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Effect of Diaminomethanal on the Vapor−Liquid Equilibria of the Ethanol + Water System at Atmospheric Pressure

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Extractive distillation processes with and without salt have been proposed to produce anhydrous ethanol. For the feasible use of anhydrous ethanol for blending in gasoline, the energy required to produce anhydrous ethanol must be less than the energy generated by its combustion. The energy required to produce anhydrous ethanol by extractive distillation with ethylene glycol is approximately 19 $\mathrm{MJ \cdot kg^{-1}}$, whereas it lies in the range of (5.02 to 9.27) $\mathrm{MJ \cdot kg^{-1}}$ for extractive distillation with salt. Thus, the energy requirement in extractive distillation with salt is reduced. However, the use of nonvolatile salts involves problems encountered in its dissolution and subsequent crystallization. It is desired to make efforts to explore organic compounds to be used as an extracting agent in the production of anhydrous ethanol that could be consumed within the process or could be recovered with least capital/energy inputs. In view of the above, diaminomethanal (commonly known as urea) has been identified, and its effect on the vapor−liquid equilibria (VLE) of the ethanol + water system at atmospheric pressure has been studied using the Othmer type recirculation still. The relative volatility of the ethanol + water solution is found to increase monotonically with the increment of diaminomethanal up to 4.16 $\mathrm{kmol \cdot m^{-3}}$. It is also found that the azeotrope formation in the ethanol + water system is completely eliminated with diaminomethanal at concentrations equal or higher than 2.26 $\mathrm{kmol \cdot m^{-3}}$.

Introduction

Anhydrous ethanol, also known as absolute ethanol, is a clear, colorless, and homogeneous liquid free from suspended matter with at least 0.995 volume fraction of ethanol at 288.75 K.[1,2] The maximum mass fraction of water, determined by Karl Fischer method (IS: 2362-1963), should be 0.0081.

Ethanol + water forms a minimum-boiling azeotrope at a mole fraction of ethanol of 0.894 at 351.35 K and standard atmospheric pressure.[3] Therefore, special processes are required for the production of anhydrous ethanol from dilute ethanol + water produced by fermentation processes.

Extractive distillation with liquid solvent is used commercially for the production of anhydrous ethanol from ethanol + water. Several liquid solvents have been used to produce anhydrous ethanol.[3−5] These include ethylene glycol, diethyl ether, toluene, and furfural.

Extractive distillation by use of a dissolved salt as an extracting agent has been studied for the production of anhydrous ethanol with the aim of energy savings. Several salts have been suggested.[6−12] These include calcium chloride, cobalt(II) chloride, cupric chloride, nickel(II) chloride, strontium bromide, sodium and potassium acetates, calcium nitrate, sodium and potassium iodides, mercuric and lithium chlorides, and mercuric and cupric chlorides. A comprehensive review of the literature related to the vapor−liquid equilibrium of salt systems and the salt extractive distillation was presented by Furter and Cook[13] and complemented by Meranda and Furter[14] and Furter.[15] It is reported that some extractive distillation processes employing the salt effect use a dissolved salt (or salts) as the extracting agent, while others use a liquid extracting agent with a salt (or salts). The relative effect of the specific kind of salt obeys the Dybel theory.[16] The presence of salt in liquid solvent enhances relative volatility.[17,18]

An energy-efficient fractional distillation scheme consumes energy of (6.0 to 8.8) $\mathrm{MJ \cdot kg^{-1}}$ of anhydrous ethanol. Since the various solvents/salts used in extractive distillation methods consume different amounts of energy, there is a possibility of minimizing the energy requirement for producing anhydrous ethanol. The energy required to produce anhydrous ethanol by extractive distillation with ethylene glycol is approximately 19 $\mathrm{MJ \cdot kg^{-1}}$, whereas it lies in the range of (5.02 to 9.27) $\mathrm{MJ \cdot kg^{-1}}$ for extractive distillation with salt.[12,19,20]

A few organic compounds such as glucose have been investigated under the saturated solubility condition of the compounds. Some of the salts/organic compounds have been reported to have an appreciable effect on relative volatility, but commercial exploitation of extractive distillation cannot overlook the enhanced cost of anhydrous ethanol due to the nonvolatile nature of salts. Hence, the desirable extracting agent would be an organic compound that could be used in the process elsewhere because of tremendous savings in processing cost. It is therefore proposed to search for an alternative organic compound for use in the extractive distillation process to produce anhydrous ethanol with reduced energy consumption.

