

Effect of Lithium chloride on Vapor Liquid Equilibria for Ethanol-Water System

V. Wankhade, R. Sirsam*

University Institute of Chemical Technology, North Maharashtra University, Jalgaon – 425001, Maharashtra, India.

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ABSTRACT

The effect of lithium chloride (LiCl) salt on vapor-liquid equilibrium (VLE) of the binary ethanol-water system has been experimentally investigated at atmospheric pressure using modified Othmer equilibrium still. An effect of salt content in the range of 0 to 10 wt % has been investigated. The addition of lithium chloride to the solvent mixture produced an important salting-out effect over the alcohol and the azeotrope tends to be shifted when the salt content increased. The experimental data were correlated by the following models Margules, Van Laar, Wilson, NRTL, UNIFAC equation.

1. Introduction

In chemical industry, the estimation of the salt effect on the vapor liquid equilibria of alcohol aqueous solution plays an important role for the distillation process [1]. For the design of distillation process it is necessary to have simple and accurate vapor liquid equilibria data of solutions [2]. Several researches have investigated the effect of various salt on VLE of various binary/tertiary system using models Margules, Van Laar [3], Wilson [4-10], NRTL [11-17], UNIFAC [18-21]. Addition of salt is the very common method to change the relative volatility and to alter the azeotropic composition [22]. Salt addition results in changing the solubility, partial and vapor pressure, density, surface tension, thermal conductivity of the mixture [23]. The force field modifies among the different solvent components due to the presence of non-electrolyte and non-volatile electrolyte, hence the solvent components are either salted-out or salted-in of the liquid and vapor composition is modified [24]. Salt addition has several advantages such as a smaller amount of separating agent, a lower energy requirement, being a solid no contamination is present in the distilled products [25]. Ethanol has several uses in chemical industry such as detergent, aerosols, medicine and food, cosmetics, perfumes, raw material, intermediate in chemical synthesis of cyclic compound chains, organics and ester [26]. In this work, the effect of LiCl at salt mass fraction from 0-10 % on VLE of ethanol-water system was experimentally investigated at atmospheric pressure using a modified Othmer equilibrium Still.

2. Experimental Methods

2.1. Materials

The chemical used are Ethanol (Merck), distilled water and lithium chloride anhydrous (Avra Synthesis Pvt. Ltd.). The chemicals were directly used without further purification.

2.2. Apparatus and Procedure

The VLE result were measured with a recirculation Othmer type still which was modified in order to minimize the volume of condensate so as to be able to consider the liquid mole fraction constant during the

experiment. So it was possible to eliminate the analysis of the liquid phase composition and also to achieve the equilibrium state more rapidly. The mixture of ethanol-water (200 mL) of different mole fraction (0.1-0.9) was added in Othmer Still. Required volume of ethanol was calculated by equation (1), desired amount of salt (0-10 wt %) was added to this mixture. Othmer Still was placed in heating mantle, gradually heat was supplied to the Still and temperature of mixture was recorded. System was operated on total reflux for 30 min to attend equilibrium condition and corresponding boiling temperature was recorded. System was then allowed to cool. Once the system attends room temperature the liquid sample was withdrawn for analysis.

$$n = \frac{\frac{\rho_e \cdot V_e}{M_e}}{\frac{\rho_e \cdot V_e}{M_e} + \frac{\rho_w \cdot (200 - V_w)}{M_w}} \quad (1)$$

where n , ρ_e , ρ_w , V_e , V_w , M_e , M_w , mole fraction of ethanol, density of ethanol, density of water, volume of ethanol, volume of water, molecular weight of ethanol, molecular weight of water respectively.

2.3. Analysis

All the samples were analyzed on Agilent 7890B GC system, using a 3 m, 1/8 in diameter, mesh 80/100, Porapak column. The temperature of oven, injector and the thermal conductivity detector were set at 180 °C (for 7 min), 200 °C and 180 °C respectively. The septum purge flow rate is 3 mL/min, the makeup flow rate is 5 mL/min, and the reference flow rate is 20 mL/min. Nitrogen was used as carrier gas for all analysis.

