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Short Communication

ESTIMATION OF AZEOTROPIC COMPOSITIONS OF THE ETHANOL-WATER SYSTEM BELOW 760MM Hg PRESSURE

H.N. Njenga, Dept. of Chemistry, University of Nairobi, Box 30197, Nairobi, Kenya

ABSTRACT

Vapour-liquid equilibrium data for the ethanol-water system was obtained at 70, 80, 90, 100, 150, 300 and 500mm Hg pressure using a modified Othmer still which was integrated with a computerized and automatic pressure control system. The pressure readings were corrected for the effects of temperature, gravity, latitude and altitude on the height of the mercury column. The measured temperatures were corrected for the effects of deviations between the set pressure and the actual pressures at which the readings were taken. Azeotropic compositions at the various set pressures were obtained from the experimental vapour-liquid equilibrium data. Using the relationship between activity coefficient and saturated vapour pressure, azeotropic compositions and temperatures at 80, 90, 100, 150, 300 and 500mm Hg pressures were obtained.

INTRODUCTION

Ethanol is a renewable energy substitute for gasoline. For use in the conventional engines, dehydrated ethanol is blended with gasoline up to a volume ratio of 1 to 4 respectively.

For environmental reasons, dehydration of ethanol by vacuum distillation would be more acceptable than using volatile, flammable and toxic liquid entrainers and solvents currently in use. Designers of ethanol vacuum dehydrating systems would require vapour-liquid equilibrium data for the ethanol-water system at low pressure as well as the relevant azeotropic data in order to establish economic viability of vacuum ethanol distillation columns.

Ethanol-water azeotropic points are hardly detectable in either y-x or t-x vapour-liquid equilibrium diagrams as they fall within regions of the two diagrams where changes in both the temperature and vapour composition are very small with respect to liquid composition. It is therefore difficult to determine the azeotropic data from such curves.

The objective of this study was to obtain accurate vapour-liquid equilibrium data at sub-atmospheric pressures and subsequently establish a method of predicting azeotropic compositions of the

ethanol water system below 760mm Hg. Lecat [1], Meissner and Greenfield [2], Prigogine and Defay [3], Malesinski [4] and Seymour et al. [5] proposed correlations between azeotropic compositions and boiling points of the pure components. These correlations give large errors when applied to systems containing polar components such as alcohols [6].

Otsuki and Williams [7] determined VLE data of the ethanol-water system above 760mm Hg. Through interpolation of the experimental relative volatility-composition and temperature-composition curves, these authors estimated azeotropic data of this system between 760 and 15510mm Hg. These workers also obtained empirical equations relating pressure and azeotropic compositions with azeotropic temperature. However, as these authors admitted, these equations cannot be used at sub-atmospheric pressures and hence cannot be used to predict the disappearance of the ethanol-water azeotrope. Earlier on, Othmer and Ten Eyck [8] had proposed an equation to correlate azeotropic composition with pressure above 760 mm Hg. Prabhu and Van winkle [9], Hirata, et al. [10] also attempted to estimate azeotropic compositions of other systems using experimental curves.

Wade and Merriman [11] determined azeotropic compositions for the

ethanol-water system around and below 760 mm Hg by fractionating mixtures whose compositions were on either side of the suspected azeotropic compositions. They obtained azeotropic compositions at various pressures by differential interpolation using density increments and relative increase in the amount distilled. These workers controlled pressure using a manostat and obtained pressure deviations of as much as ± 3 mm Hg pressure.

Assuming that the fugacity coefficient is 1 for the pressure range considered here and denoting the activity coefficient of component i to be γ_i at equilibrium, then:

$$y_i P = \gamma_i x_i P_i^\circ \quad (1)$$

where y and x are equilibrium vapour and liquid compositions respectively, P and P° are the total and saturated vapour pressures respectively.

At the azeotrope:

$$y_i = x_i \quad (2)$$

$$P = \gamma_i P_i^\circ \quad (3)$$

For a two component system:

$$P = \gamma_1 P_1^\circ = \gamma_2 P_2^\circ \quad (4)$$

$$\log \gamma_1 / \gamma_2 = \log P_2^\circ / P_1^\circ \quad (5)$$

If $\log \gamma_1 / \gamma_2$ and $\log P_2^\circ / P_1^\circ$ are simultaneously plotted against x_1 the point of their intersection is the azeotropic point.

EXPERIMENTAL

Vapour-liquid equilibrium data were obtained at 70, 80, 90, 100, 150, 300 and 500 mm Hg using a modified Othmer still whose design and operation is explained elsewhere [13]. The still had been improved by integrating it with a computerized and automatic pressure control system. Another improvement involved the incorporation of an effectively functioning Cottrell pump to enable

accurate measurement of temperatures. The final modification was a facility for simultaneous vacuum sampling of both the vapour and liquid phases.

The composition in the still was originally BDH analar grade ethanol with a minimum purity of 99.7 % by volume. The pressures mentioned above and corresponding bubble temperatures were recorded and hence became the first (T, x, y) as $(T_p, 1, 1)$. Subsequently the first of a sequence of predetermined dilutions was carried out. After equilibrium was established the temperature and pressure were read. Vapour and liquid samples were withdrawn and their density measurements taken. The ambient temperature and pressure were recorded. The samples were returned to the still after each vapour-liquid equilibrium determination. The compositions were calculated and plotted in their respective vapour equilibrium curves before proceeding with the next dilution in the sequence. If it became necessary to go to a higher region of a particular curve, for example, if from the calculations it was found out that the azeotropic point had been passed and more data points were required above it, some of the solution in the still was removed and replaced with either some absolute ethanol or concentrated ethanol solution.

