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Effect of 2,2′,2″-Nitrilotrisethanol on the Vapor−Liquid Equilibria of the Ethanol + Water System at Atmospheric Pressure

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Extractive distillation processes with a variety of extracting agents such as solvents, salts, salt(s) dissolved in solvents, and organic solutes have been studied to produce anhydrous ethanol. These studies indicate that there are merits and demerits associated with each of the extracting agents identified. An organic compound, 2,2′,2″-nitrilotrisethanol (commonly known as triethanolamine), has been identified as useful as an extracting agent for the production of anhydrous ethanol. It has infinite solubility in ethanol as well as water, and hence it can be used in any proportion. Its effect on the vapor−liquid equilibria of the ethanol + water system has been studied using an Othmer-type recirculation still. The relative volatility of ethanol + water solution of fixed composition is found to increase linearly with an increase in concentration of 2,2′,2″-nitrilotrisethanol up to 1.55 $\text{kmol}\cdot\text{m}^{-3}$. The enhancement in relative volatility of the ethanol + water system at atmospheric pressure in the presence of 2,2′,2″-nitrilotrisethanol at a concentration of more than about 0.88 $\text{kmol}\cdot\text{m}^{-3}$ is sufficient enough to eliminate the azeotrope formation completely. Therefore, anhydrous ethanol can be produced by the extractive distillation process employing 2,2′,2″-nitrilotrisethanol at the concentration of more than about 0.88 $\text{kmol}\cdot\text{m}^{-3}$.

Introduction

India has committed itself to a path of ecologically sustainable development based on a graduated shift to the extent possible from the use of fossil fuels to renewable and clean energy, including nuclear energy. Efforts are underway in India to reduce carbon dioxide emission by 99 million tons by launching a national action plan on climate change, generated by the cumulative accumulation of greenhouse gas emissions in the atmosphere, through human economic activity. Biofuel, a renewable source of energy, is a term used to describe raw biomass processed into a more convenient form to be used as a fuel. The use of biofuels instead of fossil fuels reduces net emission of carbon dioxide, resulting in a reduced impact on global climate change and improved local air quality because of reduced emissions of unburnt hydrocarbons and carbon monoxide. Biofuels are produced from local and regional biomass resources, and hence these fuels help provide energy security for the countries that use them and help reduce international trade imbalances, sometimes associated with petroleum imports. Biofuels create local and regional development opportunities; such development frequently occurs in rural areas where other options are very limited. Thus, the use of biofuels enjoys benefits in the area of environment, energy security, and economic development.[1]

Anhydrous ethanol is one of the biofuels produced today. Anhydrous ethanol for blending in gasoline consists of at least 0.995 volume fraction of ethanol at 288.75 K and at the most 0.0081 mass fraction of water, determined by the Karl Fischer method.[2] Since ethanol + water forms a minimum-boiling azeotrope at a mole fraction of ethanol of 0.894 at 351.35 K and standard atmospheric pressure, special processes are required for production of anhydrous ethanol from dilute ethanol + water solution produced by fermentation of any biological material that contains sugar, starch, or cellulose.

Extractive distillation has been studied for the production of anhydrous ethanol. The various extracting agents investigated for the ethanol + water system include liquid solvents such as ethylene glycol, diethyl ether, toluene, and furfural; salts such as calcium chloride, calcium nitrate, cobalt(II) chloride, cupric chloride, nickel(II) chloride, strontium and potassium iodides, mercuric and lithium chlorides, and mercuric and cupric chlorides; salt (or salts) dissolved in liquid solvents; and ionic liquids.[3−16] Since the various extracting agents studied consume different amounts of energy, there is a possibility of minimizing energy requirement for producing anhydrous ethanol.[13,17,18] Recently, Kumar and Prasad[19] proposed the use of organic compounds as an extracting agent and studied the effect of diaminomethanal on the vapor−liquid equilibria of the ethanol + water system at atmospheric pressure. They found that there is an upper limit of diaminomethanal concentration of 4.16 $\text{kmol}\cdot\text{m}^{-3}$ for use in the ethanol + water system. The hygroscopic nature of diaminomethanal requires its conditioning before it is dissolved in the reflux stream. Handling, metering, and dissolution of diaminomethanal are rather difficult compared to liquid extracting agents. These studies indicate that there are merits and demerits associated with each of the extracting agents. Hence, another organic compound, 2,2′,2″-nitrilotrisethanol (commonly known as triethanolamine), has been identified for use as an extracting agent for the ethanol + water system on the basis of the following:[20]

(1) 2,2′,2″-Nitrilotrisethanol is nontoxic and noncorrosive.