Azeotropism in the ethanol + water system at atmospheric pressure occurs in the high ethanol concentration region (0.894 mol fraction ethanol). Hence, efforts have been made for the enhancement in relative volatility of ethanol over water in the high ethanol concentration region. Most of the salts are soluble in water but insoluble in ethanol. It is difficult to dissolve and carry these salts into the reflux stream of the extractive distillation column. Keeping this problem in mind, organic

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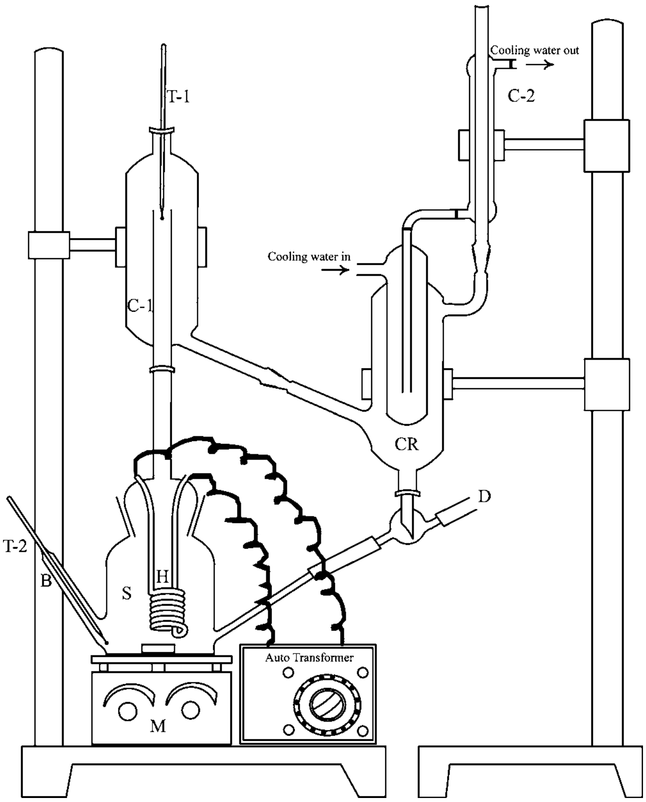

Figure 1. Schematic diagram of the Othmer type recirculation still (S: Othmer type recirculation still, B, "bottoms" sampling port; T-1 and T-2, thermometers; H, glass-sealed nichrome wire heater; C-1, air-cooled condenser; CR, water-cooled recirculation condenser; D, "distillate" sampling port; C-2, water-cooled condenser; M, magnetic stirrer).

compounds having appreciable solubility in both ethanol and water have been identified. Diaminomethanal (commonly known as urea) is one such compound.[21] Various criteria for selection of diaminomethanal include the following:

(1) Diaminomethanal is nontoxic, noncorrosive, and cheap.

(2) Diaminomethanal is available in abundance because of large-scale production.

(3) Diaminomethanal is soluble in ethanol as well as water. Its solubility in water is approximately five times as great as that in ethanol. In high concentration regions, ethanol will work as a carrier.

(4) Diaminomethanal is a nonvolatile solid. The product anhydrous ethanol will be free of diaminomethanal.

(5) Because of the high solubility of diaminomethanal in water, the appreciable fraction of diaminomethanal can be separated from the bottom stream (water) by crystallization. The remaining diaminomethanal in water can be used as a nutrient for yeast in the fermentation step.

This study presents the experimental vapor−liquid equilibria (VLE) of the ethanol + water system at atmospheric pressure in the presence of diaminomethanal.

Experimental Section

The experimental study on the effectiveness of diaminomethanal involves the following: (i) preparation of samples for VLE determination and (ii) composition analysis of the prepared samples.

