for reasons of simplicity and applicability the semi-empirical model proposed by Johnson and Furter[5] is presented below which has gained maximum popularity.

$$\ln\left(\frac{\alpha_s}{\alpha}\right) = K_s\, X_{sa} \qquad (1)$$

The proportionality constant, K_S should remain substantially constant over the entire composition range, which is often not satisfied by many systems. Hence, an attempt has been made to modify this model through inclusion of liquid phase composition in the model with better results.

OBJECTIVE OF THE PRESENT STUDY

A non-aqueous azeotropic system, namely, ethyl acetate-ethanol was selected for the study, which was observed to form a minimum boilling azeotrope at 0.547 mole fraction of ethyl acetate at 71.75°C under an observed atmospheric pressure of 98.6 ± 0.3 kPa. It was intended to identify a suitable solid inorganic salt, which was capable of eliminating the azeotrope or at least shift at to a higher concentration of ethyl acetate. After trying with several salts, it was found that the effect of three halides of lithium, namely, lithium chloride, lithium bromide and lithium iodide had pronounced effect on VLE of the system. While lithium chloride only resulted in shifting the azeotropic composition to higher values, both lithium bromide and lithium iodide succeeded in eliminating the azeotrope completely with 15% (wt %) salt concentration and above. The system was also studied and reported by Hashitani and Hirata[6,7] but with different salts, namely, zinc chloride, potassium acetate and calcium chloride.

EXPERIMENTATION

Isobaric vapour-liquid equilibrium data were obtained by using a modified Othmer Still designed and reported by Ohe, *et al*[8]. In this design, the essential features of the original design were retained but the still was suitably modified to prevent or minimize, as far as possible, the errors due to various sources identified by Ellis and Garbett[9]. A main feature of the improved design of the still was the high ratio of the pot volume to liquid condensate volume and minimum vapour hold up in the condensate chamber. This feature eliminated the necessity of analyzing the liquid composition after attainment of equilibrium since the composition of the liquid prior to the addition of the salt could well be taken as the equilibrium liquid composition without introducing appreciable error. Thus, at steady state only a few drops of condensate was required to be collected and analyzed for determining the vapour composition. Incidentally, this method also possesses the advantage of producing experimental data rapidly and giving the liquid composition directly on a salt-free basis. Detailed description of the still used in the study and method of operation is given elsewhere[10]. However, the performance of the still was first ascertained by measuring the vapour-liquid equilibrium data for the system ethanol-water in presence of barium nitrate at atmospheric pressure and comparing with the reported literature data[11] (Figure 1). Reasonably good agreement confirmed the suitability of the still used for the study undertaken.

MATERIALS USED

Both the liquids used during the study were obtained from an Indigenous organization and were claimed to be guaranteed reagents of highest purity. However, they were fractionally distilled in a laboratory fractionating column and the heart cut in the desired boiling range was used. Anhydrous reagent grade salts were used for the study. All of them were dried in a drying oven prior to the use until constant weight was obtained.
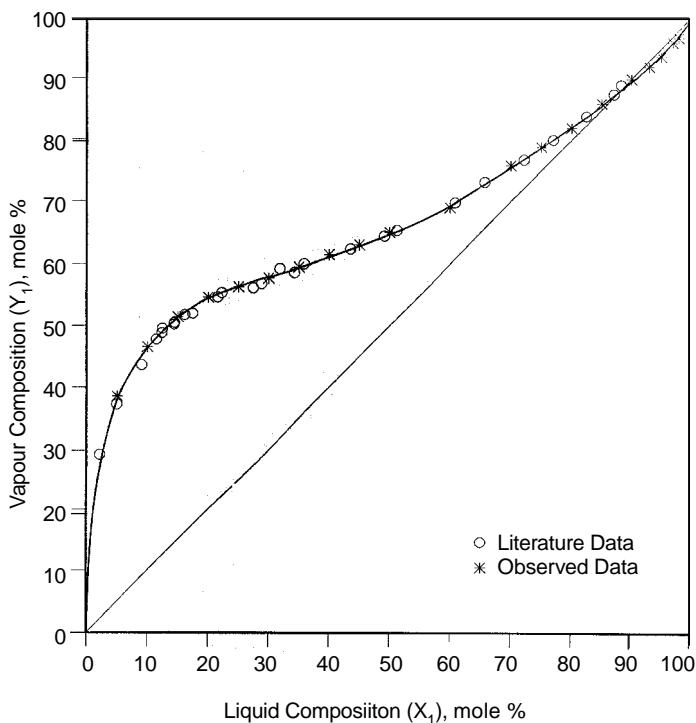
Figure 1 Still calibration diagram [System : ethanol (1) – water (2) – barium nitrate]

