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ISOTHERMAL VAPOR-LIQUID EQUILIBRIUM OF ACETONE-WATER MIXTURE IN THE PRESENCE OF MOLECULAR SIEVES

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ABSTRACT

The VLE of acetone-water mixtures was studied at 60°C in the absence and in the presence 3 Å and 4 Å molecular sieves using the Headspace gas chromatographic (HSGC) technique. Good agreement was noticed when the experimental results in the absence of molecular sieves were compared to the van Lar and UNIFAC models' predictions. These results proved the practical feasibility of using the HSGC in measuring the VLE of binary mixtures. The experimental results obtained in the presence of molecular sieves showed that the VLE of acetone-water mixtures was altered significantly in the presence of molecular sieves. A complete separation of acetone was achieved for a feed composition of about 25 mol % acetone. These results suggest the potential use of molecular sieves to alter the VLE of binary mixtures, especially those with close boiling points or systems that have azeotropic points.

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INTRODUCTION

The ease of component separation from a liquid mixture using distillation depends on the vapor-liquid equilibrium (VLE) characteristics of the liquid mixture. Solutions with maximum or minimum azeotropic point reach a state in which boiling does not change the liquid composition. Therefore, azeotropic solutions cannot be separated by conventional distillation. For these cases special techniques such as extractive, with liquid or salt, and azeotropic distillation can be used (2–8). But this will require an additional separation step, which will result in an increase in the cost.

An innovative alternative technique was proposed by Yeh et al. (8–10) and later by Abu Al-Rub and Datta (11–13), who used macroporous stainless steel plates to alter the vapor-liquid equilibrium (VLE) of ethanol-water mixture. They suggested that this was the result of solid-liquid interfacial molecular forces, that is, dispersion and polar interactions. Abu Al-Rub et al. (11) reported some experimental studies involving distillation of different liquid mixtures including ethanol-water mixture by the use of different macroporous plates, which altered the VLE of ethanol-water system in addition to other systems. Wong (14) studied the effect of capillary plates on VLE in aqueous alcohol systems using Headspace Gas Chromatography (HSGC). The results obtained showed significant alteration of the VLE in many capillary porous plates. It was found that the effect of porous materials on the VLE is more pronounced at low temperatures (15).

Abu Al-Rub (15) proposed a novel technique, called adsorptive distillation, which involves replacement of the inert packing materials in packed-bed distillation by “active” packing material. Active material means a material that can affect the force field and intermolecular forces among the system components and thus alter its VLE. Abu Al-Rub et al. (16) studied the VLE of ethanol-water in the presence of 4 Å molecular sieves using a modified Othmer still and found that the VLE for this system was significantly altered, and the azeotropic point was shifted.

Accurate vapor-liquid equilibrium data are important in the design of separation processes. Most VLE data available in the literature are obtained either by static still methods of recirculation still methods. However, both methods have their advantages and disadvantages. The main disadvantages of circulation methods involve the difficulty in obtaining steady-state conditions, especially for systems of large relative volatilities where equilibrium is almost impossible to establish, and the difficulty in analyzing the samples of the phases accurately (17,18). On the other hand, the main problem with static still methods is the need to degass the components, which requires carefully designed apparatus.

Headspace gas chromatography (HSGC) is a familiar technique and is widely used in the analysis of volatile compounds in biological objects (19) and attracted great attention in VLE studies (20,21). The use of HSGC in studying VLE of binary mixtures is simple, accurate, fast, and can save time, as equilibrium and sample analysis are done in the same apparatus. Headspace analysis in VLE studies involves sampling of the vapor phase, which is injected into the GC, in equilibrium with its liquid phase (14, 17–25). The liquid composition is determined from the mass of the pure components after correction for evaporation (18). Lepori et al. (24) and Park et al. (25) used HSGC technique to study the VLE of some binary mixtures. Recently, Wong (14) used this technique to study the VLE of some binary systems in capillary porous plates. Results obtained were in agreement with those reported in the literature.

The objective of this study is to investigate further the effect of molecular sieves on the separation of acetone-water mixture at a high temperature using the HSGC. The effect of molecular sieves weight and pore size will also be investigated.