Preparation of Samples for VLE Determination. Othmer type recirculation still S has been used for the preparation of samples for VLE determination.[22,23] Figure 1 shows the schematic diagram of Othmer type recirculation still used in this study. Mainly, it consists of a still (S) of a capacity of $1.60 \cdot 10^{-4}$ m^3 having side-angled openings to accommodate the thermometer (T-2) as well as to draw the sample as "bottoms" from left port (B) and to receive condensate recycle on the right side, where the glass-sealed nichrome wire heater (H) fused in the reducer socket allows the vapors formed to reach the air-cooled condenser (C-1). The air-cooled condenser is also fitted with a thermometer (T-1). The condensate and uncondensed vapors pass to the water-cooled recirculation condenser (CR) where almost all of the vapors are condensed and condensate flows down to the distillate sample bulb having a "distillate" sampling port (D). A small pool of liquid, approximately $2.0 \cdot 10^{-6}$ m^3, is held up, and the remainder is recycled to the still S. Traces of uncondensed vapors are condensed in the water-cooled condenser (C-2). The contents of the still are stirred with the help of magnetic stirrer (M) (model 2MLH-REMI Instruments, Bombay, India). The electricity supply to the glass-sealed nichrome wire heater H is given through the autotransformer (input 240 V, output (0 to 260) ± 1 V/2 A). The whole assembly is mounted on stands.

Ethanol + water blends of several compositions were prepared using rectified spirit and water for compositions below azeotrope and using rectified spirit and anhydrous ethanol for concentrations above azeotrope. The calculated quantity of diaminomethanal was added. The relative combined uncertainty in diaminomethanal concentration was within ± 0.02. A portion of $1.60 \cdot 10^{-4}$ m^3 of the prepared blend was taken in the Othmer still S, and the whole setup was assembled as shown in Figure 1. Cooling water was run into the condensers CR and C-2. The contents of the still S were heated with stirring with the help of magnetic stirrer M. Vapors generated were condensed in the air-cooled condenser C-1 and water-cooled condensers CR and C-2. The condensate was recycled to the still S leaving a small pool of condensate in the sample bulb. The evaporation and condensation cycle was continued at least for 1200 s to establish the equilibrium. The boiling point of the ethanol + water + diaminomethanal system was recorded. The uncertainty in temperatures of equilibrium phases was within ± 0.2 K. The uncertainty in the barometric pressure during the period of experiment was within ± 0.1 kPa. The setup was allowed to cool to room temperature. Two samples, one each from the still and the distillate sampling bulb, were drawn. The sample from the still was marked as "bottoms" and that from distillate sampling bulb marked as "distillate". The samples were collected in airtight-stoppered sample bottles (capacity of $5.0 \cdot 10^{-6}$ m^3) using a syringe. The samples thus prepared were analyzed for composition on a gas chromatograph.

Composition Analysis of the Prepared Samples. The samples marked as "bottoms" and "distillate" have been analyzed using AIMIL-NUCON model 5765 GC with the data station "DASTA". Hydrogen gas (Analar grade: volume fraction of hydrogen of greater than 0.9998) was used as a carrier at the inlet pressure of 240 kPa and flow rate of $4.7 \cdot 10^{-7}$ m$^3 \cdot$s^{-1}. A Porapak QS packed in SS column (2 m × 0.032 m) was used as separating media. Temperatures of the injector, oven, and detector were maintained, respectively, at (423.15, 398.15, and 423.15) K. The uncertainty in the temperatures of injector, oven, and detector was within ± 1 K. The eluted components were detected on a thermal conductivity detector. The uncertainty in mole fractions of ethanol in the liquid and vapor phases was within ± 0.003.

The materials used in this study include: (i) rectified spirit (mass fraction of ethanol > 0.92; procured from the central store of our Institute), (ii) absolute ethanol (analytical reagent: mass fraction of ethanol of > 0.998; Changsu Yangyuan Chemical,

Table 1. Effect of Diaminomethanal Concentration c on the Relative Volatility α of the Ethanol (1) + Water (2) System at Atmospheric Pressure (98.5 kPa): c = (0 to 4.16) kmol·m^{-3}

c/kmol·m^{-3}	x_1'[a]	y_1[b]	α[c]
0.00	0.848	0.865	1.145
0.33	0.848	0.864	1.143
0.80	0.846	0.869	1.214
2.26	0.849	0.889	1.428
4.16	0.850	0.910	1.784

[a] Mole fraction of ethanol in the liquid phase on a diaminomethanal-free basis. [b] Mole fraction of ethanol in the vapor phase. [c] Relative volatility $\alpha = y_1(1 - x_1')/x_1'(1 - y_1)$; uncertainties: $\sigma_{c,r}(c) = 0.02$, $\sigma(x_1') = 0.003$, $\sigma(y_1) = 0.003$, $\sigma_{c,r}(\alpha) = 0.025$.

