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Effect of Vinyl Alcohol + Sodium Acrylate Copolymer Gel on the Vapor−Liquid Equilibrium of 1-Propanol + Water

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The activities of 1-propanol and water in the solvent + polymeric gel (vinyl alcohol + sodium acrylate copolymer) binary systems and the vapor−liquid equilibrium (VLE) compositions of 1-propanol + water system containing polymeric gel were measured at 298.15 K by using flow type equipment which 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. The activity of 1-propanol in the 1-propanol + polymeric gel solution scarcely changed with an increase of polymeric gel, while the activity of water decreased with an increase in the concentration of polymeric gel in the binary systems. It was found that the mole fraction of 1-propanol in the vapor phase increases with an increase in the concentration of polymeric gel in the liquid phase of the ternary system.

Introduction

Recently, polymeric gels have been attracting attention in many fields and they are being considered in applications such as water adsorbent, artificial musculature, and mechanochemicals. Many investigators have explored the properties of the gel, such as the volume change behavior (Amiya et al., 1987; Ishidao et al., 1989, 1993). But the effect of the polymeric gel on the vapor-liquid equilibrium (VLE) compositions has seldom been examined. In order to consider the use of a polymeric gel in the distillation process for mixtures containing azeotropic compounds, the isothermal VLE measurements on the mixtures are required. In this work, the activities of 1-propanol and water in the solvent + polymeric gel (vinyl alcohol + sodium acrylate copolymer) solutions and the VLE compositions of the aqueous 1-propanol solution containing the polymeric gel were experimentally determined by flow type equipment at 298.15 K.

Experimental Section

Materials. The special grade 1-propanol was purchased from Wako Pure Chemical Ind. Ltd. and believed to be more than 99.5% purity. 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% aqueous ethanol 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} segments·g^{-1}. Water was purified with an ultrapure water apparatus (Mill-Q Laboratories, Nihon Millipore Ltd.).

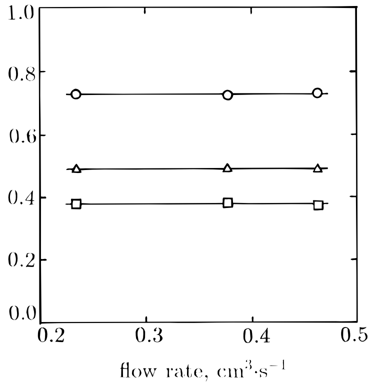

Figure 1. Relationship between the vapor mole fraction of 1-propanol and the flow rate of helium gas: (□) $x_A° = 0.2$; (△) $x_A° = 0.6$; (○) $x_A° = 0.9$.

Apparatus and Procedure. Details of the flow type equipment used in the measurements and of measuring procedures of the VLE compositions for the aqueous alcohol solutions were described in our previous papers (Mishima et al., 1987; Kumagae et al., 1992; Matsuyama et al., 1995). In this work, measurements were carried out by modifying the parts for control of the flow rate of the carrier gas. The flow rate of the carrier gas was controlled by a mass flow controller (SEC 310, Estec Co.). The VLE measurements were carried out under several flow rates of carrier gas. From these measurements, the VLE compositions obtained are independent of flow rates, as shown in Figure 1. In

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Table 1. Vapor Pressure p_A and Activity a_A of 1-Propanol in 1-Propanol (A) + Vinyl Alcohol + Sodium Acrylate Copolymer Gel (C) Solutions at 298.15 K

$100w_C$	p_A/kPa	a_A
4.977	2.73	1.000
9.923	2.73	1.000
15.066	2.73	1.000
20.022	2.73	1.000

Table 2. Vapor Pressure p_B and Activity a_B of Water in Water (B) + Vinyl Alcohol + Sodium Acrylate Copolymer Gel (C) Solutions at 298.15 K

$100w_C$	p_B/kPa	a_B
0.0687	3.13	0.987
0.0943	3.12	0.984
0.1397	3.09	0.977
0.1961	3.08	0.972

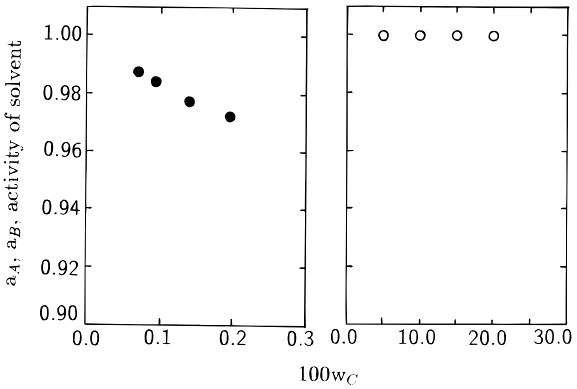

Figure 2. Activities of 1-propanol (A) a_A and water (B) a_B in solvent + vinyl alcohol + sodium acrylate copolymer gel (C) solutions at 298.15 K: (○) 1-propanol; (●) water.