RESULTS AND DISCUSSION

The ambient temperature varied between 20 and 30 °C during the period when the measurements were undertaken. There was also an average deviation of ± 0.5 mm Hg between the set pressure and the actual pressure read just before sampling. For each data point and for all the data sets, pressure and temperature corrections were made. First, individual measured pressures were corrected for the effects of temperature, gravity, latitude and altitude on the mercury column as recommended by Hala et al [14] to the reference temperature of 0° C. Next the

experimental temperatures were corrected for the difference between the corrected pressures and the set pressures as described by Njenga [13].

Thermodynamic consistency tests of the experimental data were carried out using Herington's [15] method. All seven data sets passed this test [13]. The $\log \gamma_1/\gamma_2$ and $\log P_2/P_1^\circ$ for each data set were fitted against the liquid composition x_1 . The intersection of the two curves for each data set indicated the azeotropic composition. Using this procedure, the data set at 100, 150, 300, and 500 mm Hg clearly indicated

the existence of the azeotrope. At 70, 80 and 90mm Hg, there was experimental scatter around $x=1$ and therefore no conclusion could be drawn at this stage on whether or not azeotropes existed at these pressures.

Detailed plots of $\log \gamma_1/\gamma_2$ and $\log P_2/P_1^\circ$ against x_1 for the data sets at 100, 150, 300, and 500mm

Hg was made from around 0.6 to 1.0 liquid mole fractions. By interpolation, more accurate estimates of the azeotropic compositions at these pressures were obtained. Figure 1 is a detailed plot at 500mm mercury pressure.

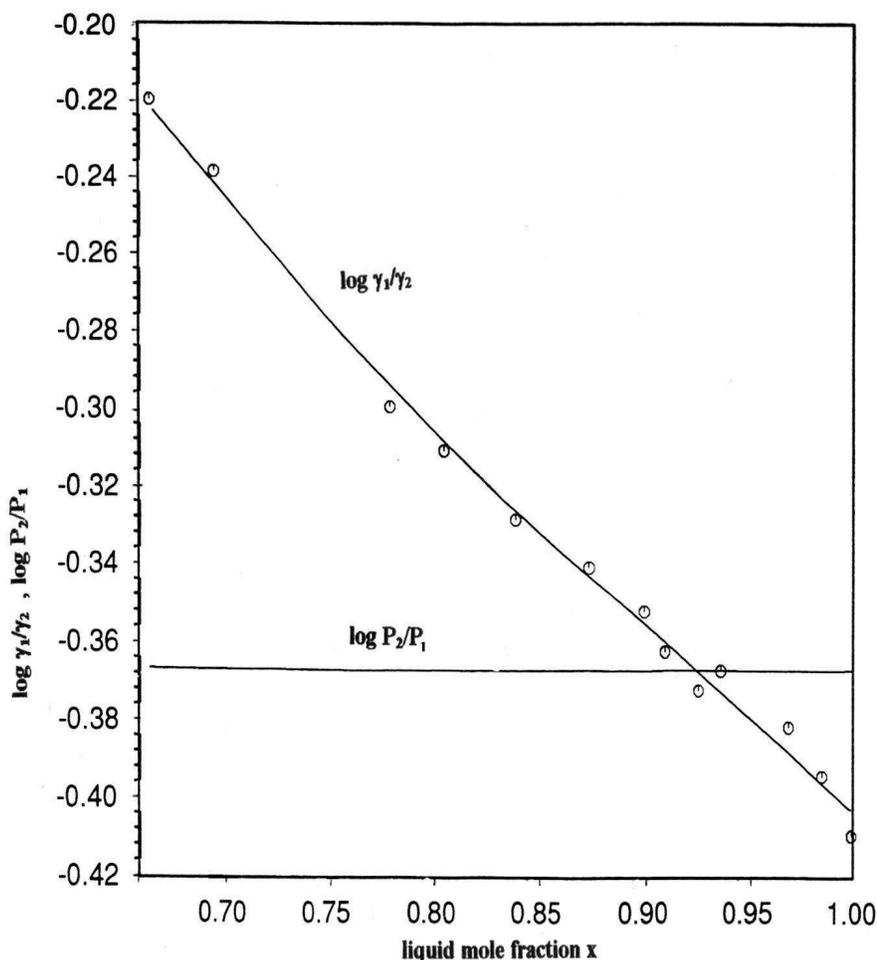


Figure 1 Azeotropic composition of the ethanol-water system at 500mm Hg pressure

These azeotropic compositions and corresponding temperatures are shown in Table 1. No azeotrope was detected at 80mm Hg. Pressure deviations of ± 0.5 mm Hg were observed in this study and this indicated a significant improvement to the ± 3 mm Hg achieved by Wade and Merriman [11]. The sample sizes averaged 6.6g

compared to 25g sampled by the above workers. It is to be expected that the larger the sample size, the higher the deviation from the equilibrium value. Azeotropic temperatures were easier to estimate from experimental data plots [13] since the changes were minimal at the ethanol-rich region of the experimental data.

Table 1. Azeotropic compositions and equilibrium temperatures for the ethanol-water system at various pressures

<u>Pressure, mm Hg</u>	<u>mole fraction</u>	<u>Temperature, °C</u>
80	1.0	30.3
90	0.993	32.4
100	0.985	34.2
150	0.960	41.9
300	0.925	56.5
500	0.906	67.7

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GLOSSARY:

P = total pressure, P_i^o = saturated vapour pressure of component i, x = equilibrium liquid mole fraction, y = equilibrium vapour mole fraction and γ = activity coefficient.