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VAPOR-LIQUID EQUILIBRIUM DATA OF CHLOROFORM-ETHANOL MIXTURES INSIDE POLAR AND NONPOLAR POROUS PLATES

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ABSTRACT

Vapor-liquid equilibrium (VLE) data of chloroform-ethanol mixtures at different temperatures were experimentally measured in 3 different macroporous plates: a 13.5-μm pore diameter, sintered, stainless-steel plate; a 30-μm pore diameter, porous, carbon plate; and a 30-μm pore diameter, porous, Teflon plate. The experimental results showed that the VLE of this system in the stainless steel plate was dramatically altered and the azeotropic point was eliminated. However, the effect of the porous Teflon plate or porous carbon plate on the VLE of this system was insignificant. The VLE for the studied system was predicted through the theory of Abu Al-Rub and Datta and gave a good agreement with the experimental data.

Key Words: Chloroform; Porous plates; Ethanol; Azeotrope

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INTRODUCTION

The capillary distillation process has proven itself a strong alternative for the separation of mixtures with azeotropic points (1–12). The capillary process depends on utilization of solid-liquid, interfacial, intermolecular forces that alter the vapor-liquid equilibrium (VLE) of a given system. Due to the porous solid-liquid interactions, a layer with different physicochemical properties from those in the bulk phases may be created adjacent to the solid surface. In principle, the interface curvature is also responsible for altering the VLE in a porous material. The interaction can be described by the Kelvin equation (1–12):

$$\ln\left(\frac{p^{\mathrm{r}}_{\mathrm{v,o}}}{p^{\infty}_{\mathrm{v,o}}}\right) = -\frac{2\sigma_{\mathrm{o}}\tilde{V}_{1,\mathrm{o}}}{rRT} \tag{1}$$

where $p^{\mathrm{r}}_{\mathrm{v,o}}$ is vapor pressure in the capillary in the absence of external fields; r is the pore radius; $\tilde{V}$ is molar volume; and σ is the surface energy or tension. However, the studies of Yeh et al. (10–12), Abu Al-Rub et al. (1), Abu Al-Rub and Datta (2–7), and Wong (9) showed that the Kelvin effect is negligible for pores of radii > 0.1 μm.

Yeh et al. (10–12), Abu Al-Rub and Datta (2–7), Abu Al-Rub et al. (1), and Wong (9) proved the feasibility of using capillary porous plates to alter the VLE of binary solutions. Yeh et al. (11) conducted some experimental studies on distillation of different liquid mixtures, including some azeotropic mixtures, by the use of macroporous fractionating plates of sintered stainless steel. The results obtained showed alteration of VLE in the porous plates and resulted in high separation efficiencies for most of the systems studied. Abu Al-Rub et al. (1) and Abu Al-Rub and Datta (2) studied the distillation of different liquid mixtures of different polarity, including some azeotropic mixtures, by the use of capillary porous plates. They found that the polar, capillary, porous plates usually could enhance the separation and in some cases eliminate the azeotropic point. Recently, Abu Al-Rub and Datta (3,7) reported some experimental results on the effect of different porous plates on the VLE of 2 binary mixtures: One consisted of components of different polarity, e.g., ethanol and water, while the other contained components of similar polarity, such as ethanol and acetone. They found that while polar, capillary, porous plates could alter the VLE of ethanol-water mixtures, nonpolar porous plates resulted in insignificant alteration of the VLE. For acetone-ethanol mixtures, neither polar nor nonpolar plates resulted in significant changes in the VLE of this system. These results show that for substantial alteration of the VLE binary mixtures inside porous plates, 2 conditions are required: The liquid components must be of different polarity and the porous plate should possess high polarization (3,7).

