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Vapor-Liquid Equilibria of Isopropanol-Water Mixtures in the presence of Tetrasodium Ethylenediaminetetraacetic Acid

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Abstract: The recent COVID-19 pandemic has emphasized the importance of antiseptics, one of which being isopropyl alcohol or isopropanol (IPA), which is derived from the indirect hydration of propylene. Due to its miscibility with water, IPA can only be conventionally distilled at a maximum of 67.20% mol at its azeotropic point with a bubble point of 80.2°C. Azeotropic distillation is commonly employed to further purify IPA through the addition of entrainers to shift or eliminate the azeotrope of the binary system. A special type of this process is salt distillation, which utilize the preferential interaction between ionic compounds and polar water molecules to isolate the IPA molecules. In this paper, the ability of tetrasodium ethylenediaminetetraacetic acid (EDTA) salt as a mass separating agent was evaluated for the IPA-water system. To particularly quantify this potential, the vapor-liquid equilibrium of the binary system at different salt concentrations were determined both experimentally and through simulation. Experimental vapor-liquid equilibrium (VLE) data were obtained using solutions with IPA fractions ranging from 0.0375 to 0.9000 at 0.005, 0.010, and 0.020 molal concentrations of tetrasodium EDTA in an ebulliometer at total reflux. The concentrations of the liquid and vapor phases at equilibrium were measured using refractive index. The VLE was modelled to satisfy the Modified Raoult's Law where the vapor phase was assumed ideal and the activity coefficients were determined through the UNIFAC-Dortmund model. The addition of tetrasodium EDTA to the IPA-water system resulted in higher concentrations of alcohol achieved in the vapor phase as compared to the salt-free binary system. The azeotrope was shifted from 0.6720 mole fraction with respect to IPA to 0.8400 and 0.9050 for systems with 0.005 and 0.01 m of salt, respectively. Elimination of azeotrope was observed at 0.02 m of tetrasodium EDTA.

Key Words: isopropanol; tetrasodium EDTA; vapor-liquid equilibrium; UNIFAC-Dortmund

1. INTRODUCTION

The demand for alcohol increases in the recent years, not only in pharmaceutical uses due to the COVID-19 pandemic, but also in solvent applications and the manufacture of agricultural products, semiconductors, and process catalysts. The IPA-Water system produces an azeotrope at 80.23°C with a 67.20% IPA composition (Gironi & Lamberti, 1994), rendering the purification of IPA through simple distillation difficult. Current technologies like molecular sieving or adsorption using desiccants require costly operations for regeneration.

One alternative is salt distillation, which involves the addition of salts more soluble in water than in IPA, causing IPA to be salted out of the solution. Halides (Prausnitz & Targovnik, 1958; Gironi & Lamberti, 1994), nitrates (Polka & Gmehling, 1994), hydrocarbons (Zabaloy, 1993), and organic compounds such as esters and ethers (Pienaar, 2013) were found to shift the azeotropic points of the IPA-Water system at varying salt concentrations and experimental conditions.

This study investigated the potential of the tetrasodium salt of EDTA as a mass-separating agent for the distillation of the IPA-Water system at atmospheric pressure. Currently, only the application of this salt in the ethanol-water system (Bungay et al., 2010) has been investigated. The property of having many bonding sites that is attributed to chelating agents may serve to be useful in shifting or eliminating the azeotrope in the IPA-Water system.

2. METHODOLOGY

2.1 Chemicals

Reagent grade IPA (99.8%) and tetrasodium EDTA dihydrate (98.0%) were used. The salt was dried at 120°C to obtain its anhydrous form.

2.2 Apparatus and Procedures

The apparatus for achieving vapor-liquid equilibrium for prepared samples are in reference to the development of the circulating still by Novianti (2007), shown in Figure 1.