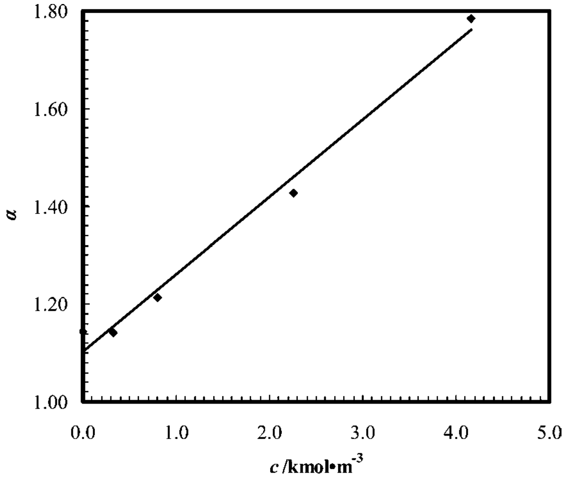

Figure 2. Effect of diaminomethanal concentration c on the relative volatility α of the ethanol (1) + water (2) system at 98.5 kPa.

China), and (iii) diaminomethanal (technical grade: mass fraction of diaminomethanal of > 0.985).

Results and Discussion

Diaminomethanal has been selected for use in the extractive distillation process to produce anhydrous ethanol. The effectiveness of diaminomethanal in the elimination of azeotrope formation in the ethanol + water system at atmospheric pressure has been determined experimentally. Since the enhancement in relative volatility of the ethanol + water system is required in the concentration range from near-azeotrope and above, the effect of the concentration of diaminomethanal on the relative volatility of the ethanol + water solution of near-azeotrope composition has been determined. Then, the VLE of the ethanol + water system at atmospheric pressure have been studied experimentally for selected concentrations of diaminomethanal.

Effect of Diaminomethanal on the Relative Volatility of the Ethanol + Water System. The effect of the concentration of diaminomethanal on the relative volatility of the ethanol + water solution in the azeotropic concentration region has been studied.

The relative volatility of close-to-azeotrope composition of the ethanol + water solution has been determined from experimental data on VLE obtained in the presence of diaminomethanal in the concentration range of (0 to 4.16) kmol·m^{-3}, and these are given in Table 1. Figure 2 is a plot of relative volatility versus concentration of diaminomethanal. This figure shows that the relative volatility of the ethanol + water solution increases with the increment of diaminomethanal up to 4.16 kmol·m^{-3}. At the diaminomethanal concentration of 4.16 kmol·m^{-3}, a small fraction of undissolved diaminomethanal has been observed in the case of pure ethanol even at its boiling point. This indicates that pure ethanol reached saturation and higher concentrations of diaminomethanal need not be tested.

Table 2. Experimental $T-x',y$ Data for Ethanol (1) + Water (2) + Diaminomethanal at Atmospheric Pressure (98.5 kPa)[a]

experimental data		
x_1'	y_1	T/K
	c = 2.26 kmol·m^{-3}	
0.000	0.000	372.85
0.039	0.236	364.65
0.109	0.390	359.75
0.195	0.513	357.15
0.360	0.616	355.15
0.417	0.678	354.15
0.519	0.707	353.95
0.629	0.772	353.75
0.843	0.881	353.75
0.918	0.936	353.75
0.957	0.964	353.75
1.000	1.000	353.75
	c = 4.16 kmol·m^{-3}	
0.000	0.000	373.65
0.004	0.073	371.85
0.013	0.124	370.05
0.026	0.163	367.25
0.041	0.242	365.85
0.082	0.358	362.60
0.207	0.609	357.35
0.273	0.629	356.35
0.425	0.696	355.95
0.502	0.737	355.55
0.598	0.800	355.35
0.733	0.860	355.35
0.817	0.897	354.95
0.929	0.959	354.75
1.000	1.000	354.75

[a] Uncertainties: $\sigma_{c,r}(c) = 0.02$, $\sigma(x_1') = 0.003$, $\sigma(y_1) = 0.003$, $\sigma(T) = 0.2$ K.