The physical properties of the liquid components used are compared with literature[12] data and those are given in Table 1.

TREATMENT OF EXPERIMENTAL DATA

Jaques and Furter[13] and Rousseau, *et al*[14], suggested a technique for treating systems consisting of two liquids and a salt as 'special binaries' in which it is assumed that a salt added to a mixture of solvents get associated with the liquid components in proportion to its maximum solubility in the individual components, at the existing temperature. The temperature in question was taken as the boiling point of the system. Using this concept various authours have successfully correlated and predicted salt effect on VLE using Wilson[3] equation.

For the salt containing systems, the liquid phase activity coefficients were calculated by applying a correction factor to the vapour pressure of the pure component as suggested by Jaques and Furter[15]. The relationship used can be represented as

Table 1   Physical properties of the liquids used

Compo-nent	Boiling Point, °C		Refractive Index at 20°C		Specific Gravity	
	Present Study	Litera-ture[12]	Present Study	Litera-ture[12]	Present Study	Litera-ture[12]
Ethyl acetate	75.90	76.10	1.3725	1.3728	0.901	0.901
Ethanol	78.40	78.40	1.3612	1.3510	0.787	0.788

$$\gamma_i = \frac{Y_i\, P_T}{X_i\, p_i'} \qquad (2)$$

where p_i' is the corrected vapour pressure expressed as

$$p_i' = p_i\, \varepsilon_i \qquad (3)$$

and

$$\varepsilon_i = \frac{P_T}{P_i^o} \qquad (4)$$

The vapour pressure values at any desired temperature were calculated using Antoine Equation, the constant being taken from literature[12]. The correction factor (ε_i) calculated by using the method as stated above are given in Table 2. The expression used for calculation of relative volatility of the system is given as

$$\alpha_{12} = \frac{X_1}{Y_1} \times \frac{Y_2}{X_2} \qquad (5)$$

The system ethyl acetate—ethanol under no salt condition was found to be consistent according to the Herington[16] as well as Jaques and Furter[15] criteria. The calculated constant values are shown below.

$|D| = 10.156$

$J = 2.958$

$K = 1.479$

where

$$D = \frac{\left| \int_0^1 \log \frac{\gamma_1}{\gamma_2}\, dx_1 \right|}{\Sigma} \times 100 \qquad (6)$$

Table 2   Correction factor for calculation of activity coefficients [Systen : ethy acetate (1)—ethanol (2)]

Salt	Concentration, %	Correction Factor	
		ε_1	ε_2
Lithium chloride	5	0.9986	0.9301
	10	0.9986	0.8371
	15	0.9986	0.8116
	20	0.9986	0.7077
Lithium bromide	5	0.9496	0.9792
	10	0.9281	0.9500
	15	0.9056	0.9314
	20	0.8612	0.8383
Lithium iodide	5	0.9920	0.9768
	10	0.9820	0.9501
	15	0.9760	0.9279
	20	0.9661	0.8993

Table 3 Salt effect parameter of the proposed model, root mean square and average deviation in calculation of vapour phase mole fraction and equilibrium temperature at atmospheric pressure