(2) 2,2′,2″-Nitrilotrisethanol is completely soluble in ethanol and a mixture of ethanol + water.

(3) The boiling temperature of 2,2′,2″-nitrilotrisethanol is 613.15 K, which is quite high compared to that of ethanol (351.55 K) and water (373.15 K). Hence, 2,2′,2″-nitrilotrisethanol can be easily recovered by evaporation.

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(4) Because of the large difference in boiling temperatures of 2,2′,2″-nitrilotrisethanol and ethanol, the 2,2′,2″-nitrilotrisethanol impurity level in the product anhydrous ethanol will be low as compared to other extracting agents, for example, ethylene glycol.

(5) The makeup quantity of 2,2′,2″-nitrilotrisethanol required because of losses will also be low as compared to other extracting agents.

This study presents the experimental vapor−liquid equilibria of the ethanol + water system at atmospheric pressure in the presence of 2,2′,2″-nitrilotrisethanol.

Experimental Section

The experimental study on the effectiveness of 2,2′,2″-nitrilotrisethanol involves: (i) preparation of samples for vapor−liquid equilibria (VLE) determination and (ii) composition analysis of prepared samples.

Preparation of Samples for VLE Determination. An Othmer-type recirculation still has been used for preparation of samples for VLE determination.[21,22] The details of the experimental setup and its working are available elsewhere.[19]

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 compositions above azeotrope. In these blends, a calculated quantity of 2,2′,2″-nitrilotrisethanol was added. The relative combined uncertainty in 2,2′,2″-nitrilotrisethanol concentration was within ± 0.03. An amount of $1.60 \cdot 10^{-4}$ m^3 of each blend was used to prepare the samples of liquid (“bottoms”) and equilibrium vapor phase (“distillate”). The boiling point of the ethanol + water + 2,2′,2″-nitrilotrisethanol 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. These prepared samples were analyzed for composition on GLC.

Composition Analysis of Prepared Samples. The samples marked as “bottoms” and “distillate” have been analyzed using the AIMIL-NUCON model 5765 gas chromatograph (GC) with Data-Station “DASTA”. Hydrogen gas (Analar grade: volume fraction of hydrogen of greater than 0.9998) was used as the carrier at inlet pressure of 240 kPa and flow rate of 28 mL·min^{-1}. PORAPAK QS packed in an SS column (2 m × 3.2 mm) was used as separating media. Temperatures of the injector, oven, and detector were maintained at (423.15, 398.15, and 423.15) K, respectively. The uncertainty in temperatures of the 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 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 Central Store of our Institute), (ii) absolute ethanol (analytical reagent: mass fraction of ethanol > 0.998; Changsu Yangyuan Chemical, China), (iii) 2,2′,2″-nitrilotrisethanol (laboratory reagent: mass fraction of 2,2′,2″-nitrilotrisethanol > 0.97).

Results and Discussion

The effect of the concentration of 2,2′,2″-nitrilotrisethanol on the relative volatility of ethanol + water solution of near-azeotrope composition has been determined. Then, the vapor−liquid equilibria of the ethanol + water system at atmospheric pressure have been determined experimentally for selected concentrations of 2,2′,2″-nitrilotrisethanol of (0.88 and 1.55) kmol·m^{-3}.

Table 1. Effect of 2,2′,2″-Nitrilotrisethanol Concentration *c* on Relative Volatility α of the Ethanol (1) + Water (2) System at Atmospheric Pressure (98.5 kPa): *c* = (0 to 1.55) kmol·m^{-3}

c / (kmol·m^{-3})	x_1'[a]	y_1[b]	α[c]
0.00	0.833	0.850	1.136
0.13	0.844	0.863	1.164
0.34	0.823	0.848	1.200
0.63	0.813	0.853	1.335
0.88	0.837	0.877	1.389
1.55	0.840	0.895	1.624

[a] Mole fraction of ethanol in the liquid phase on a 2,2′,2″-nitrilotrisethanol-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: $\sigma_{c,r}(c) = 0.03$, $\sigma(x_1') = 0.003$, $\sigma(y_1) = 0.003$, $\sigma_{c,r}(\alpha) = 0.019$.