3. Results and Discussion

Fig. 1 shows the equilibrium composition of ethanol-water at different LiCl concentration. It has been observed that the addition of salt (0-10 wt %) changes the composition of ethanol in vapor phase at all liquid composition (0.1-0.9 mole fraction). The azeotropic point was shifted from 0.905 to 0.845, 0.840, 0.850 and 0.855 by addition of 2.5%, 5%, 7.5% and 10% LiCl salt respectively. The solution is saturated at 10 wt % LiCl which shows maximum positive deviation for the system. These changes in vapor composition may be due to the attraction of more polar component (water) by the electrostatic field of ions. Therefore the compositions of less polar component (ethanol) increase in vapor phase [2]. All the further experiments were carried out at the saturated condition.

*Corresponding Author

Email Address: rajkumarsirsam@gmail.com (R. Sirsam)

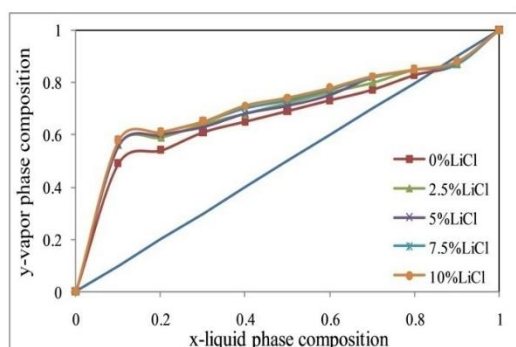


Fig. 1 VLE diagram for Ethanol-Water at atmospheric pressure

The experimental activity coefficient of pure liquid in non-ideal mixture at boiling point temperature (T) and local atmospheric pressure (P) was calculated by using equation (2).

$$y_i P = x_i \gamma_i P_i^{\text{sat}} \quad (2)$$

where y is the vapor phase composition, x liquid phase composition, P local atmospheric pressure, P^{sat} saturated vapor pressure for solvent pair i - j (ethanol-water) respectively.

Saturated vapor pressure P^{sat} was calculated for solvent pair (i - j) from Antoine equation (3).

$$\log(P_i^{\text{sat}}) = A_i - B_i / (T + C_i) \quad (3)$$

Different activity coefficient models were used to predict the activity coefficient viz Margule (Eq. 4-5), Van Laar (Eq. 6-7), Wilson (Eq. 8-10), NRTL (Eq. 11-16), UNIFAC (Eq. 17-27) for ethanol and water respectively.

$$\log_{10} \gamma_1^* = x_2^2 [A_{12} + 2 x_1 (A_{21} - A_{12})] \quad (4)$$

$$\log_{10} \gamma_2^* = x_1^2 [A_{21} + 2 x_2 (A_{12} - A_{21})] \quad (5)$$

$$\log_{10} \gamma_1^* = \frac{\bar{A}_{12}}{(1 + \frac{x_1 \bar{A}_{12}}{x_2 \bar{A}_{21}})^2} \quad (6)$$

$$\log_{10} \gamma_2^* = \frac{\bar{A}_{21}}{(1 + \frac{x_2 \bar{A}_{21}}{x_1 \bar{A}_{12}})^2} \quad (7)$$

$$\ln \gamma_1^* = -\ln(x_1 + \Lambda_{12} x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21} x_1} \right] \quad (8)$$

$$\ln \gamma_2^* = -\ln(x_2 + \Lambda_{21} x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21} x_1} \right] \quad (9)$$

$$\text{where } \Lambda_{ij} = \frac{v_j^L}{v_i^L} \exp \left[-\frac{(\lambda_{ij} - \lambda_{ii})}{RT} \right] \quad (10)$$

$$\ln \gamma_1^* = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{(x_1 + x_2 G_{21})^2} \right) + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \quad (11)$$

$$\ln \gamma_2^* = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{(x_2 + x_1 G_{12})^2} \right) + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \quad (12)$$