Salt	K	a	b	c	ΔY_1		ΔT, °C	
					RMSD	AD	RMSD	AD
Lithium chloride, (5%-20%)	0.9998	− 0.0027	0.0026	0.0302	0.0293	0.0197	1.2045	0.9245
Lithium bromide, (5%-20%)	1.0013	− 0.0141	0.0155	0.0624	0.0218	0.0168	1.5592	1.0367
Lithium iodide, (5%-20%)	1.0020	− 0.0152	0.0175	0.0744	0.0880	0.0143	1.1656	1.0118

$$J = \frac{150|\theta|}{T_{\min}} \qquad (7)$$

$$K = \frac{75|\theta|}{T_{\min}} \qquad (8)$$

CORRELATION OF VLE DATA

The salt effect on vapour-liquid equilibrium has been a subject of intense investigation from the consideration of both experimental data collection and modelling. Unfortunately, the absence of a sound theoretical basis based on the possiblities of self-interactions, pair-interactions and multi-species interaction among the solvent species, undissociated salt molecules and both ion species within the liquid phase is mainly responsible for a slow progress in this direction. Despite the lack of inadequate mechanism to explain the effect of salt addition, the need for characterization of such systems are realized and widely attempted for the sake of designing separation process equipments. As a result, correlation and development of models for vapour-liquid equilibrium data for the salt-

containing systems by means of well accepted integral form of the Gibbs-Duhem equation has been attempted.

In this regard, the well accepted Johnson and Furter[15] model [expressed by equation (1)] was tried. But it failed to correlate the experimental data in the entire range of composition of the liquid mixture under study in the concentration range of 5%-20% of the salts. This might be due to various types of molecular interactions and salt-solvent interaction forces existing within the system, which are also dependent on the relative proportion of the two volatile liquid compoonents in the liquid mixture as well as the concentration of the salt present. Hence, the Furter model [equation (1)] was modified in order to account for the inclusion of liquid phase composition. The proposed model is, therefore, expressed as

$$\frac{\gamma_1^s}{\gamma_1^o} = K_s \, X_1^a \, X_2^b \, X_{sa}^c \qquad (9)$$

The calculated activity coefficient values under salt and no-salt condition for the system under study were used to evaluate the constants by writing a small program. The values of the
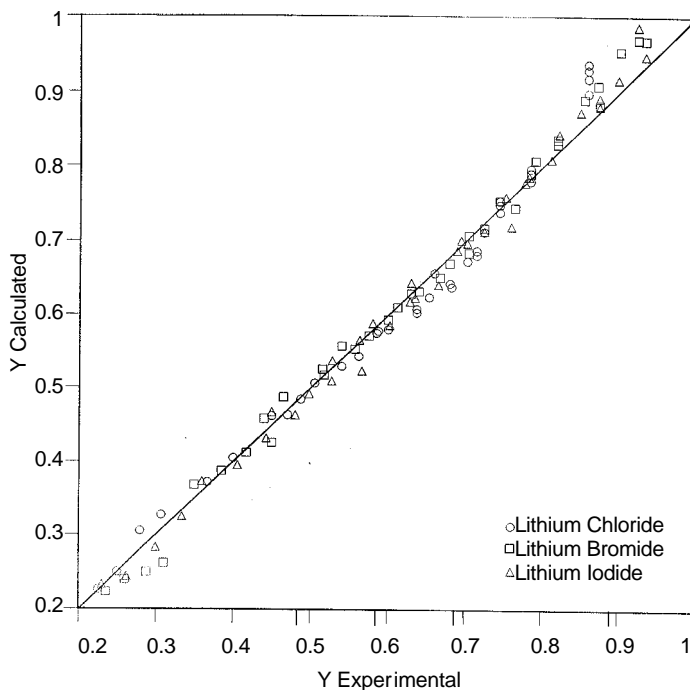