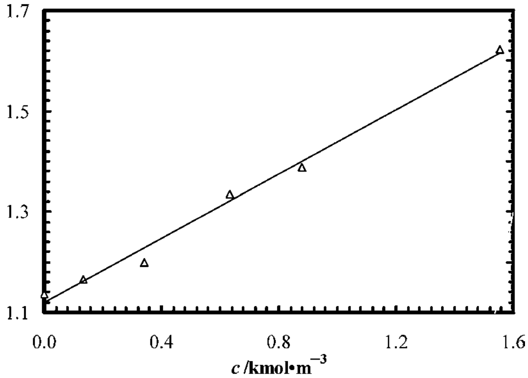

Figure 1. Effect of 2,2′,2″-nitrilotrisethanol concentration *c* on relative volatility α of the ethanol (1) + water (2) system at 98.5 kPa.

Effect of 2,2′,2″-Nitrilotrisethanol on the Relative Volatility of the Ethanol + Water System. The effect of concentration of 2,2′,2″-nitrilotrisethanol on the relative volatility of ethanol + water solution in the azeotropic concentration region has been studied.

The relative volatility of ethanol + water solution of ethanol mole fraction of 0.84 has been determined from experimental data on vapor−liquid equilibria obtained in the presence of 2,2′,2″-nitrilotrisethanol in the concentration range of (0 to 1.55) kmol·m^{-3}, and these are given in Table 1. Figure 1 is a plot of relative volatility versus concentration of 2,2′,2″-nitrilotrisethanol. This figure shows that the relative volatility of the ethanol + water solution increases linearly with the increment of 2,2′,2″-nitrilotrisethanol up to 1.55 kmol·m^{-3}. Although 2,2′,2″-nitrilotrisethanol has infinite solubility, both in ethanol and water, its concentration has been varied up to 1.55 kmol·m^{-3}. Since the increased concentration of 2,2′,2″-nitrilotrisethanol in the reflux stream decreases tray efficiency and increases relative volatility of ethanol + water mixtures, there must be an optimum concentration of 2,2′,2″-nitrilotrisethanol. This is a separate issue of investigation. Nevertheless, the VLE relationship as a function of concentration of 2,2′,2″-nitrilotrisethanol is a prerequisite.

VLE of the Ethanol + Water System in the Presence of 2,2′,2″-Nitrilotrisethanol. The vapor−liquid equilibrium data of the ethanol + water system in the presence of 2,2′,2″-nitrilotrisethanol at concentrations of (0.88 and 1.55) 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 2 and 3 are plots of temperature versus composition of liquid and vapor phases in equilibrium

Table 2. Experimental *T*, *x*′, *y* Data for Ethanol (1) + Water (2) + 2,2′,2″-Nitrilotrisethanol at 98.5 kPa[a]

experimental data		
x_1'	y_1	T/K
	$c = 0.88\ \text{kmol}\cdot\text{m}^{-3}$	
0.000	0.000	371.9
0.007	0.123	368.8
0.017	0.225	366.4
0.066	0.335	362.8
0.116	0.428	359.2
0.160	0.478	358.0
0.258	0.545	356.0
0.368	0.612	354.8
0.529	0.689	353.8
0.676	0.775	353.4
0.837	0.877	353.2
0.911	0.926	353.2
0.947	0.961	353.2
1.000	1.000	353.2
	$c = 1.55\ \text{kmol}\cdot\text{m}^{-3}$	
0.000	0.000	372.65
0.020	0.139	369.25
0.049	0.280	364.80
0.085	0.393	362.20
0.169	0.491	359.40
0.214	0.515	358.40
0.364	0.625	355.55
0.514	0.697	354.95
0.613	0.745	354.55
0.667	0.778	354.55
0.818	0.875	354.35
0.936	0.960	354.15
1.000	1.000	354.15

[a] Uncertainties: $\sigma_{c,r}(c) = 0.03$, $\sigma(x_1') = 0.003$, $\sigma(y_1) = 0.003$, $\sigma(T) = 0.2$ K.