Abu Al-Rub and Datta (4,5) developed a theory based on a molecular thermodynamic approach to investigate the VLE of mixtures in the presence of external fields. They applied their theory to the case of VLE inside capillary porous media. According to their theory, the criterion for VLE inside capillary porous plates requires that (5)

$$y_i p = \gamma_i x_i p_{i\mathrm{v}} \qquad i = 1,2,\ldots,n \tag{2}$$

Equation (2) is of a form equivalent to that under normal conditions, i.e., without the capillary porous plates. It reduces to

$$y_i p_\mathrm{o} = \gamma_{i,\mathrm{o}} x_i p_{i\mathrm{v,o}} \qquad i = 1,2,\ldots,n \tag{3}$$

The vapor pressure, the total pressure, and the activity coefficients, γ, are all, in general, affected when fluids are placed inside capillary porous plates.

Abu Al-Rub and Datta (5) showed that the effect of the capillary porous plates on mixture VLE values can be analyzed with the equation

$$\ln \frac{\alpha_{ij}}{\alpha_{ij,\mathrm{o}}} \cong (\kappa_\mathrm{c} - \kappa_\mathrm{s})\left(\frac{\tilde{P}_i^\mathrm{l}}{\tilde{V}_i^\mathrm{l}} - \frac{\tilde{P}_j^\mathrm{l}}{\tilde{V}_j^\mathrm{l}}\right)$$

where α is the relative volatility; $\kappa_\mathrm{c} - \kappa_\mathrm{s}$ is a constant that depends on the binary system and the porous plates; $\tilde{P}$ is the molar polarization; and $\tilde{V}$ is the molar volume. Thus, Eq. (4) can be used to predict the VLE of a mixture inside capillary porous plates using its normal VLE data.

Our objective in this study was to measure the VLE of chloroform-ethanol mixtures at 318.15K under “normal” conditions and at different temperatures inside different capillary porous plates. The measured VLE data inside porous capillary plates were compared to predicted data through the use of the Abu Al-Rub and Datta theory.

EXPERIMENTAL

Chemicals

Chloroform (purity: >99.9%, Aldrich) and ethanol (purity >99.9, Aldrich) were used in this study. Chloroform was used without further purification after gas chromatography failed to show any significant impurities. The ethanol was dried with 3Å and 4Å molecular sieves (Aldrich) before use.

Procedure

Isothermal VLE measurements inside and without the porous plates were obtained experimentally using the static still method. The still used in this study consisted of 2 Pyrex chambers with ground glass joints between which the porous plate was mounted and sealed. The mixture solution, after being degassed, was charged into the lower chamber while the upper chamber contained the vapor, the vapor-liquid interface being located within the porous plate. The apparatus had ports for evacuation, pressure measurements, liquid introduction, and sample withdrawal, and upon charging it is placed in a thermostatically controlled constant-temperature air bath. A detailed description of the procedure and the still used to study VLE in capillary porous plates can be found elsewhere (3,8,10).

The sintered stainless steel plates were porous and polar. The specifications of the stainless steel plates are listed in Table 1. These plates were air blown to remove any dust and then washed in a beaker containing acetone for 24 hours. The plates were dried in a vacuum and then immersed in boiling distilled water for 8 hours, then water was replaced with fresh water, and the plates were immersed for another 8 hours. We tested the cleanliness of the plates by using fresh distilled water and observing the ability of the plates to be wetted completely and instantly by water.

Teflon plates are porous and nonpolar. The specifications of the Teflon plates are listed in Table 2. These porous plates were machined from a large sheet of Teflon. They were air blown to remove dust, washed with distilled water, dried, immersed in 2-propanol for 1 hour, washed again with water, dried, and put in sulfuric acid for 1 hour. Then the plates were immersed in boiling distilled water for 8 hours; the water was refreshed; and the plates were resubmerged for another 8 hours. The plates were then tested for perfect cleanliness. After they were prepared, the plates were mounted in the static apparatus. The apparatus was then closed, evacuated, and placed in the constant temperature air bath. The maximum error in temperature measurements was estimated to be ±0.1K. After equilibrium was reached (24 hours), samples of the liquid and vapor were withdrawn for analysis by a Perkin Elmer Auto System Gas Chromatograph. The accuracy of the analysis was estimated to be within a 0.0002-mol fraction.