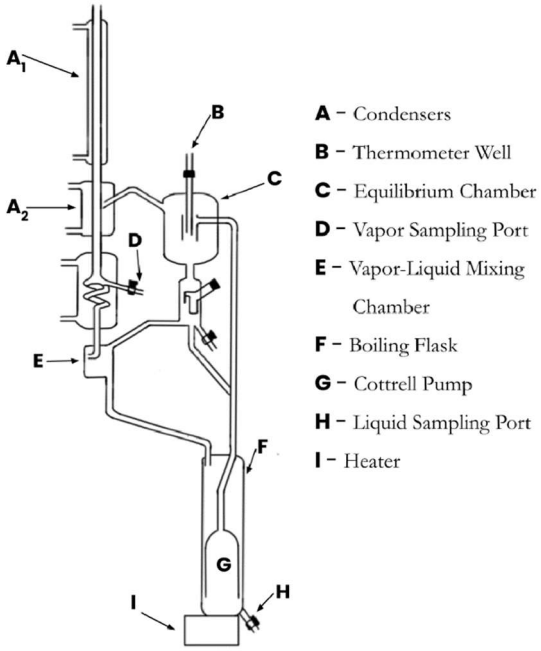

Fig. 1. VLE Experimental Apparatus

In each experiment, the ternary mixture of IPA + water + tetrasodium EDTA was poured into the boiling flask (**F**) in contact with a heater (**I**) underneath. The Cottrell pump (**G**) withdrew vapor from the boiling flask into the equilibrium chamber (**C**), where the vapor temperature was taken. The vapor condensed in the condensers (**A**) and into the vapor-liquid mixing chamber (**E**), and then to the boiling flask again. This cycle was repeated until thermometer (**B**) shows uniform temperature readings in the apparatus. The vapor and liquid products were then collected from their respective outlets (**D**, **H**).

Salt-free equilibrium liquid samples were initially isolated using a rotary evaporator. The composition of vapor and liquid were identified via refractometry using the Atago DR-A1 Abbe Refractometer. The concentrations of the liquid and vapor samples were determined with the calibration curve obtained from salt-free concentrations of IPA.

3. RESULTS AND DISCUSSION

3.1 VLE of IPA-Water Systems

The equilibrium compositions of the salt-free IPA-water system obtained from experiments, the from modelling, and from Gironi (1994) were plotted in Figure 2 which exhibit similar VLE behavior. The azeotrope is determined to be at 0.675 mole fraction with respect to IPA, with a bubble point of 80.85 ˚C.

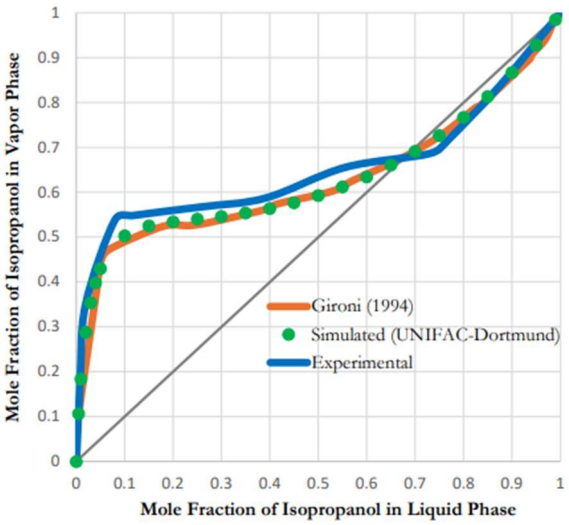

Figure 2. x-y Diagram of IPA-Water System

3.2 VLE of IPA-Water Systems with Tetrasodium EDTA

Experimental VLE data of IPA-water mixtures with tetrasodium EDTA were obtained for IPA-water mixtures with tetrasodium EDTA salt at 0.005, 0.01, and 0.02 molal concentrations. For comparison, the VLE were also modeled with activity coefficients calculated using the UNIFAC-Dortmund method.

Adding tetrasodium EDTA salt in IPA-water mixtures increased concentrations of alcohol in the vapor phase which is desired in producing high-purity IPA. Higher salt concentrations enhance this effect by salting in more water in the liquid phase and salting out IPA. This behavior is shown in Figures 3 and 4 plotting alcohol concentrations in the vapor phase, y, against equilibrium liquid concentrations, x.