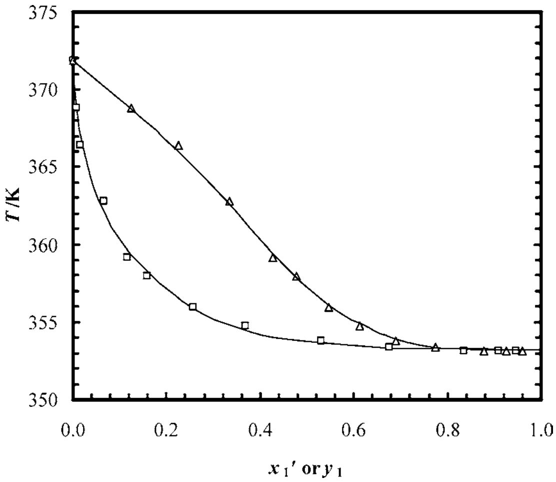

Figure 2. Experimental *T*, *x*′, *y* diagram for ethanol (1) + water (2) + 2,2′,2″-nitrilotrisethanol at 98.5 kPa: 2,2′,2″-nitrilotrisethanol concentration $c = 0.88\ \text{kmol}\cdot\text{m}^{-3}$; Δ, *T*, y_1; □, *T*, x_1'.

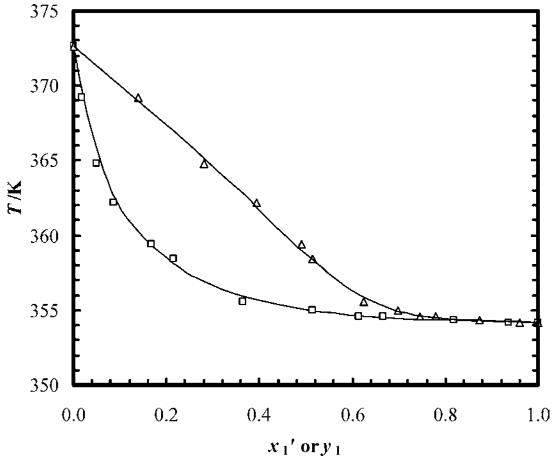

Figure 3. Experimental *T*, *x*′, *y* diagram for ethanol (1) + water (2) + 2,2′,2″-nitrilotrisethanol at 98.5 kPa: 2,2′,2″-nitrilotrisethanol concentration $c = 1.55\ \text{kmol}\cdot\text{m}^{-3}$; Δ, *T*, y_1; □, *T*, x_1'.

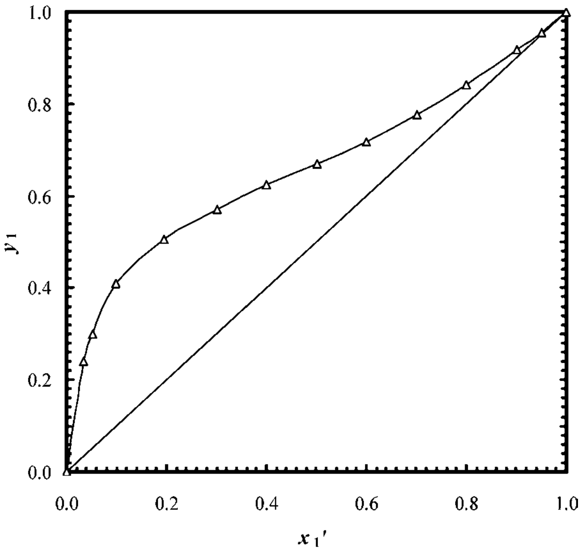

Figure 4. Equilibrium vapor−liquid composition diagram for ethanol (1) + water (2) + 2,2′,2″-nitrilotrisethanol at 98.5 kPa: 2,2′,2″-nitrilotrisethanol concentration $c = 0.88\ \text{kmol}\cdot\text{m}^{-3}$.