$$\text{Here } \tau_{12} = \frac{(g_{12} - g_{22})}{RT} \quad (13)$$

$$\tau_{21} = \frac{(g_{12} - g_{11})}{RT} \quad (14)$$

$$\text{and } G_{12} = \exp(-\alpha_{12}^* \tau_{12}) \quad (15)$$

$$G_{21} = \exp(-\alpha_{12}^* \tau_{21}) \quad (16)$$

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (17)$$

$$\ln \gamma_i^C = \ln \frac{\Phi_i^L}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i^L} + l_i - \frac{\Phi_i^L}{x_i} \sum_j x_j l_j \quad (18)$$

$$\ln \gamma_i^R = q_i [1 - \ln(\sum_j \theta_j \tau_{ji}) - \sum_j (\theta_j \tau_{ij} / \sum_k \theta_k \tau_{kj})] \quad (19)$$

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1); z = 10 \quad (20)$$

$$\text{Here } \theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad (21)$$

$$\Phi_i^L = \frac{r_i x_i}{\sum_j r_j x_j} \quad (22)$$

$$\text{and } \tau_{ji} = \exp \left[-\left(\frac{u_{ji} - u_{ii}}{RT} \right) \right] \quad (23)$$

$$r_i = \sum_k v_k^{(i)} R_k \quad (24)$$

$$q_i = \sum_k v_k^{(i)} Q_k \quad (25)$$

$$R_k = V_{wk} / 15.17 \quad (26)$$

$$Q_k = A_{wk} / (2.5 \times 10^9) \quad (27)$$

The theoretical vapor phase composition was calculated by following equation (28, 29).

$$y_1^* = x_1 \gamma_1 P_1^{\text{sat}} / (x_1 \gamma_1 P_1^{\text{sat}} + x_2 \gamma_2 P_2^{\text{sat}}) \quad (28)$$

$$y_1^* = x_1 \gamma_1 P_1^{\text{sat}} / (x_1 \gamma_1 P_1^{\text{sat}} + x_2 \gamma_2 P_2^{\text{sat}}) \quad (29)$$

All the models constant are listed in table 1.

Table 1 Model constants for different equation [3]

Model	Component Parameters	
	Ethanol(1)	Water(2)
Margules	$A_{12} = 0.6848$	$A_{21} = 0.3781$
Vanlaar	$\bar{A}_{12} = .7292$	$\bar{A}_{21} = 0.4140$
Wilson	$\lambda_{12} - \lambda_{11} = 382.30$ $v_1^L = 58.39$	$\lambda_{21} - \lambda_{22} = 955.45$ $v_1^L = 18.060$
NRTL*	$\lambda_{12} - \lambda_{11} = 382.30$ $\alpha_{12} = 0.30$	$\lambda_{21} - \lambda_{22} = 955.45$
UNIFAC	$\lambda_{12} - \lambda_{11} = 382.30$	$\lambda_{21} - \lambda_{22} = 955.45$
Antoine Constants	$A = 8.04494$	$A = 7.96681$
	$B = 1554.30$	$B = 1668.21$
	$C = 222.65$	$C = 228.00$

*significance of g_{ij} is similar to that of λ_{ij} in Wilson's equation.

Fig. 2 shows experimental liquid composition versus calculated vapor phase composition for various models at 10 wt % LiCl, Margules and Van Laar predicts complete elimination of azeotropic point where as other model shows close relation with experimental values. Fig. 3 shows plot of experimental and calculated vapor phase composition. It is observed that most of the data falls near the diagonal line, which implies the fairly good indication agreement of the model.