EXPERIMENTAL

The vapor phase in equilibrium with liquid phase is referred to as the "headspace." The principle behind headspace analysis is that at any temperature and pressure when a fixed volume of solution is sealed in a fixed-volume vial, there will be only one vapor composition corresponding to that liquid composition. The experiments conducted in this study consisted of analyzing the vapor composition above liquid mixtures of acetone and water. In predetermined time intervals, the dosing follows one after another, where all the necessary steps are automated. The vapor was sampled using a Genesis Headspace Autosampler and the amount of acetone was determined using a Varian 3400 Gas Chromatograph (GC). Specifications for the headspace autosampler and the gas chromatograph are listed in Tables 1 and 2, respectively.

Procedure

Liquid samples of the acetone-water mixture, with and without molecular sieves, were placed in a closed vial and introduced into a 50-position rotating car-

Table 1. Headspace Autosampler Specifications

Model	Genesis Headspace Autosampler with 50 Position Carousel
Injector inlet connection	Septum needle adapter
Carrier gas	Ultrahigh purity helium (Matheson)
Sample vial size	22 ml vials
Sample loop volume	20 μl

Table 2. Gas Chromatograph Specifications

Model	Varian 3400 Gas Chromatograph
Detector	Flame Ionization Detector (FID)
Column	DB-624 glass capillary column, length = 75 m, diameter = 530 μm
Make-up gas	Helium

rousel. One at a time, the vials moved onto a platen, which heated them to a specified temperature. Sufficient time was allowed for the solutes to diffuse into the vial's atmosphere. The amount of time required to reach equilibrium was determined by plotting an area count for the same sample concentration as a function of time spent on the platen. When the curve levels out, equilibrium has been reached. In addition to residence time on the platen and platen temperature, other parameters of the headspace autosampler such as loop fill time, loop equilibrium time, injection time, line temperature, and valve temperature must be established. Following equilibration, an aliquot of the vapor in the vial headspace was automatically transferred with a gas sample valve and passed through a transfer line into the GC, where the analysis took place. Reproducibility of data showed that the accuracy of the measurements was within ±0.1%. The experimental setup is illustrated in Fig. 1.

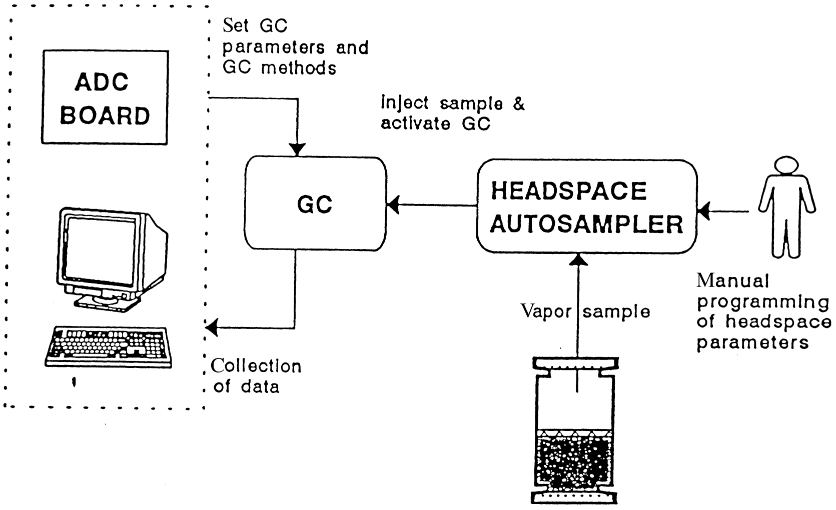

Figure 1. Experimental setup.

Table 3. Parameters Used for Acetone Composition Determination

Headspace Autosampler	
Platen temperature	60.0 ± 0.1°C
Equilibrium time	90 min
Loop fill time	0.25 min
Loop equilibrium time	0.3 min
Inject time	2.00 min
Line temperature	150.0 ± 0.1°C
Valve temperature	150.0 ± 0.1°C
Gas Chromatograph	
Column temperature	65.0 ± 0.1°C. The column was ramped to 75.0 ± 0.1°C and held for 3.5 min at that temperature after each 10 min run to prevent carryover between samples
Injector temperature	140 ± 0.1°C
Detector temperature	250 ± 0.1°C

When a fixed volume of sample vapor was automatically injected into the GC column, a second method involving injector, detector, and oven temperatures was invoked. The GC output, in the form of analog signal, was acquired by a Star Chromatography Workstation through an ADC board and processed for storage as digitized data. The Star Workstation software was acquired from Varian along with the chromatographic equipment.

By testing various instrument settings, the analytical method that yielded the most reproducible data was determined. Table 3 lists these parameters for acetone-water system.