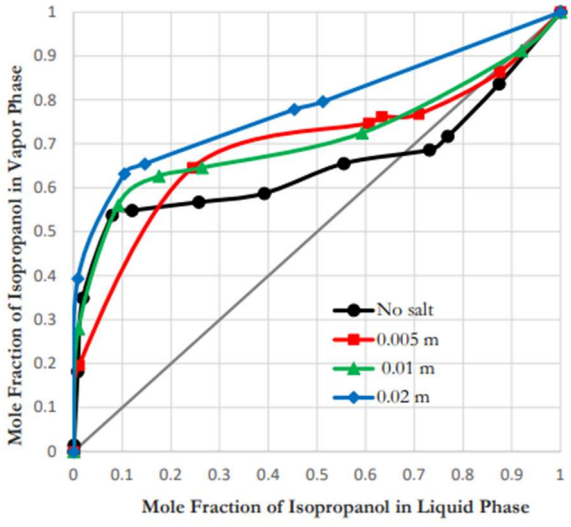

Figure 3. Experimental x-y Diagrams of IPA-Water System with Tetrasodium EDTA

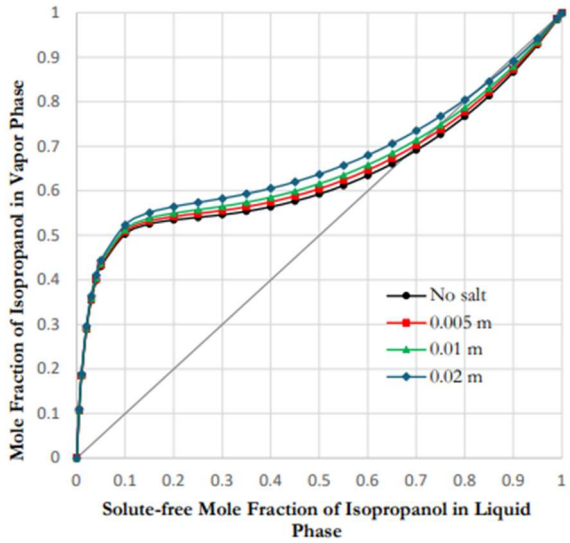

Figure 4. Simulated x-y Diagrams of IPA-Water System with Tetrasodium EDTA

3.3 Evaluation of Azeotropes

The azeotropes were determined to quantify the effect of adding tetrasodium EDTA salt in IPA-water mixtures, as azeotropes limit the highest concentration of IPA that can be extracted from crude mixtures through distillation processes.

The azeotropic points of the experimental data deviated from the simulations, as summarized in Table 1, with the elimination of the azeotrope being achieved at 0.02 m with a bubble point of 81.95 °C. From the simulation results, the azeotrope was found to be eliminated at salt concentration of 0.04 m or higher, with the bubble point of 81.09 °C.

This can serve as preliminary data whether the tetrasodium EDTA can eliminate the azeotrope of IPA-water mixtures. Further development in the simulation is recommended with the currently unavailable interaction parameters between CH_2N and Na^+ groups.

Table 1. Azeotropes of IPA-Water System at Varying Concentrations of Tetrasodium EDTA

Salt Concentration (m)	Experimental		Model	
	Azeotropic IPA Mole Fraction	T (°C)	Azeotropic IPA Mole Fraction	T (°C)
0	0.675	80.85	0.677	80.35
0.005	0.84	80.35	0.7098	80.41
0.01	0.905	81.15	0.745	80.47
0.02	0.9999	81.95	0.823	80.64

3.4 Predictive Calculation of VLE

The modified Raoult's Law, shown in Equation 1, considers the nonideal behavior of the liquid phase with the activity coefficient. With atmospheric pressure, it can be assumed that the vapor phase fugacity and the Poynting factor to be unity. The value of the vapor pressure for pure components were calculated with the Antoine equation as shown in Equation 2.

In two-component systems, the sum of the mole fractions in the vapor phase must be equal to one. In the process, an iterative algorithm was used to determine the temperature at which this condition is observed.

$$y_i P_T = \gamma_i x_i P_i^{sat} \quad \text{(Eq. 1)}$$

where:

P_T = Total pressure
P_i^{sat} = Saturation vapor pressure (i)
y_i = Vapor-phase mole fraction of i
x_i = Liquid-phase mole fraction of i
γ_i = Activity coefficient of i

$$\log P^{sat}\,(bar) = A - \frac{B}{T\,(°C) + C} \quad \text{(Eq. 2)}$$

where:

P^{sat} = Saturation vapor pressure
T = Temperature
A, B, C = Antoine Constants

The Antoine constants in Equation 2 for IPA and water are shown in Table 2.

