Effect of Vinyl Alcohol + Sodium Acrylate Copolymer Gel on the Vapor−Liquid Equilibrium Compositions of Ethanol + Water and 2-Propanol + Water Systems

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The vapor−liquid equilibrium (VLE) compositions of ethanol + water and 2-propanol + water systems containing polymeric gel (vinyl alcohol + sodium acrylate copolymer) were measured at 298.15 K by using flow-type equipment that can detect the concentrations of solvents in the vapor phase and the partial pressures of each solvent. Helium gas was used as the carrier gas. The mole fraction of the vapor phase was determined by gas chromatography with a concentration accuracy of ±0.4%, and the mole fraction of the liquid phase was obtained from feed compositions. It was found that the mole fraction of alcohol in the vapor phase increases with an increase in the concentration of polymeric gel in the liquid phase.

Introduction

Many investigators have explored the properties of polymeric gels such as the volume change behavior[1−3] because gels have been attracting attention in many fields. Recently, polymeric gels and polymers were applied to the distillation process for mixtures containing alcohol + water azeotropic compounds.[4,5] To consider the use of a polymeric gel in the distillation process, the isothermal vapor−liquid equilibrium (VLE) measurements on the mixtures are needed as fundamental knowledge. In previous work, we have been reported the VLE composition of the 1-propanol + water system containing a polymeric gel at 298.15 K.[4]

In this work, the VLE compositions of ethanol + water and 2-propanol + water systems containing the polymeric gel (vinyl alcohol + sodium acrylate copolymer) were experimentally determined by flow-type equipment at 298.15 K.

Experimental Section

Materials. Special-grade ethanol and 2-propanol were purchased from Wako Pure Chemical Ind. Ltd. and were believed to be more than 99.5% pure. Ethanol and 2-propanol were used without further purification. The used polymeric gel was vinyl alcohol + sodium acrylate copolymer and was supplied by Sumitomo Chemical Co. Ltd. Prior to measurements, gels were washed in 80 mass % aqueous ethanol and/or 2-propanol solution six times. The compounding ratio (vinyl alcohol/sodium acrylate) of the gel was 3:2. The gel was considered to be cross linked by hydrogen bonds, and the number of segments of the gel per gram was 9.4×10^{21}. These values were obtained from the supplier. Water was purified with an ultrapure water apparatus (Mill-Q Laboratories, Nihon Millipore Ltd.).

Apparatus and Procedure. Details of the flow-type equipment used in the measurements and measuring procedures of the VLE compositions for the aqueous alcohol solutions were described in our previous papers.[4,6−8] In the flow-type equipment for VLE, the three glass equilibrium cells were held in a water bath with a temperature control accuracy of ±0.05 K. One cell contained a solution with a known concentration of alcohol, water, and polymeric gels. The other two cells contained pure alcohol and water, respectively. These cells gave the peak areas in gas chromatography for each solvent at several temperatures. Helium gas leaving a gas cylinder and filters passed through each equilibrium cell. The helium gas saturated with solvent vapor was introduced into a gas chromatograph. The concentration of solvents in the vapor phase was determined as the peak area. The partial pressures of the solvents contained in the solution could be calculated from the peak area of the pure solvent by using the temperature data of the pure solvent and a vapor pressure equation, such as the Antoine equation.[9] The accuracy of the concentration in the vapor phase was believed to be less than ±0.4%. The experimental values of vapor pressure were obtained from the arithmetic average of several measurements at each liquid composition. In general, it may take considerable time for the polymeric gel solution to attain equilibrium, and its swelling rate depends on the size of the polymeric gel. The polymeric microsphere gel had a mean diameter of about 4.0×10^{-4} m in ethanol and/or 2-propanol. Prior to loading, dried gels were immersed and agitated with a magnetic stirrer in alcohol + water. The solution at the equilibrium cell was left to stand for more than 48 h at 298.15 K. During measurements, the solution in a cell was agitated by a magnetic stirrer. When the flow-type equipment was used for the VLE measurements, the mole fraction change in the liquid phase was less than 10^{-5} and was negligibly small throughout the VLE measurements, so the liquid-phase compositions should be considered to be identical to the feed compositions. To confirm the mole fraction in the liquid phase, composition analysis was carried out by using liquid and gas chromatography. The equilibrium compositions in the liquid phase obtained in this study were reproducible within ±0.2% for each composition on repeated runs.