in the presence of 2,2′,2″-nitrilotrisethanol at concentrations of (0.88 and 1.55) $\text{kmol}\cdot\text{m}^{-3}$, respectively. The composition of liquid solution is expressed in terms of mole fraction of ethanol on a 2,2′,2″-nitrilotrisethanol-free basis. Because of the large difference in boiling points of 2,2′,2″-nitrilotrisethanol and ethanol, 2,2′,2″-nitrilotrisethanol will appear in anhydrous ethanol in traces only. For all practical purposes, it is considered to be present in liquid phase only. The vapor composition is expressed in terms of 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 concentrations. These curves are widely separated for ethanol mole fraction in liquid phase up to about 0.80 for 2,2′,2″-nitrilotrisethanol concentrations of (0.88 and 1.55) $\text{kmol}\cdot\text{m}^{-3}$. Above this value, there is no measurable change in the temperatures, but there is a sufficient difference in equilibrium vapor−liquid compositions which can be viewed in Figures 4 and 5. These figures show the distribution diagrams for the ethanol + water system at atmospheric pressure in the presence of 2,2′,2″-nitrilotrisethanol at concentrations of (0.88 and 1.55) $\text{kmol}\cdot\text{m}^{-3}$, respectively. It can be seen from these figures that the distribution diagrams of the ethanol + water system at 2,2′,2″-nitrilotrisethanol concentrations of (0.88 and 1.55) $\text{kmol}\cdot\text{m}^{-3}$ are lying above the diagonal line for the entire range of composition. This indicates the elimination of azeotrope formation at these concentrations of 2,2′,2″-nitrilotrisethanol.

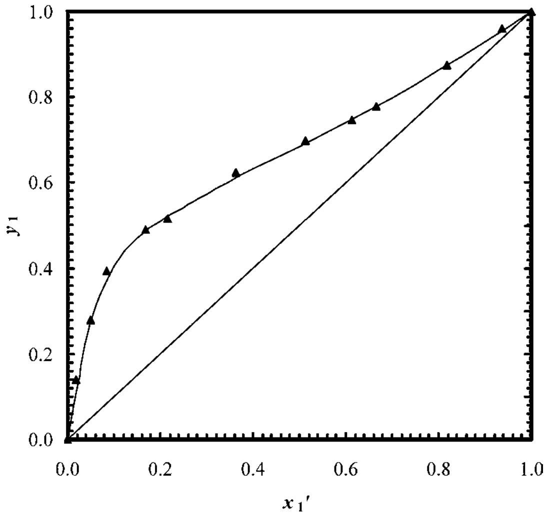

Figure 5. Equilibrium vapor−liquid composition diagram for ethanol (1) + water (2) + 2,2′,2″-nitrilotrisethanol at 98.5 kPa: 2,2′,2″-nitrilotrisethanol concentration $c = 1.55$ kmol·m^{-3}.

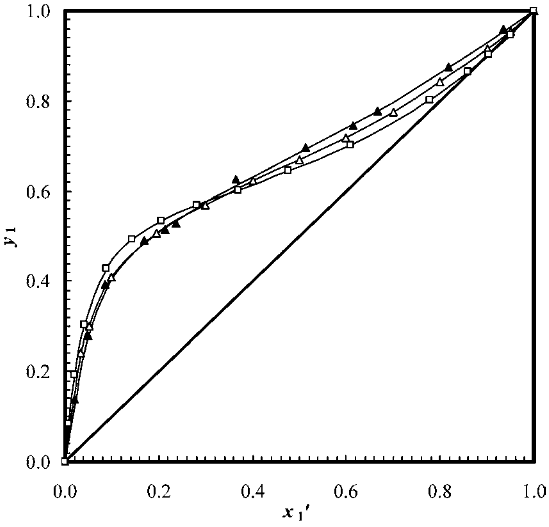

Figure 6. Comparison of equilibrium vapor−liquid composition diagrams for ethanol (1) + water (2) + 2,2′,2″-nitrilotrisethanol at 98.5 kPa: 2,2′,2″-nitrilotrisethanol concentrations (▲, 1.55; Δ, 0.88; and □, 0) kmol·m^{-3}.