Table 2. Antoine Constants for IPA and Water

Component	A	B	C
Isopropanol	5.24268	1580.920	219.610
Water	5.11564	1687.537	230.17

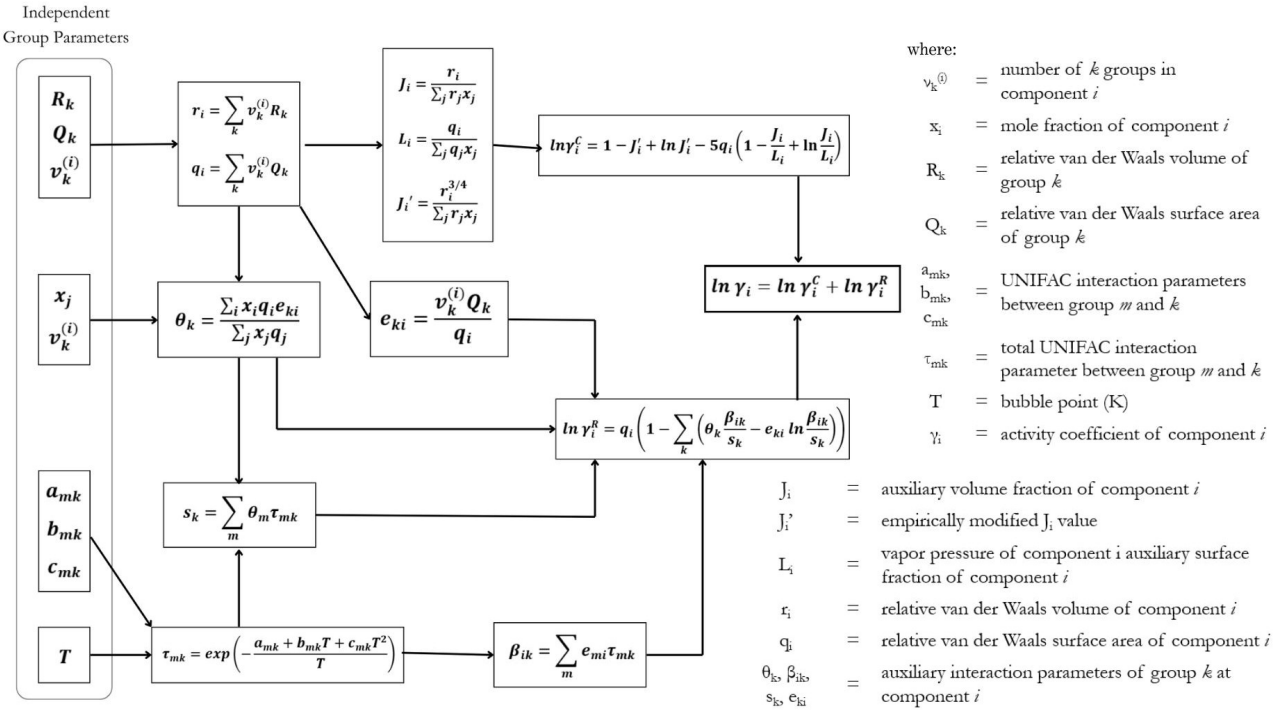

Figure 5. UNIFAC-Dortmund formulas (Smith et al., 1949)

The activity coefficient, γ_i, was evaluated using the UNIFAC-Dortmund model, with the formulas summarized in Figure 5. The parameters for UNIFAC-Dortmund were collated from Dortmund Data Bank Software and Separation Technology (DDBST) and from different papers by Gmehling et al. (1993), Aznar & Telles (2001), Jakob et al. (2006), and Balboa (2022). The values for modelling parameters are shown in Tables 3 to 6.