Table 3. Vapor–Liquid Equilibrium Data for 1-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	1.67	2.87	0.368
	0.300	1.75	2.81	0.384
	0.400	1.86	2.74	0.404
	0.500	1.95	2.69	0.420
	0.599	2.00	2.43	0.451
	0.700	2.12	2.09	0.504
	0.799	2.39	1.54	0.608
10	0.200	1.72	2.87	0.375
	0.300	1.81	2.79	0.393
	0.395	1.90	2.85	0.400
	0.498	1.79	2.30	0.438
	0.595	2.04	2.13	0.489
	0.700	2.32	1.92	0.547
	0.800	2.32	1.37	0.629
15	0.201	1.76	2.85	0.379
	0.299	1.86	2.75	0.403
	0.400	1.91	2.63	0.421
	0.500	2.03	2.19	0.481
	0.600	2.19	1.97	0.526
	0.698	2.31	1.59	0.592
	0.801	2.46	1.31	0.653

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 the solution of the known concentration of 1-propanol, water, and polymeric gels. The other two cells contained pure 1-propanol and water, respectively. These cells gave the peak areas in gas chromatography for each solvent at several temperatures. The impurities in helium gas used as the carrier gas were removed by a gas filter and a dryer placed in the flow line. 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. The accuracy of the concentration in the vapor phase was believed to be less than ±0.4%. 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 the mean diameter of 4.06×10^{-4} m in 1-propanol. Prior to loading, dried gels were immersed and agitated with a magnetic stirrer in the 1-propanol + water solution at the equilibrium cell and were 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 $\pm 10^{-5}$ in mole fraction and was negligibly small throughout the VLE measurements. So the liquid phase compositions should be considered to be identical with the feed compositions. In order to confirm the mole fraction in the liquid phase, composition analysis was carried out by using liquid chromatography and gas chromatography. The equilibrium compositions in the vapor phase obtained in this study were reproducible within ±0.2% for each composition on repeated runs.

Results and Discussion

Activities of solvents in the solvent + polymeric gel binary systems at 298.15 K are shown in Tables 1 and 2 and Figure 2. At equilibrium between the vapor and liquid phases at temperature T, the activity a_i of solvent i was calculated from

$$a_i = \frac{p}{p_i^0}\left\{\exp\frac{(B - V^L)(p - p_i^0)}{RT}\right\} \qquad (1)$$

where p is the vapor pressure, p_i^0 is the saturated vapor pressure of pure solvent i (Kagaku-Binran, 1984), R is the universal gas constant, V^L is the liquid molar volume (Kagaku-Binran, 1984), and B is the second virial coefficient calculated by the Tsonopoulos method (Tsonopoulos, 1974). The values of B in $cm^3 \cdot mol^{-1}$ are −3811 (1-propanol) and −2997 (water). The activity of water decreases with an increase in the concentration of the polymeric gel in the liquid phase, while that of 1-propanol hardly changes with a change in the polymeric gel concentration, as the aqueous polymer solution such as poly(ethylene glycol), which does not release ions (Hao et al., 1992). The VLE compositions of the 1-propanol (A) + water (B) + gel (vinyl alcohol + sodium acrylate copolymer) (C) ternary system were obtained at 298.15 K, as shown in Table 3 and Figure 3.

The compositions of the 1-propanol (A) + water (B) binary system are literature data (Hongo et al., 1989). In Table 3, x_A° and $100w_C$ denote the polymer-free basis mole fraction of 1-propanol and the concentration of the polymeric gel (mass per cent); p_A and p_B are the partial pressures of 1-propanol and water. After VLE measurements, no lighter component of the polymer in aqueous solution can be detected by liquid chromatography and gas chromatography. The mole fraction of 1-propanol in the vapor phase, y_A, and the azeotropic point increase with an increase in the concentration of the polymeric gel. The volatility of 1-propanol is enhanced by the gel, and the salting-out effect is observed. Similar results were obtained in the alcohol (A) + water (B) + electrolyte (C)

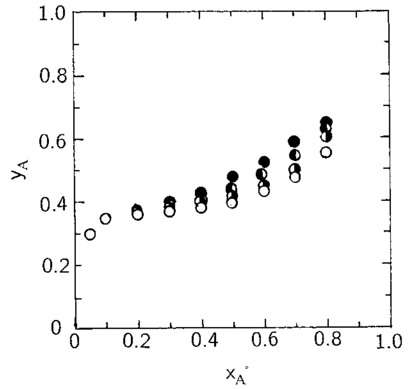

Figure 3. Vapor−liquid equilibrium data for 1-propanol (A) + water (B) + vinyl alcohol−sodium acrylate copolymer gel (C) at 298.15 K: (○) 0% gel, Hongo et al.; (◑) 5% gel, (◐) 10% gel, (●) 15% gel, this work.

systems (Mishima et al., 1987; Kumagae et al., 1992; Matsuyama et al., 1995). 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.

The salting-out effect of the gel was compared with that of the electrolyte by using measurements of the electric conductivity of the aqueous 1-propanol solution. From our measurements of electric conductivity, it was considered that the cause of the change of vapor pressure is not only a partial release of sodium ions from the gel but also the effect of selective adsorption of molecules on the polymeric gel. In the case of the aqueous solution containing 3.0 g of gel, 46 g of 1-propanol, and 14 g of water, the electric conductivity was 2.0 $mS{\cdot}m^{-1}$. The same value was obtained for the aqueous 1-propanol solution containing about 0.003 g of NaCl. But the salting-out effect of the gel on the VLE of the 1-propanol water system is much larger than that of NaCl at the same ion concentration. So it is difficult to explain the salting-out effect of the gel only by the release of sodium ions.

Conclusion

The activities of 1-propanol and water in the solvent + gel (vinyl alcohol + sodium acrylate copolymer) binary systems and VLE compositions of the 1-propanol + water + gel (vinyl alcohol + sodium acrylate copolymer) ternary system were measured by using flow type equipment at 298.15 K. In binary systems, the vapor pressure of water decreased with an increase in the concentration of the polymeric gel, while that of 1-propanol scarcely changed. Furthermore, the mole fraction of 1-propanol in the vapor phase increased with an increase in the concentration of polymeric gel in the liquid phase of the ternary system. The volatility of 1-propanol was enhanced by the added gel, and the salting-out effect of the gel on VLE of the 1-propanol + water system was observed.

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