Table 1. Specifications of Sintered Stainless Steel Plates

Manufacturer	Technetics Corporation
Product number	FM 1104
Plate thickness	4.9×10^{-5}m
Area density	439.2 kg/m^2
Median pore size	13 μm
Pore size range	7–72 μm
Tensile strength	4.136×10^9 N/m^2
Surface area	13 300 m^2/kg

Table 2. Specifications of Porous Carbon and Teflon Plates

a. Porous Carbon Plate	
Manufacturer	Union Carbide Corporation
Porosity	52%
Plate thickness	4.9×10^{-5} m
Bulk density	1050 kg/m^3
Median pore size	30 μm
Flexural strength	2.76×10^8 N/m^2
Compressive strength	4.136×10^8 N/m^2
b. Porous Teflon Plate	
Manufacturer	Engineering Seal Products Inc
Porosity	52%
Plate thickness	4.9×10^{-5} m
Median pore size	30 μm

RESULTS AND DISCUSSION

Normal VLE of Chloroform-Ethanol Mixtures

The experimental isothermal VLE data for chloroform-ethanol mixtures at 318.15K without the porous plates are shown in Fig. 1. Figure 1 shows that the experimental data of this work are in agreement with experimental data from the literature (13). Moreover, this figure shows that the chloroform-ethanol system at 318.15K exhibits an azeotropic point at a composition of 86.99% (mol) chloroform. These results suggest that at this composition the components of this binary mixture would be impossible to separate through the use of conventional distillation processes.

VLE of Chloroform-Ethanol Mixtures Inside Capillary Porous Plates

The effect of capillary porous plates on the VLE of the studied system is shown in Fig. 2, which presents the x-y diagram for the studied system in the presence and in the absence of the porous plates. As can be seen from this figure, the VLE for the chloroform-ethanol system in the sintered stainless plates is quite dif-

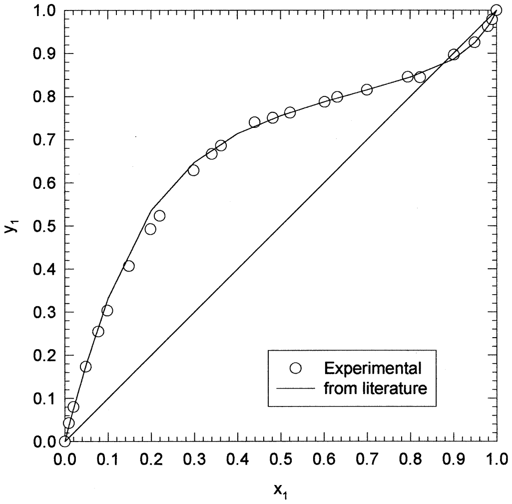

Figure 1. x_1-y_1 diagram (isothermal) for chloroform-ethanol mixtures at 318.15K. The normal curve is from Ohe (13).

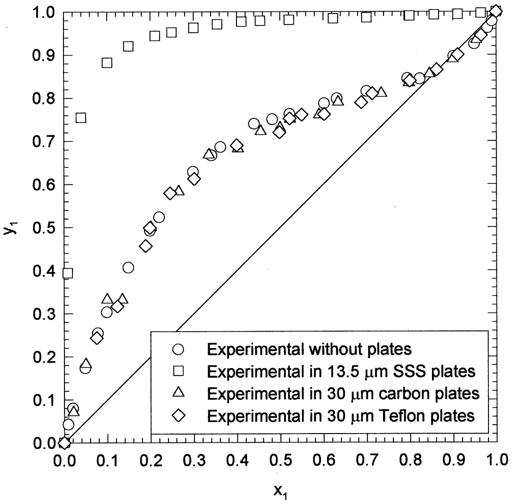

Figure 2. x_1-y_1 diagram (isothermal) for chloroform-ethanol mixtures inside porous plates at 318.15 K.

ferent from the VLE of carbon and Teflon plates and the azeotropic point is eliminated. A vapor phase with 92.0% mol chloroform was obtained for a liquid phase of 15.0% mol chloroform. Figure 3 shows the relative volatility of chloroform with respect to ethanol at 318.15 K. It shows that the relative volatility of chloroform is substantially increased (20-fold) at low concentrations. Furthermore, the azeotropic point in this case has been eliminated.