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10.1021/je049858k CCC: $27.50

Table 1. Vapor−Liquid Equilibrium Data for Ethanol (A) + Water (B) + Vinyl Alcohol + Sodium Acrylate Copolymer Gel (C) at 298.15 K

$100w_c$	x_A°	p_A/kPa	p_B/kPa	y_A
5	0.400	4.65	2.39	0.661
	0.500	5.21	2.24	0.699
	0.600	5.75	2.07	0.735
	0.700	6.26	1.71	0.785
	0.800	6.77	1.30	0.839
10	0.400	4.99	2.39	0.676
	0.500	5.26	2.04	0.721
	0.600	5.89	1.86	0.760
	0.700	6.23	1.60	0.796
	0.800	6.93	1.15	0.858
15	0.400	5.07	2.20	0.697
	0.500	5.57	2.03	0.733
	0.600	6.01	1.68	0.782
	0.700	6.51	1.41	0.822
	0.800	6.64	1.08	0.860

Table 2. Vapor−Liquid Equilibrium Data for 2-Propanol (A) + Water (B) + Vinyl Alcohol + Sodium Acrylate Copolymer Gel (C) at 298.15 K

$100w_c$	x_A°	p_A/kPa	p_B/kPa	y_A
5	0.200	3.44	2.72	0.558
	0.299	3.68	2.63	0.599
	0.399	3.82	2.44	0.610
	0.500	4.13	2.40	0.632
	0.599	4.50	2.23	0.669
	0.700	4.81	1.81	0.727
	0.797	5.35	1.47	0.784
10	0.200	3.51	2.76	0.560
	0.300	3.72	2.57	0.591
	0.400	4.04	2.50	0.618
	0.500	4.34	2.34	0.650
	0.599	4.46	1.99	0.691
	0.700	4.93	1.73	0.740
	0.799	5.24	1.28	0.804
15	0.200	3.70	2.69	0.579
	0.299	3.98	2.62	0.603
	0.400	4.12	2.42	0.630
	0.500	4.73	2.14	0.689
	0.600	4.94	1.94	0.718
	0.700	4.99	1.57	0.761
	0.800	5.28	1.15	0.821

Results and Discussion

Before the measurement of VLE compositions, we checked the volume of the gel in the equilibrium cell containing aqueous alcohols solution, and the solution containing the gel was left to stand for more than 48 h at 298.15 K. After equilibrium, we measured the VLE compositions. The experimental data of the volume change of the gel in the aqueous alcohol solution have been reported in a previous paper.[2]

The VLE compositions of the ethanol (A) + water (B) + gel(vinyl alcohol + sodium acrylate copolymer) (C) and 2-propanol (A) + water (B) + gel (C) ternary systems were obtained at 298.15 K, as shown in Tables 1 and 2 and Figures 1 and 2. The compositions of the ethanol (A) + water (B) and 2-propanol (A) + water (B) binary systems are literature data.[7,10] In Tables 1 and 2, x_A° and $100w_c$ denote the polymer-free-basis mole fraction of alcohol (ethanol and/or 2-propanol) and the concentration of the polymeric gel (mass percent); p_A and p_B are the partial pressures of alcohol and water. After VLE measurement, no lighter component of the polymer in aqueous solution can be detected by liquid and gas chromatography. The mole fraction of alcohols in the vapor phase, y_A, and the azeotropic point increase with an increase in the concentration of the polymeric gel. The volatility of alcohols is enhanced by the gel, and a salting-out effect is observed. Similar results were obtained in the alcohol (A) + water (B) + electrolyte (C)[6−8] and 1-propanol (A) + water (B) + polymeric gel (C)[4] systems. It appears that the polymeric gel is an effective substance for the distillation processes containing the mixtures of azeotropic compounds as well as the electrolyte. Though the electrolyte will cause the corrosion of the material, the polymeric gel may scarcely cause corrosion.