Chemicals

Distilled water and acetone with 99.9 purity (Sigma) were used. The active packing material used in this study was 3 Å and 4 Å molecular sieves with specifications listed in Table 4.

Table 4. Molecular Sieves Specifications

Type	Base	Cation	Supplier
Molecular sieves 3 Å	Alumina-silicate	Potassium	Fisher Scientific
Molecular sieves 4 Å	Alumina-silicate	Sodium	Fisher Scientific

RESULTS AND DISCUSSION

The experimental VLE data for acetone-water system with the absence of molecular sieves at 60°C are presented in Fig. 2 as an x-y diagram. The main objective for studying the VLE for this system in the absence of molecular sieves was first to check for the practical "feasibility" of using Headspace GC to study the VLE of binary mixtures. This was done by comparing the results obtained using this technique with the predictions obtained from van Lar and UNIFAC models (26, 27) as no experimental results were found at the specified temperature. It is noticed that the predicted results are in good agreement with the experimental ones (Fig. 2). These results proved the practical feasibility of using this apparatus to study the effect of molecular sieves on the VLE of binary mixtures.

The experimental VLE data for acetone-water system in the presence of molecular sieves at 60°C are presented in Fig. 3 as an x-y diagram. The abscissa of Fig. 3 is the acetone mole fraction prior to equilibration. Actually, the liquid phase mole fraction that should be plotted is the mole fraction of acetone after equilibration. However, owing to the large difference in the molar volumes of a liquid and a gas, the loss of the volatile component in the solution can be neglected, provided that concentrated solutions are involved. Wong (14) and Kolb (28) have adequately discussed this point.

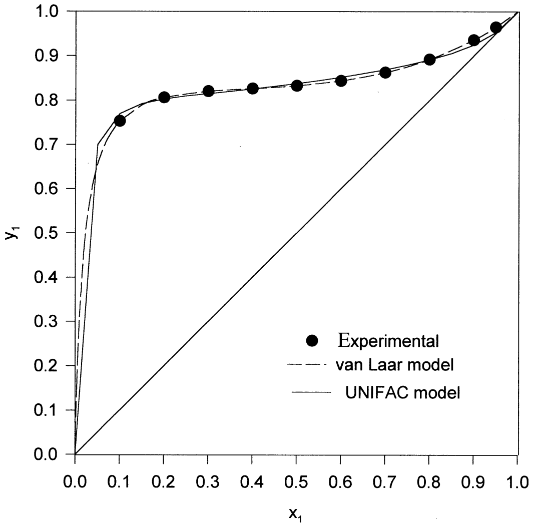

Figure 2. Experimental vapor-liquid equilibrium data for acetone-water system at 60°C.

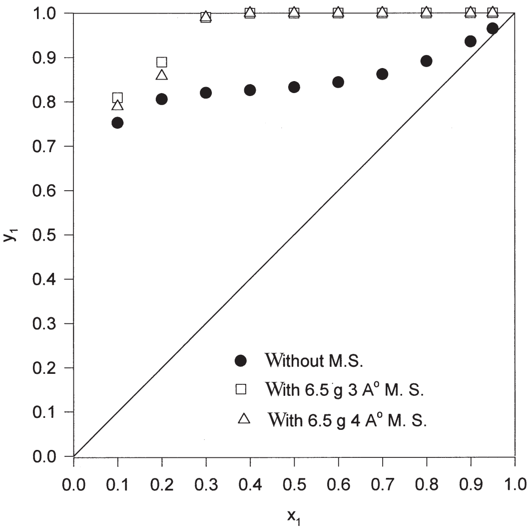

Figure 3. Experimental vapor-liquid equilibrium data for acetone-water with 3Å and 4Å molecular sieves.

As can be seen from this figure, the VLE diagram has been altered. The altering of VLE in the presence of molecular sieves was due to the effect of the force field created by the molecular sieves on the mixture components. This effect is a function of the polarity of each component. The intermolecular interactions between the molecular sieves and the most polar compound will be greater than the one between the molecular sieves and the component of less polarity (12). Thus, the composition of the most polar compound in the vapor phase will be less than that in the absence of the molecular sieves under the same conditions. For acetone-water system, the composition of water, which is more polar than acetone in the vapor phase in the presence of molecular sieves, is expected to be less than that in the absence of molecular sieves. The theoretical analysis of this effect has been studied in detail by Abu Al-Rub and Datta (12,13).
The relative volatility defined as

$$\alpha_{12} \equiv \frac{y_1/x_1}{y_2/x_2} \tag{1}$$

can be used as a measure of the separation efficiency. Although the maximum value of the relative volatility in the absence of molecular sieves was found to be about 27, infinite values were obtained in the presence of the molecular sieves of either of the pore sizes used. This indicates that using the molecular sieves in separating acetone-water mixtures will be very easy and will not require the same amount of energy needed without the molecular sieves.