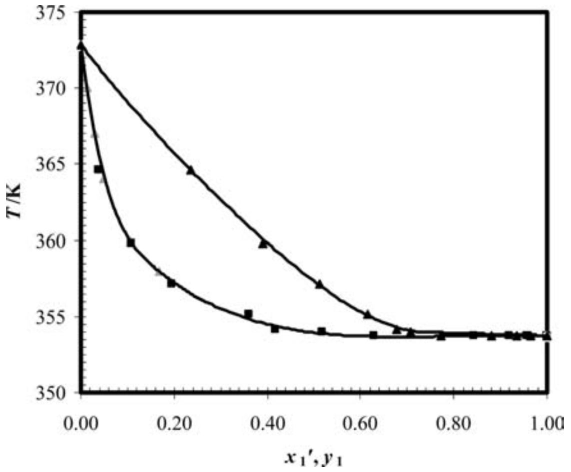

Figure 3. Experimental $T-x',y$ diagram for ethanol (1) + water (2) + diaminomethanal at 98.5 kPa: diaminomethanal concentration c = 2.26 kmol·m^{-3}; ▲, $T-y_1$; ■, $T-x_1'$.

VLE of the Ethanol + Water System in the Presence of Diaminomethanal. The vapor–liquid equilibrium data of ethanol + water system in the presence of diaminomethanal at a concentration of (2.26 and 4.16) kmol·m^{-3} at atmospheric pressure have been determined experimentally, and these are listed in Table 2. These data have been used to draw temperature–composition and equilibrium vapor–liquid composition diagrams. Figures 3 and 4 are plots of temperature versus composition of liquid and vapor phases in equilibrium in the presence of diaminomethanal at concentrations of (2.26 and 4.16) kmol·m^{-3}, respectively. The composition of liquid

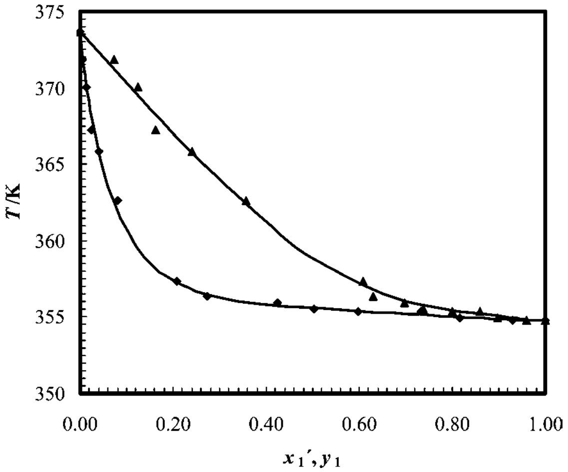

Figure 4. Experimental $T-x',y$ diagram for ethanol (1) + water (2) + diaminomethanal at 98.5 kPa: diaminomethanal concentration $c = 4.16$ kmol·m^{-3}; ▲, $T-y_1$; ♦, $T-x_1'$.

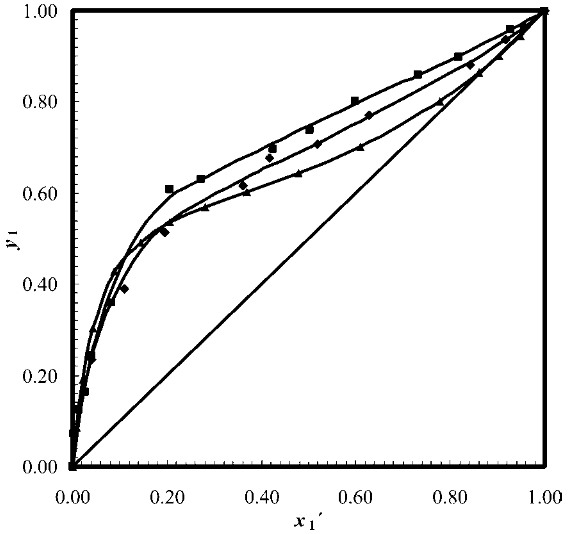

Figure 5. Equilibrium vapor−liquid composition diagram for ethanol (1) + water (2) + diaminomethanal at diaminomethanal concentrations (■, 4.16; ♦, 2.26; and ▲, 0) kmol·m^{-3} and 98.5 kPa.