The effect of concentration of 2,2′,2″-nitrilotrisethanol on the distribution diagrams of the ethanol + water system at atmospheric pressure can be viewed in Figure 6 which shows the distribution diagrams in the absence and presence of 2,2′,2″-nitrilotrisethanol. It can be seen from this figure that the distribution diagram of the ethanol + water system is crossing the diagonal line at an ethanol mole fraction of 0.894,[23] but the distribution diagrams of ethanol + water system in the presence of 2,2′,2″-nitrilotrisethanol at concentrations of (0.88 and 1.55) kmol·m^{-3} are not crossing the diagonal line for the entire range of compositions. For ethanol mole fraction of more than about 0.26 in the liquid phase, the deviation of the distribution diagram from the diagonal line is more for 2,2′,2″-nitrilotrisethanol concentration of 1.55 kmol·m^{-3} than that for 2,2′,2″-nitrilotrisethanol concentration of 0.88 kmol·m^{-3}, and the reverse is true for ethanol mole fraction of less than about 0.26. This indicates higher relative volatility at 2,2′,2″-nitrilotrisethanol concentration of 1.55 kmol·m^{-3} for ethanol mole fraction of more than about 0.26 and lower relative volatility at 2,2′,2″-nitrilotrisethanol concentration of 1.55 kmol·m^{-3} for ethanol mole fraction of less than about 0.26. The distribution diagrams in the presence of 2,2′,2″-nitrilotrisethanol are lying below the distribution diagram in its absence for ethanol mole fractions of 0.33 and 0.30 in the liquid phase for 2,2′,2″-nitrilotrisethanol concentrations of (0.88 and 1.55) kmol·m^{-3}, respectively, indicating a decrease in relative volatility.

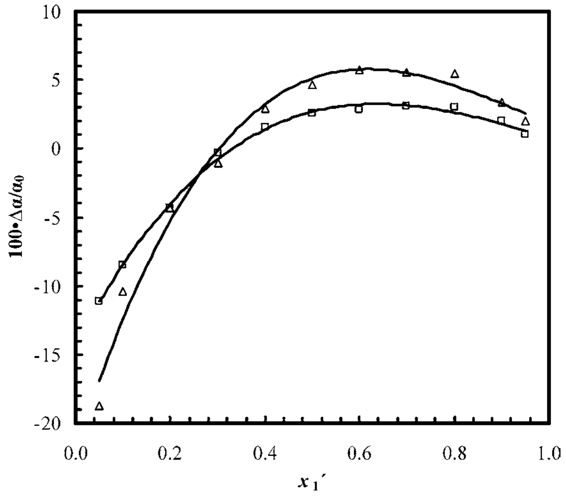

Figure 7. Effect of 2,2′,2″-nitrilotrisethanol concentration on fractional enhancement in relative volatility of the ethanol (1) + water (2) system at 98.5 kPa: $\Delta\alpha = \alpha - \alpha_0$; α = relative volatility of the ethanol + water system at 2,2′,2″-nitrilotrisethanol concentration c; α_0 = relative volatility of ethanol + water system at $c = 0$; c = (□, 0.88 and Δ, 1.55) kmol·m^{-3}.

The fractional enhancement in relative volatility, expressed in percent, of the ethanol + water system at atmospheric pressure in the presence of 2,2′,2″-nitrilotrisethanol is shown in Figure 7, which is a plot of fractional enhancement in relative volatility versus ethanol mole fraction in the liquid phase with concentration of 2,2′,2″-nitrilotrisethanol as a parameter. The two curves for 2,2′,2″-nitrilotrisethanol concentrations of (0.88 and 1.55) kmol·m^{-3} intersect at an ethanol mole fraction of about 0.26 at which the enhancement in relative volatility is the same for the concentrations of 2,2′,2″-nitrilotrisethanol of (0.88 and 1.55) kmol·m^{-3}. For ethanol mole fraction of more than about 0.26 in the liquid phase, higher enhancement in relative volatility is obtained for 2,2′,2″-nitrilotrisethanol concentration of 1.55 kmol·m^{-3}. For 2,2′,2″-nitrilotrisethanol concentrations of (0.88 and 1.55) kmol·m^{-3}, the fractional enhancement in relative volatility is positive for ethanol mole fractions of more than about (0.33 and 0.30), respectively. The negative fractional enhancement in relative volatility indicates the decrease in relative volatility with the addition of 2,2′,2″-nitrilotrisethanol. In fact, ethanol and water are oxygenates (having oxygen in its molecules) and do not follow Raoult's law due to molecular association leading to nonideal behavior and existence of azeotrope. The marginal decrease in relative volatility in the presence of 2,2′,2″-nitrilotrisethanol may be attributed to alteration in 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 2,2′,2″-nitrilotrisethanol at a concentration of more than about 0.88 kmol·m^{-3} is sufficient enough to eliminate the azeotrope formation completely. Therefore, anhydrous ethanol can be produced by an extractive distillation process employing 2,2′,2″-nitrilotrisethanol at a concentration of more than about 0.88 kmol·m^{-3}.