Effect of the Molecular Sieves Weight

The effect of the molecular sieves weight on the separation efficiency of this system was studied for liquid composition of 30 mol % acetone. The liquid volume was 3 mL and kept constant during the experiments. The results, shown in Fig. 4, show that no further improvement on the separation was achieved by increasing the weight of molecular sieves beyond 6.5 g. This can be explained as follows: when the molecular sieves amount is less than the optimum amount, "free" liquid regions exist that will reduce the separation efficiency. By free liquid region we mean a region where the equilibrium between the vapor and the liquid does not occur in the pores of the molecular sieves. This is because the height of the bed of the molecular sieves is not enough to prevent vapor molecules from escaping without being contacted with the molecular sieves. At the optimum weight, we reach to the bed height were no vapors can escape from contacting the molecular sieves. Thus, increasing the amount of the molecular sieves beyond the optimum amount will introduce no enhancement on the separation efficiency.

Effect of the Pore Size

The effect of pore size of the molecular sieves on the VLE of acetone-water system is shown in Fig. 3. As can be seen, the alteration of VLE of acetone-water

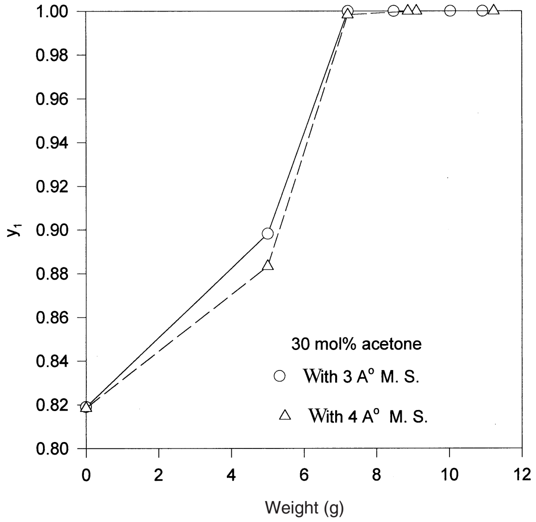

Figure 4. Effect of molecular sieves weight on vapor acetone mole fraction at 60°C.

system in the presence of 3 Å molecular sieves was "greater" than that of the 4 Å in the low acetone concentration region ($<$30 mol % acetone). This may be attributed to two factors: 1) the intermolecular interactions between the solid and the liquid are inversely proportional to the pore diameter (12). Thus, the intermolecular interactions of the liquids with 3 Å molecular sieves will be greater than these with 4 Å, and 2) according to Kelvin equation, the vapor pressure of the pure components in microporous media is given by

$$\ln\left(\frac{P^{r}_{v,o}}{P^{\infty}_{v,o}}\right) = -\frac{2\sigma_o \tilde{V}_{l,o}}{rRT} \tag{2}$$

This equation relates the vapor pressure in microporous media to the vapor pressure over a flat interface. As is evident from this equation, the reduction of the vapor pressure of the pure liquids in the presence of 3 Å molecular sieves will be greater than that in the presence of 4 Å molecular sieves, thus the VLE of the binary mixture in the 3 Å molecular sieves will be different from that in the 4 Å molecular sieves. However, at high acetone concentration, the effect of the pore size was negligible, and similar values of the vapor composition were obtained for the same liquid composition. This means that at acetone concentration $>$30 mol %, the effect of the long-range intermolecular forces is dominant.

CONCLUSIONS

The experimental results obtained for the VLE of an acetone-water system using the Headspace GC apparatus showed the practical feasibility of using this technique in studying the isothermal VLE of binary mixtures. The experimental results obtained for VLE of acetone-water system at 60°C in the presence of 6.5 gm 3 Å and 4 Å molecular sieves showed considerable change from those without the molecular sieves. Moreover, no further improvement on the separation was achieved by increasing the weight of molecular sieves beyond the ratio of 2.2 g/mL. The alteration of VLE is a result of the external force field exerted by the molecular sieves on the mixture components. These results proved the feasibility of using active packing materials to alter the VLE of binary mixtures.