solution is expressed in terms of mole fraction of ethanol on diaminomethanal-free basis. Since diaminomethanal is not present in the vapor phase because of its nonvolatile nature, the vapor composition is expressed in terms of the mole fraction of ethanol. The upper curve in these figures is a saturated vapor curve, known as the dew-point curve, and it provides the temperature−vapor composition relationship. The lower curve in these figures is a saturated liquid curve, known as the bubble-point curve, and it provides the temperature−liquid composition relationship. Liquid and vapor mixtures at equilibrium are at the same temperature and pressure throughout. It can be seen from these figures that the dew-point curve lies above the bubble-point curve for the entire range of concentration. These curves are widely separated for ethanol mole fraction in the liquid phase up to about 0.90 for a diaminomethanal concentration of 4.16 kmol·m^{-3}. Above this value there is a sufficient difference in equilibrium vapor−liquid compositions, but there is no measurable change in the temperatures.

The effectiveness of diaminomethanal in enhancing the relative volatility of the ethanol + water system at atmospheric pressure can be viewed in Figure 5, which shows the distribution diagrams for the ethanol + water system at atmospheric pressure in the absence and presence of diaminomethanal at a concentration of (2.26 and 4.16) kmol·m^{-3}. It can be seen from this figure that the distribution diagram of the ethanol + water system in the absence of diaminomethanal is crossing the diagonal line at 89.4 mol % ethanol, but the distribution diagrams for diaminomethanal concentrations of (2.26 and 4.16) kmol·m^{-3} are lying above the diagonal line for the entire range of composition. The deviation of the distribution curve from the diagonal line is more for a diaminomethanal concentration of 4.16 kmol·m^{-3} than the deviation obtained for a diaminomethanal concentration of 2.26 kmol·m^{-3}, and this indicates a higher relative volatility at a diaminomethanal concentration of 4.16 kmol·m^{-3}. For liquid compositions below about 11 mol % ethanol, the distribution diagrams of ethanol + water + diaminomethanal systems at a diaminomethanal concentration of 4.16 kmol·m^{-3} are lying below the distribution diagram of the ethanol + water system. In fact, ethanol and water are oxygenates (having oxygen in its molecules) and do not follow the Raoult's law because of molecular association leading to nonideal behavior and the existence of an azeotrope. The marginal decrease in relative volatility in the presence of diaminomethanal is probably due to alteration in the degree of molecular association of ethanol and water.

The enhancement in relative volatility of the ethanol + water system at atmospheric pressure in the presence of diaminomethanal at a concentration of more than about 2.26 kmol·m^{-3} is sufficient enough to eliminate the azeotrope formation completely. Therefore, anhydrous ethanol can be produced by the extractive distillation process employing diaminomethanal at a concentration of about 2.26 kmol·m^{-3}. The upper limit of diaminomethanal concentration is 4.16 kmol·m^{-3} because of the solubility saturation at the boiling point of pure ethanol.

Conclusions

Diaminomethanal has been identified for use in the extractive distillation of the ethanol + water solution to produce anhydrous ethanol. Its effect on the VLE of the ethanol + water system has been studied using the Othmer type recirculation still. The relative volatility of the ethanol + water solution is found to increase monotonically with an increase in concentration of diaminomethanal up to 4.16 kmol·m^{-3}. The enhancement in relative volatility of the ethanol + water system at atmospheric pressure in the presence of diaminomethanal at a concentration of more than about 2.26 kmol·m^{-3} is sufficient enough to eliminate the azeotrope formation completely. Therefore, anhydrous ethanol can be produced by the extractive distillation process employing diaminomethanal in the concentration range of (2.26 to 4.16) kmol·m^{-3}.

Supporting Information Available:

Experimental data summary. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) IS: 321-1964 (Indian Standard-Specification for Absolute Alcohol); Bureau of Indian Standards: New Delhi.
(2) IS: 15464-2004 (Indian Standard-Specification for Anhydrous Alcohol for Automotive Use); Bureau of Indian Standards: New Delhi.
(3) Treybal, R. E. *Mass-Transfer Operations*; McGraw-Hill Book Co.: New York, 1980.
(4) Rousseau, R. W., Ed. *Handbook of Separation Process Technology*; John Wiley & Sons: New York, 1987.
(5) Lee, F. M.; Pahl, R. H. Solvent Screening Study and Conceptual Extractive Distillation Process to Produce Anhydrous Ethanol from Fermentation Broth. *Ind. Eng. Chem. Process Des. Dev.* **1985**, *24*, 168–172.