Table 3. Antoine Constants and Some Physical Properties of Pure Substances[20]

	ethanol	water	2,2′,2″-nitrilotrisethanol
Antoine constants:			
A	8.11220	7.96681	8.44235
B	1592.864	1668.210	2922.52
C	226.184	228.000	185.639
density @ 293.15 K, $\text{kg}\cdot\text{m}^{-3}$	789.3	998.2	1127
refractive index	1.359	1.333	1.481−1.4860
normal boiling temperature, K	373.15	351.55	613.15

Thermodynamic Consistency and Correlation of VLE Data. The experimental T, x', y data of Table 2 have been used to develop correlations and to test their thermodynamic consistency. The experimental activity coefficients γ_1^* and γ_2^* have been obtained using modified Raoult's law

$$Py_i = x_i\gamma_i^* P_i^{\text{sat}} \qquad i = 1,2 \tag{1}$$

where x_i is the mole fraction of component i in the liquid phase. The vapor pressures of ethanol and water have been calculated using the Antoine equation

$$\log P_i^{\text{sat}} = A_i - \frac{B_i}{t + C_i} \qquad i = 1,2 \tag{2}$$

where P_i^{sat} is the vapor pressure of component i in mmHg and t is temperature in °C. The Antoine constants A_i, B_i, and C_i and some physical properties of pure substances are given in Table 3. γ_1^* and γ_2^* have been used to calculate experimental dimensionless excess Gibbs energy $(G^E/RT)^*$ using the equation

$$\left(\frac{G^E}{RT}\right)^* = x_1' \ln\gamma_1^* + x_2' \ln\gamma_2^* \tag{3}$$

The values of $(G^E/RT)^*$ so calculated are divided by $x_1'x_2'$ to provide the experimental values of $[G^E/(x_1'x_2'RT)]^*$. Figure 8 is a plot of $[G^E/(x_1'x_2'RT)]^*$, $(G^E/RT)^*$, $\ln\gamma_1^*$, and $\ln\gamma_2^*$ versus x_1' for the concentration of 2,2′,2″-nitrilotrisethanol of 1.55 $\text{kmol}\cdot\text{m}^{-3}$. These experimental values have been correlated with the Wilson model. The values of Wilson parameters obtained are given in Table 4.

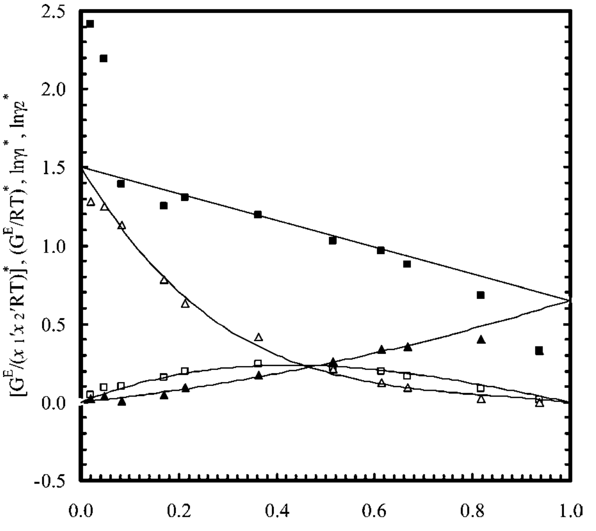

Figure 8. Variation of experimental dimensionless excess Gibbs energy and activity coefficients with liquid phase ethanol composition for ethanol (1) + water (2) + 2,2′,2″-nitrilotrisethanol. ■, $[G^E/(x_1'x_2'RT)]^*$, x_1'; □, $(G^E/RT)^*$, x_1'; Δ, $\ln\gamma_1^*$, x_1'; and ▲, $\ln\gamma_2^*$, x_1'.