NOTATION

p = pressure, mm Hg
R = universal gas constant = 8.3143 J/mol K
T = temperature, K
x = mole fraction in the liquid phase
y = mole fraction in the vapor phase

Greek Letters

α = relative volatility
σ = surface tension of liquid, dyne/cm

Subscripts

1 = ethanol
2 = water
~ = molar property
r = property evaluated at radius r
∞ = property evaluated at flat interface

Abbreviations

HSGC = Headspace Gas Chromatography
M.S = molecular sieves
VLE = vapor-liquid equilibrium

REFERENCES

1. Johnson, A. I.; Furter, W. F. Can. J. Technol. **1957,** *35*, 413.
2. Cook, R. A.; Furter, W. F. Can. J. Chem. Eng. **1968,** *46*, 119.
3. Hashitani, M.; Hirata, M. J. Chem. Eng. Jpn. **1968,** *1*, 116.
4. Hashitani, M.; Hirata, M.; J. Chem. Eng. Jpn. **1969,** *2*, 149.
5. Ohe, S.; Yokoyama, K.; Nakamura, S. J. Chem. Eng. Jpn. **1969,** *2*, 1.
6. Ohe, S.; Yokoyama, K.; Nakamura, S. J. Chem. Eng. Data **1971,** *16*, 70.
7. Jaques, D.; Furter, W. F. AIChE J. **1972,** *18*, 343.
8. Yeh, G. C.; Shah, M. S.; Yeh, B. V. Langmuir **1986,** *2*, 90.
9. Yeh, G. C.; Yeh, B. V.; Ratigan, B. J.; Correnti, S. J.; Yeh, M. S.; Pitakowski, D. W.; Fleming, W.; Ritz, D. B.; Lariviere, J. A. Desalination **1991,** *81*, 129.
10. Yeh, G. C.; Yeh, B. V.; Schmidt, S. T.; Yeh, M. S.; McCarthy, A. M.; Celenza, W. J. Desalination **1991,** *81*, 161.
11. Abu Al-Rub, F. A.; Akili, J.; Datta, R. Sep. Sci. & Technol. **1998,** *33*, 1529.
12. Abu Al-Rub, F. A.; Datta, R. Fluid Phase Equilibria **1998,** *147*, 65.
13. Abu Al-Rub, F. A.; Datta, R. Fluid Phase Equilibria **1999,** *162*, 83.
14. Wong, N. S.; The Effects of Capillary Plates on Vapor-Liquid Equilibrium in Aqueous Alcohol Systems. M. Eng. Thesis, Dept. Chem. Eng., McGill University: Montreal, 1997.

15. Abu Al-Rub, F. A. Distillation in Capillary Porous Media For Separation of Biomass Ethanol-Water Mixtures. Ph.D. Thesis, The University of Iowa: Iowa City, Iowa 1994.
16. Abu Al-Rub, F. A.; Banat, F. A.; Jumah, R. Sep. Sci. & Technol. **1999,** *34*, 2355.
17. Hachenberg, H.; Schmidt, A. P. *Gas Chromatographic Headspace Analysis*; Heyden and Son Ltd.: London, England, 1977.
18. Gironi, F.; Lamberti, L. Fluid Phase Equilibria **1995,** *105*, 273.
19. Vitenberg, A. G.; Loffe, B. V.; Borisov, V. Chromatographia **1974,** *7*, 610.
20. Chai, X.; Zhu, J. Anal. Chem. **1998,** *70*, 3481.
21. Kolb, B.; Ettre, L. *Static Headspace Gas Chromatography: Theory and Practice*; Wiley-VCH: New York, 1997
22. Marsh, K. N. Fluid Phase Equilibria **1989,** *52*, 169.
23. Ettre, L. S.; Kolb, B.; Hurt, S. G. Am. Lab. **1983,** *15*.
24. Lepori, L.; Matteoli, E.; Marongiu, B. Fluid Phase Equilibria **1988,** *42*, 229.
25. Park, S. J.; Chol, B. H.; Rhee, B. S. Hwahak Konghak **1987,** *25*, 512.
26. Ohe, S. *Vapor-Liquid Equilibrium Data*; Elsevier: Amsterdam, 1989.
27. Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977.
28. Kolb, B. J. Chromatography **1975,** *112*, 287.

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