(6) Nishi, Y. Vapor-Liquid Equilibrium Relations for the System Accompanied by Hypothetical Chemical Reactions Containing Salts. *J. Chem. Eng. Jpn.* **1975**, *8*, 187–191.

(7) Jaques, D.; Galan, M. A. Isobaric LVE Data for Ethanol-Water Systems Saturated with a Salt Which Appear to Contradict the Gibbs-Konovolov Theorem. *Chem. Eng. Sci.* **1980**, *35*, 1803–1804.

(8) Galan, M. A.; Labrador, M. D.; Alvarez, J. R. Salt Effect in Liquid-Vapor Equilibrium: Ethanol-Water System Saturated with Strontium Bromide, Barium Nitrate and Strontium Nitrate. *J. Chem. Eng. Data* **1980**, *25*, 7–9.

(9) Meranda, D.; Furter, W. F. Vapor-Liquid Equilibrium Data for System: Ethanol-Water Saturated with Potassium Acetate. *Can. J. Chem. Eng.* **1966**, *44*, 298–300.

(10) Meranda, D.; Furter, W. F. Vapor-Liquid Equilibrium in Alcohol-Water Systems Containing Dissolved Halide Salts and Salt Mixtures. *AIChE J.* **1972**, *18*, 111–116.

(11) Tan, T. C.; Teo, W. K.; Ti, H. C. Vapor-Liquid Equilibria of Ethanol-Water System Saturated with Glucose at Subatmospheric Pressures. *Chem. Eng. Res. Des.* **1988**, *66*, 75–83.

(12) Barba, D.; Brandini, V.; DiGiacomo, G. Hyperazeotropic Ethanol Salted-out by Extractive Distillation: Theoretical Evaluation and Experimental Check. *Chem. Eng. Sci.* **1985**, *40*, 2287–2292.

(13) Furter, W. F.; Cook, R. A. Salt Effect in Distillation: A Literature Review. *Int. J. Heat Mass Transfer* **1967**, *10*, 23–36.

(14) Meranda, D.; Furter, W. F. Salt Effect on Vapor-Liquid Equilibrium: Some Anomalies. *AIChE J.* **1974**, *20*, 103–108.

(15) Furter, W. F. Salt Effect in Distillation: A Literature Review II. *Can. J. Chem. Eng.* **1977**, *55*, 229–239.

(16) Ziqing, H. *Introduction of Electrolyte Solution Theory*; Science Press: Beijing, 1983.

(17) Lei, Z.; Wang, H.; Zhou, R.; Duan, Z. Influence of Salt Added to Solvent on Extractive Distillation. *Chem. Eng. J.* **2002**, *87*, 149–156.

(18) Gil, I. D.; Uyazan, A. M.; Aguilar, J. L.; Rodríguez, G.; Caicedo, L. A. Separation of Ethanol and Water by Extractive Distillation with Salt and Solvent as Entrainer. *Braz. J. Chem. Eng.* **2008**, *25*, 207–215.

(19) Black, C. Distillation Modeling of Ethanol Recovery and Dehydration Processes for Ethanol and Gasohol. *Chem. Eng. Prog.* **1980**, *76*, 78–85.

(20) Ligero, E. L.; Ravagnani, T. M. K. Dehydration of Ethanol with Salt Extractive Distillation- A Comparative Analysis between Processes with Salt Recovery. *Chem. Eng. Process.* **2003**, *42*, 543–552.

(21) Perry, R. H.; Don, W. G., Eds. *Perry's Chemical Engineers' Handbook*; McGraw-Hill Book Co.: New York, 1999.

(22) Othmer, D. F. Composition of Vapors from Boiling Solutions. Improved Equilibrium Still. *Ind. Eng. Chem., Anal. Ed.* **1948**, *20*, 763–766.

(23) Othmer, D. F.; Gilmont, R.; Conti, J. J. An Adiabatic Equilibrium Still. *Ind. Eng. Chem.* **1960**, *52*, 625–628.

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