Table 3. Group Volume and Surface Parameters for Isopropanol and Water

Molecule	Subgroup	Group Volume Parameters (R_K)	Surface Area Parameters (Q_K)
Isopropanol	CH_3	0.6325	1.0608
	CH	0.6325	0.3554
	OH	1.063	0.8663
Water	H_2O	1.7334	2.4561
	CH_2N	1.0746	0.824
Tetrasodium EDTA	CH_2COO^-	1.27	1.4228
	Na^+	3	3

Table 4. Interaction Parameter, a_{mn}

a_{mn}		n						
		CH_3	CH	OH	H_2O	CH_2N	CH_2COO^-	Na^+
m	CH_3	0	0	2777	1391.3	-175.7	98.65601	6767.4
	CH	0	0	2777	1391.3	-175.7	98.65601	6767.4
	OH	1606	1606	0	-801.9	104.6	973.8	-7007.6
	H_2O	-17.253	-17.253	1460	0	274.5	-433.288	-1970.2
	CH_2N	205.65	205.65	1876	-446	0	160.8	*ND**
	CH_2COO^-	632.22	632.22	310.4	311.974	152.8	0	-2354.6
	Na^+	-1899	-1899	-2974.7	-552.42	*ND**	1264.4	0

*No data

Table 5. Interaction Parameter, b_{mn}

b_{mn}		n						
		CH_3	CH	OH	H_2O	CH_2N	CH_2COO^-	Na^+
m	CH_3	0	0	-4.674	-3.6156	1.857	1.9294	49.151
	CH	0	0	-4.674	-3.6156	1.857	1.9294	49.151
	OH	-4.746	-4.746	0	3.824	-5.014	-5.633	14.412
	H_2O	0.8389	0.8389	-8.673	0	-0.5905	3.0862	2.0391
	CH_2N	-1.4436	-1.4436	11.5	-0.7738	0	0.8719	*ND**
	CH_2COO^-	-3.3912	-3.3912	1.538	-1.3412	-1.099	0	0
	Na^+	72.291	72.291	9.2317	0.32527	*ND**	0	0

*No data

Table 6. Interaction Parameter, c_{mn}

c_{mn}		n						
		CH_3	CH	OH	H_2O	CH_2N	CH_2COO^-	Na^+
m	CH_3	0	0	0.00155	0.00114	0	-0.00313	0
	CH	0	0	0.00155	0.00114	0	-0.00313	0
	OH	0.000918	0.000918	0	-0.00751	0.06366	0.00769	0
	H_2O	0.000902	0.000902	0.0164	0	0.002205	-0.00201	0
	CH_2N	0	0	0.06382	0.002634	0	0	*ND**
	CH_2COO^-	0.0039282	0.0039282	-0.0049	0.001074	0	0	0
	Na^+	0	0	0	0	*ND**	0	0

*No data

Similar to other group contribution models, the UNIFAC-Dortmund model uses the sum of the combinatorial term and the residual term. The combinatorial term considers the size and geometry of species, while the residual term considers the energies involved in the interaction of species. The missing interaction parameters for $CH_2N\text{-}Na^+$ may significantly affect the evaluation of the residual term, resulting to the deviation between experimental and simulated data. The model also does not account for the Debye-Huckel long-range electrostatic interactions considering its negligible effect on the equilibrium parameters (Mock et al., 1986).

4. CONCLUSIONS

The vapor-liquid equilibria of the isopropanol-water system with tetrasodium EDTA were determined at IPA mole of 0.035 to 0.9. The alcohol concentration in the vapor phase were shown to be increasing as the concentration of the salt increases. The azeotrope was shifted from 0.6770 to 0.9999 mole fraction of IPA at 0.02 m tetrasodium EDTA at a bubble point of 81.95 ºC experimentally, while the predictive VLE had the azeotrope eliminated at 0.04 m at a bubble point of 81.09 ºC.

Both the experiment and predictive calculations have shown tetrasodium EDTA to increase the concentration of alcohol in the vapor phase and eliminate the azeotrope in the system, therefore validating the salting-out capacity of the tetrasodium EDTA salt in the system. The results and corresponding interpretations from this study support the potential of tetrasodium EDTA as a mass-separating agent for the salt distillation of isopropanol and water, which opens the possibility of a safer and cheaper method for separating the system.

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