Figure 2 Comparison of experimental and calculated values of vapour phase composition in presence of salts
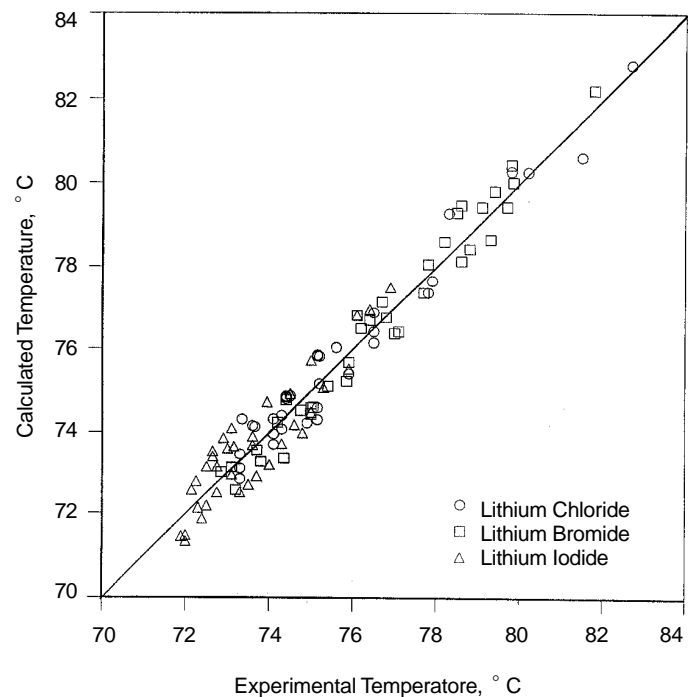

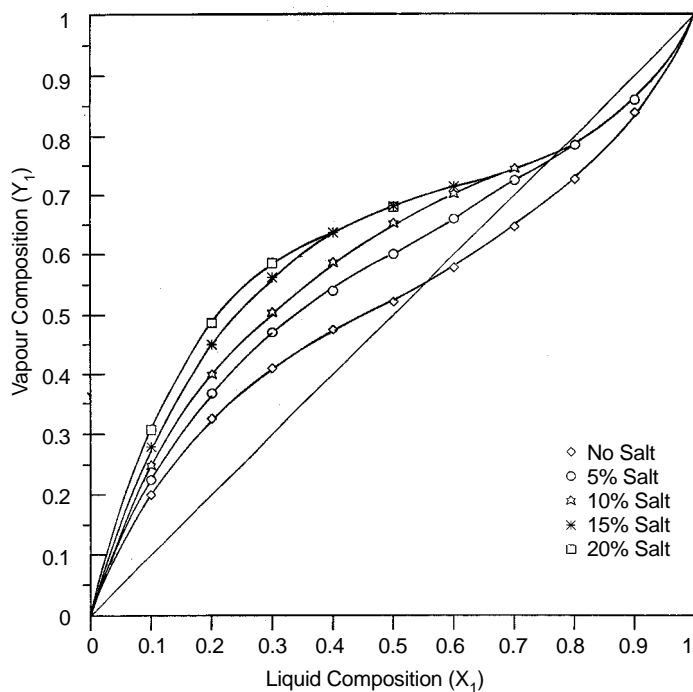**Figure 3** Comparison of experimental and calculated values of boiling point of the system in presence of salts