However, in porous carbon or Teflon plates, the VLE change in the chloroform-ethanol system was rather insignificant, and no discernible shift in the azeotropic point was found.

These experimental results can be qualitatively rationalized through the theories of Abu Al-Rub and Datta (4,5), who showed that the long-range surface forces exerted by the porous material have 2 effects: 1) They reduce the vapor pressure of each component, and 2) they alter the intermolecular interaction of the mixture components, thereby changing their activity coefficients. They showed that the vapor pressure reduction can be explained in terms of the excess enthalpy of vaporization in porous solids, which is a function of both the solid and the liquid polarization. Thus, Abu Al-Rub and Datta (4,5) showed that excess enthalpy of vaporization in porous sintered stainless steel is high, increasing directly with liquid polarity. This would result in a large reduction in the vapor pressure of polar liquids in these plates. However, the excess enthalpy of vaporization in nonpolar plates is relatively low and largely independent of the liquid polarity. Nonpolar liquids have low excess enthalpy of vaporization that is relatively independent of the polarization of the porous material.

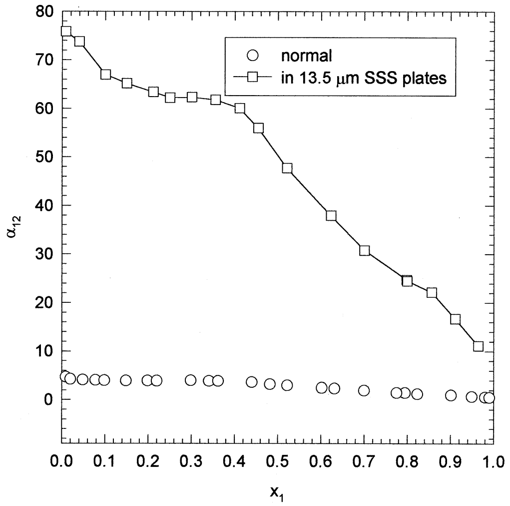

Figure 3. Relative volatility of chloroform with respect to ethanol at 318.15K.

However, Abu Al-Rub and Datta (5) showed that the variation of the activity coefficients depends upon the change of intermolecular interactions of the mixture components, and hence, upon the difference between the effects of the porous material on individual components of the mixture. For the chloroform-ethanol system, in which the components have a considerable difference in polarization, the change in relative volatility is high in the porous, sintered, stainless-steel plate that results in the elimination of the azeotrope. However, in the porous carbon plate the azeotrope was not nullified.

Effect of Temperature on VLE

The effect of temperature on VLE was studied for the chloroform-ethanol mixtures in the porous sintered stainless steel plates at 318.15–328.15K. The experimental data for these temperatures are presented in Fig. (4), which shows that increasing the temperature results in a slight decrease in the effect of the porous plates on the VLE of the studied system. Increasing the temperature decreases the intermolecular forces. Thus, the intermolecular interactions between the mixture components and the porous plates are expected to decrease by increased temperature. Also, increasing the temperature results in a decrease in the vapor pressure reduction of the pure components inside the porous plates (4).

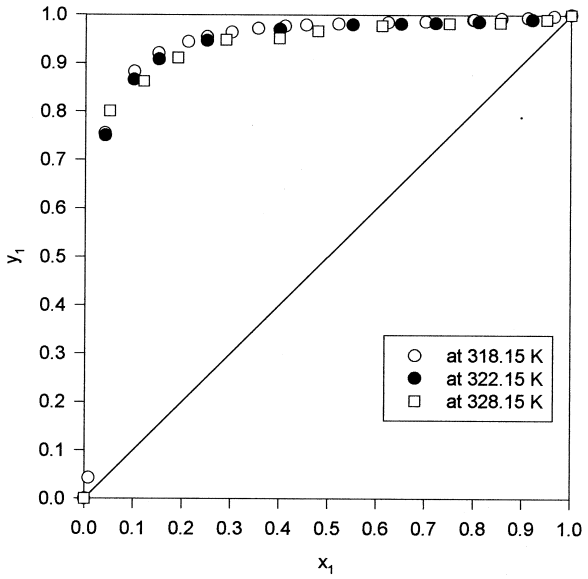

Figure 4. Effect of temperature on x_1-y_1 data for chloroform-ethanol system in sintered, porous, stainless-steel plates of 13.5-μm pore diameter.