Table 4. Wilson Parameters for Ethanol (1) + Water (2) + 2,2′,2″-Nitrilotrisethanol

Wilson parameters		
Λ_{12}	Λ_{21}	mean absolute deviation in y_1
	$c = 0$ $\text{kmol}\cdot\text{m}^{-3\,a}$	
0.2067	0.9261	0.014
	$c = 0.88$ $\text{kmol}\cdot\text{m}^{-3}$	
0.2035	0.9610	0.023
	$c = 1.55$ $\text{kmol}\cdot\text{m}^{-3}$	
0.2182	1.0240	0.016

[a] Determined for VLE data of ref 23.

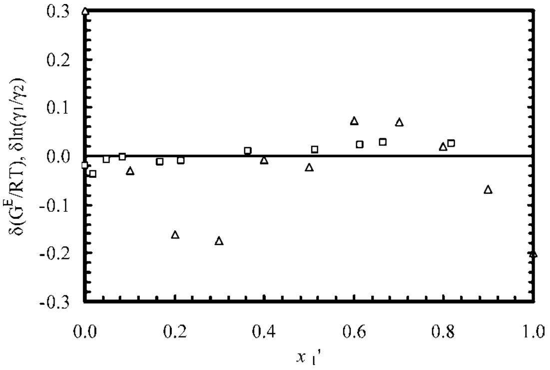

Figure 9. Thermodynamic consistency of T, x_1', y_1 of ethanol (1) + water (2) + 2,2,2-nitrilotrisethanol. □, $\delta(G^E/RT)$, x_1'; Δ, $\delta\ln(\gamma_1/\gamma_2)$, x_1' for $c = 1.55$ $\text{kmol}\cdot\text{m}^{-3}$.

For the testing of thermodynamic consistency of experimental data, the residuals $\delta(G^E/RT)$ and $\delta\ln(\gamma_1/\gamma_2)$ are defined by[24]

$$\delta\left(\frac{G^E}{RT}\right) = \frac{G^E}{RT} - \left(\frac{G^E}{RT}\right)^* \tag{4}$$

$$\delta\ln\left(\frac{\gamma_1}{\gamma_2}\right) = x_1'\frac{d\ln\gamma_1^*}{dx_1'} + x_2'\frac{d\ln\gamma_2^*}{dx_1'} \tag{5}$$

where

$$\frac{G^E}{RT} = -x_1'\ln(x_1' + \Lambda_{12}x_2') - x_2'\ln(x_2' + \Lambda_{21}x_1') \tag{6}$$

in which Λ_{12} and Λ_{21} are Wilson parameters. The residuals $\delta(G^E/RT)$ and $\delta\ln(\gamma_1/\gamma_2)$ have been calculated, and these quantities are plotted against x_1' in Figure 9. The residuals $\delta(G^E/RT)$ distribute themselves about zero. The average absolute value of these residuals less than 0.017 indicates the data of high degree of consistency. The average absolute value of the residuals $\delta\ln(\gamma_1/\gamma_2)$ is 0.06, which also satisfies the thermodynamic consistency requirement. For the concentration of 2,2′,2″-nitrilotrisethanol of 0.88 $\text{kmol}\cdot\text{m}^{-3}$, the average absolute values of 0.034 and 0.09 of the residuals $\delta(G^E/RT)$ and $\delta\ln(\gamma_1/\gamma_2)$, respectively, satisfy the thermodynamic consistency requirements.

Conclusions

2,2′,2″-Nitrilotrisethanol has been identified as an extracting agent for use in extractive distillation of ethanol + water solution to produce anhydrous ethanol. Its effect on the vapor−liquid equilibria of the ethanol + water system has been studied using the Othmer-type recirculation still. The relative volatility of ethanol + water solution of fixed composition is found to increase linearly with increase in concentration of 2,2′,2″-nitrilotrisethanol up to 1.55 $\text{kmol}\cdot\text{m}^{-3}$. The enhancement in relative volatility of the ethanol + water system at atmospheric pressure in the presence of 2,2′,2″-nitrilotrisethanol at a concentration of more than about 0.88 kmol·m^{-3} is sufficient enough to eliminate the azeotrope formation completely. Therefore, anhydrous ethanol can be produced by an extractive distillation process employing 2,2′,2″-nitrilotrisethanol at the concentration of more than about 0.88 kmol·m^{-3}. However, economics of the proposed process will dictate the favorable concentration of 2,2′,2″-nitrilotrisethanol for anhydrous ethanol production.

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