Figure 4 Vapour-liquid equilibrium diagram [System : ethyl acetate (1)-ethanol (2)-lithium chloride
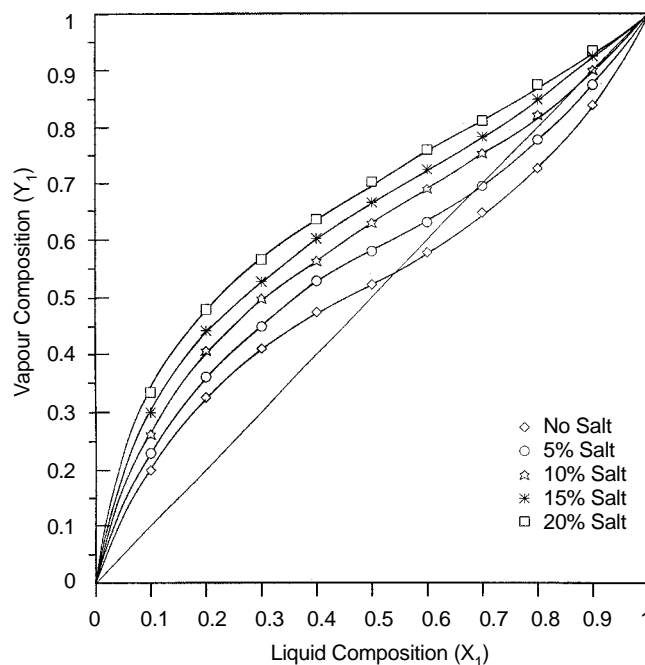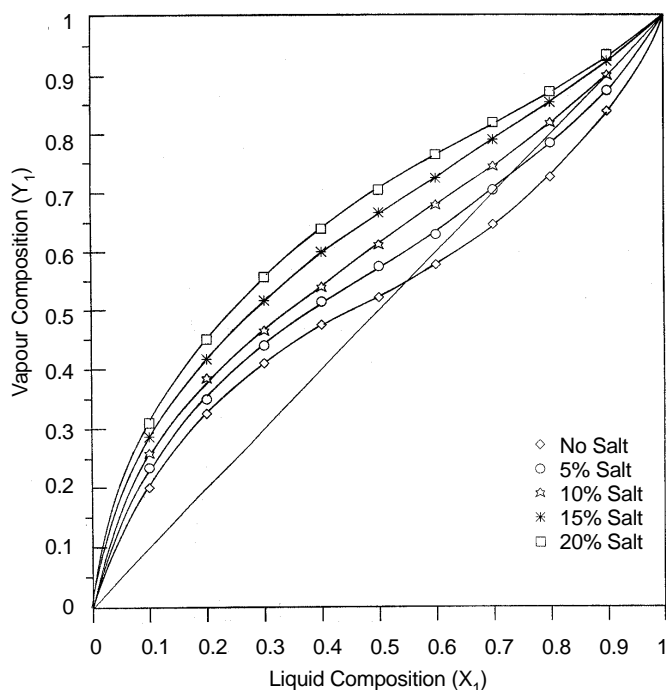

Figure 5 Vapour-liquid equilibrium diagram [System : ethyl acetate (1)-ethanol (2)-lithium bromide

constants so obtained for all systems are given in Table 3. Having known the constant values, it was possible to calculate back the ratio of γ_1^s / γ_1^o for any liquid composition for any known concentration of the salt. Thus, the vapour composition (Y_{cal}) could be predicted from the ratio under the assumption of ideal behaviour of the vapour phase and knowledge of the bubble point of the system.

Figure 6 Vapour-liquid equilibrium diagram [System : ethyl acetate (1)-ethanol (2)-lithium iodide

In a similar way, the equilibrium boiling point of the system (T_{cal}) could also be predicted having known the calculated vapour composition (Y_{cal}). Figure 2 and Figure 3 show the calculated and experimental values of vapour phase composition and bubble points, respectively for all the systems under study. The root mean square deviation and average deviation between the experimental and calculated values are also given in Table 3.

CONCLUSION

Experimentally the system ethyl acetate-ethanol is observed to form a minimum boiling azeotrope at 0.547 mole fraction of ethyl acetate at 71.75° C and atmospheric pressure of 98.6 ± 0.03 kPa. All the three salts employed, namely, lithium chloride, lithium bromide and lithium iodied are preferentially soluble in ethanol, the less volatile component of the liquid mixture. Consequently it resulted in salting-out of ethyl acetate and thus increasing the relative volatility of the system. The extent of salt effect is also observed to be proportionally higher with increased concentration of the salts in the liquid mixture.

Addition of lithium chloride only resulted in shifting the azeotropic composition to higher values. It failed to eliminate it even with addition of 20% (wt %) salt in liquid mixture. Lithium bromide on the other hand is successful in eliminating the azeotrope with 15% salt concentration and above. Addition of 5% and 10% salt only result in shifting the azeotrope to 0.759 and 0.935 mole fraction of ethyl acetate, respectively. Lithium iodide also exhibits a similar trend. Azeotrope is eliminated with 15% salt concentration and above. Addition of 5% or 10% salt only affects a shifting of

azeotropic composition to 0.697 and 0.900 mole fraction of ethyl acetate, respectively. However, all the three salts selected for the study has pronounced effect on the VLE of the system. The effect is evident right from the lowest concentration of the ester to the highest concentration. The VLE diagram for all the systems mentioned previously are shown in Figures 4-6.

Thus, it is concluded that from the view point of separation of the binary mixture of ethyl acetate-ethanol to its components by distillation, all the three halides of lithium are equally effective.

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