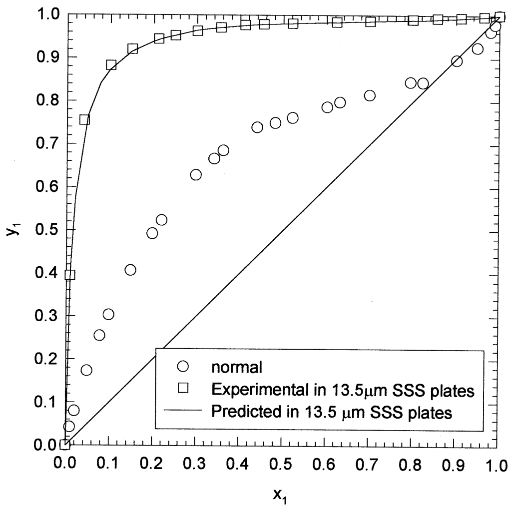

Figure 5. Comparison between experimental and predicted VLE data using the Abu Al-Rub and Datta theory for the chloroform-ethanol system in sintered stainless-steel plates of 13.5-μm pore diameter at 318.15K.

Prediction of VLE Data of Chloroform-Ethanol Mixtures Inside Steel Plates

Equation (4) was used to predict the VLE of chloroform-ethanol mixtures at 318.15K inside the capillary, sintered, stainless steel plates. This system is considered a nonpolar-polar mixture because the dielectric constant, which is a measure of polarity (4), equals 4.31 for chloroform at 323.15 K and 20.21 for ethanol at 328.15 K (14). For such systems in polar capillary plates, Abu Al-Rub and Datta (5) showed that the constant $\kappa_c - \kappa_s$, which is temperature dependent, has a value in the range of (−0.500)–(−0.850). An optimum value, i.e., a value that best fits the experimental data, of (−0.550) was taken and used to predict the *x-y* data for chloroform-ethanol mixtures at 318.15 K inside the sintered stainless-steel plates. As can be seen from Fig. 5, which shows a comparison between the experimental and predicted data, the theory of Abu Al-Rub and Datta could successfully predict the *x-y* data for chloroform-ethanol mixtures inside sintered stainless-steel plates.

CONCLUSIONS

The effect of capillary porous plates on the VLE of chloroform-ethanol mixtures was investigated by studying the effect of 3 porous plates: sintered stainless steel, carbon, and Teflon. The experimental data showed that the sintered stainless-steel plates could substantially alter the VLE of this system and could eliminate the azeotropic point. However, neither the porous carbon nor the porous Teflon plates could significantly alter the VLE. The experimental data were compared with those predicted by the Abu Al-Rub and Datta theory and the agreement to values in the literature was good.

NOMENCLATURE

n	number of components
p	pressure (kPa; mm Hg)
$p^{r}_{v,o}$	vapor pressure in the absence of external fields (kPa; mmHg)
$\tilde{P}$	molar polarization (m^3/mol)
r	radius of curvature; pore radius (m)
R	universal gas constant = 8.3143 J/mol·K
T	temperature (K)
V	volume (m^3)
$\tilde{V}$	molar volume (m^3/mol)
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase

Greek Letters

$\alpha_{1,2}$	relative volatility of component 1 with respect to component 2
κ_{χ}, κ_{s}	constants, dimensionless
σ	surface energy or tension (mJ/m^2 or mN/m)

Subscripts

i	species i
l	liquid phase
o	property in the absence of external fields
v	capillary porous plates

Superscripts

r	property inside a pore of radius r
∞	property with infinite radius of curvature, plane interface
$\sim$	molar thermodynamic property

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