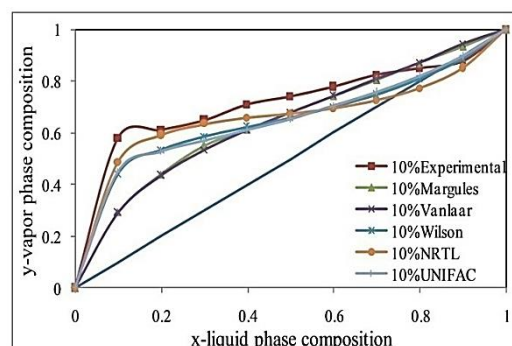


Fig. 2 Experimental and Calculated vapor composition for ethanol-water system

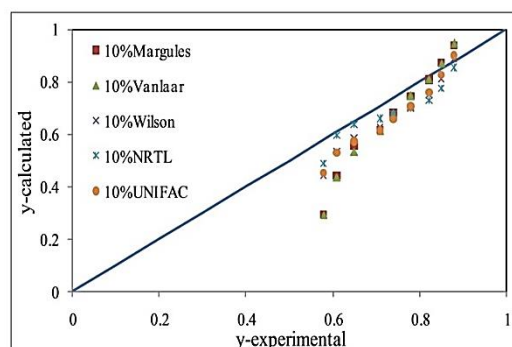


Fig. 3 Comparison of experimental and calculated vapor composition for ethanol-water system

The Activity coefficient calculated by all the models were used to correlate the experimental activity coefficient and vapor liquid equilibrium data. It can be seen from Fig. 4 that the activity coefficient calculated by NRTL, Wilson and UNIFAC model are in good agreement with experimental data. However, the Margules and the Van Laar model shows good agreement at higher concentration. Over the composition range of 0.1 to 0.9 mole fraction, the positive value of Activity coefficient shows the positive deviation for the system.

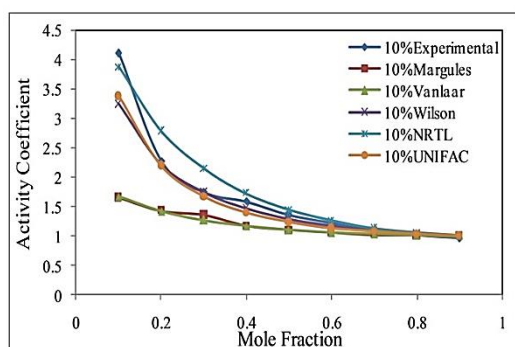


Fig. 4 The Activity Coefficient in propanol-water system

4. Conclusion

VLE data were measured for ethanol-water mixture at 10 wt % Lithium chloride salt, which shows considerable salting-out effect for Ethanol. The Margules, Van Laar, Wilson, NRTL, UNIFAC models were used to predict the vapor phase composition and Activity coefficients. The predicted vapor composition data by NRTL model satisfactory agree with the experimental one. The calculated activity coefficient by UNIFAC, NRTL and Wilson model are comparable with experimental data.

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Nomenclature

A	= Antoine constant
A_{wk}	= surface area
A_{12}, A_{21}	= parameters in the Margules equation
$\bar{A}_{12}, \bar{A}_{21}$	= parameters in the Van Laar equation
B, C	= Antoine constant, °C
P_i	= vapor pressure of i^{th} component, cc/g mol
q	= pure component area parameter
Q	= group area parameter
R	= gas law constant, cal/g mol K
r_i	= pure component parameter
R_k	= group volume parameter (with subscript)
T	= temperature, °C
v_i^L	= liquid molar volume of the i^{th} component, c/g mol
V_{wk}	= van der waals group volume
x_i	= liquid mole fraction of the i^{th} component
y_i	= vapor mole fraction of the i^{th} component
z	= lattice coordination number, a constant here set equal to ten
γ_i	= activity coefficient of the i^{th} component
Γ_k	= activity coefficient of group k
$\Gamma_k^{(i)}$	= activity coefficient of group k in pure component i
θ_i	= area fraction of component i
Φ_k	= segment fraction of component k
Θ_k	= area fraction of group k
$\nu_k^{(i)}$	= number of group of kind k in a molecule of component i
τ_{ij}, τ_{ji}	= binary parameter
Ψ_{mn}	= interaction parameter
Λ_{ij}	= variables defined by Wilson equation
$(\lambda_{ij} - \lambda_{ji})$	= parameter in the Wilson equation, cal/g mol

Superscripts

C	= combinatorial
R	= residual

Subscripts

i, j, k	= component i, j, and k
k, m, n	= group k, m and n

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