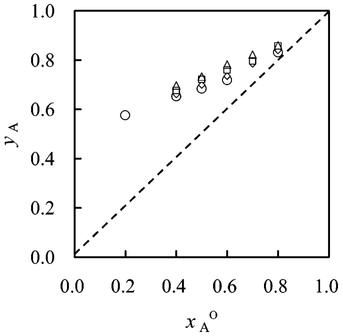

Figure 1. Vapor−liquid equilibrium data for ethanol (A) + water (B) + vinyl alcohol−sodium acrylate copolymer gel (C) at 298.15 K: ○, 0 gel, Kumagae et al.;[7] ◇, 5% gel; □, 10 gel; △, 15% gel, this work.

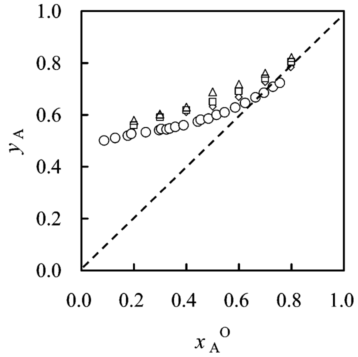

Figure 2. Vapor−liquid equilibrium data for 2-propanol (A) + water (B) + vinyl alcohol−sodium acrylate copolymer gel (C) at 298.15 K: ○, 0 gel, Gmehling et al.;[10] ◇, 5% gel; □, 10 gel; △, 15% gel, this work.

The salting-out effect of the gel was compared with that of the electrolyte by using measurements of the electrical conductivity of the aqueous alcohol solution. From our measurements of electrical conductivity, it was considered that the cause of the change in vapor pressure is not only a partial release of sodium ions from the gel but also the effect of the selective adsorption of molecules on the polymeric gel. In the case of the aqueous solution containing 3.0 g of gel, about 46 g of ethanol and/or 2-propanol, and 14 g of water, the electric conductivity was about 2.0 mS/m. Small amounts of ions were detected by conductivity measurement, despite the fact that the gels were washed with an aqueous alcohol solution six times. The same value was obtained for the aqueous alcohols solution containing about 0.003 g of NaCl, but the salting-out effect of the gel on the VLE of the alcohol + water systems is much larger than that of NaCl at the same ion concentration. Therefore, it is difficult to explain the salting-out effect of the gel only by the release of sodium ions. It is well known that vinyl alcohol + sodium acrylate copolymer gel is water absorbent. In previous work, we reported the volume of gels in equilibrium with an alcohol + water solution and the concentrations of alcohol inside and gels outside in equilibrium.[2] The gel shows a large volume change according to alcohol concentrations and a discontinuous volume-phase transition. The alcohol concentrations inside the gel in the shrinked state were much smaller than those outside the gel. Under our experimental conditions, the gel is in the shrinked state, thus indicating the selective adsorption of water in the gels.

Conclusions

The VLE compositions of the ethanol + water + gel (vinyl alcohol + sodium acrylate copolymer) and 2-propanol + water + gel ternary systems were measured by using flow-type equipment at 298.15 K. Furthermore, the mole fraction of ethanol and/or 2-propanol in the vapor phase is increased with an increase in the concentration of polymeric gel in the liquid phase of the ternary system. The volatility of ethanol and/or 2-propanol was enhanced by the added gel, and a salting-out effect of the gel on the VLE of the alcohol + water systems was observed.

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Received for review April 6, 2004. Accepted August 4, 2004. This work was partially supported by a Grant-in-Aid for Scientific Research (no. 16560664) from the Ministry of Education, Sports, Science, and Culture of Japan.

JE049858K