Technical Paper

Vapor-Solution Equilibrium of Isobutyl Alcohol-Water System and Effect of Cobalt Nitrate Hexahydrate at 25°C

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Vapor-solution equilibrium of isobutyl alcohol-water system and effect of cobalt nitrate hexahydrate on the system have been investigated at atmospheric pressure and 25°C by a modified Randall's method. This method consists of passing a measured amount of air through a solution, collecting the transported vapors by condensation, and determining their weight and compositions. Solvent compositions were determined by gas chromatographic and refractometric methods. The activities of solvents showed positive deviation from Raoult's law, similar to other isomeric butyl alcohol-water systems. There was a sign of salting-out of isobutyl alcohol by addition of cobalt nitrate. It then appears that hexahydrated water molecules in the cobalt nitrate were not readily substituted by isobutyl alcohol molecules.

1 Introduction

A number of investigations have been performed for the ternary systems involving butyl alcohol, water, and various solutes (alkalihalide¹⁾, acids²⁾, alkali hydroxide³⁾) with the purpose of obtaining the knowledge of distribution behaviors of the solutes. As the result of measurements of solvent composition, it was found that the change of distribution ratio of solute was accompanied with the transfer of water from butyl alcohol phase to the aqueous one. The authors then thermodynamically correlated the transfer with the change of distribution ratio or salting-out of butyl alcohol in the aqueous phase. Moreover, from the conductometric measurements of the salt in the butyl alcohol phase, the salt distributed in butyl alcohol phase seemed to be generally weak electrolyte and to be dissociated into ions to some extent⁴⁾. However, there is no information on what interaction exists between salt and solvent, whether definite species are formed, and how they are bonded. When the solute is non-volatile, the activity of solvent or the behavior of solute can be obtained from the measurements of the change of the vapor pressure caused by the presence of the solute. From the above point of view, it is desirable to determine the vapor-solution equilibrium data of such systems. Since the vapor-solution equilibrium for *n*-butyl alcohol-water and tert-butyl alcohol-water systems have been previously reported^{5),6)}, the authors took up the system of isobutyl alcohol-water and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as the

third component of the system.

2 Experimental

2.1 Reagents

Isobutyl alcohol and cobalt nitrate hexahydrate and reagent grade chemicals were used without further purification. The conductivity water was prepared by passing the distilled water through mixed-bed ion exchange resins.

2.2 Procedure

Vapor pressures of isobutyl alcohol and water system have been determined by a modified Randall's method^{7),14)} as shown in Fig. 1. The present method consists of passing a given amount of air through a solution, collecting the absorbed vapors in wet air by condensation, and determining its weight and composition. The glass packing tower was packed with tube rings of glass, and was 2 cm in inside diameter and 100 cm in height. Air was passed through a wet gas meter A, a calcium tube B, a soda lime tube C, a bubbling tube L which contained the same solution as was circulated through the packing tower I, and then to the packing tower I. The saturated air was led into trap J, where solvents were condensed out of the air by use of a methanol solution of dry ice (contained in the Dewar vessel). The air then was passed to the vacuum line, its pressure being measured by the manometer K. The sample was stored in the upper tank G and was passed through the packing tower, then collected in the lower tank E, from which it was returned to the upper tank G by a pump. The flow of air was adjusted to

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Fig. 1 Apparatus for measuring vapor pressure

A: Wet gas meter, B: CaCl_2 tube, C: Soda lime tube, D, H: Flow regulator, E: Lower sample tank, G: Upper sample tank, I: Packing tower, J: Trap (Dewar vessel), K: Manometer, L: Bubbling tube

approximately 5 l/hr, and that of solution to 50 ml/min, respectively, which were below the safe maximum rates, and above these rates flooding occurred. After air of about 10 l had been passed, the flow of air was interrupted and the trap was disconnected, the trap was weighed and the condensate was analyzed. The accuracy of the method was checked by determining the vapor pressure of pure water at 25°C, which agreed well with literature value of 23.7 mmHg. The partial pressures of solvents were calculated in the following way. If a volume V of dry air was saturated with the vapor of the solution at temperature $t^\circ\text{C}$ and pressure P mmHg and the condensate contained w_1 g of water and w_2 g of isobutyl alcohol, the volumes of water and isobutyl alcohol (molecular weight M_1 and M_2 respectively) in vapor are given (in ml) by,

$$v_1 = w_1 \times 22,400(273+t) \times 760 / (M_1 \times 273 \times P) \quad (1)$$

$$v_2 = w_2 \times 22,400(273+t) \times 760 / (M_2 \times 273 \times P) \quad (2)$$

respectively.

Then, the total volume of the saturated air is $V+v_1+v_2$ and the partial pressures are given by,

$$p_1 = P \cdot v_1 / (V + v_1 + v_2) \quad (3)$$

$$p_2 = P \cdot v_2 / (V + v_1 + v_2) \quad (4)$$

respectively.

2.3 Analysis

The condensates from the high isobutyl alcohol solu-

tion and from the high water solution were of single phase and were analyzed by an Abbe refractometer. Most of the condensates separated into two phases by standing at a room temperature. These were diluted with a sufficient volume of tert-butyl alcohol to produce a homogeneous solution and then the solutions were analyzed by gas chromatography. A column used for gas chromatography consists of 20% by weight of the stationary liquid phase (cetyl alcohol) and 80% by weight of treated 60~80 mesh cellite. The column was made of 2 m $\times$ 0.6 cm ϕ stainless steel tube in U shape. The conditions of operation were similar to the case previously reported^{17,18}.

3 Results and Discussion

3.1 Isobutyl alcohol-water system

The experimental value is a mean of two or three runs which are determined for each composition. The data satisfied well the Gibbs-Duhem equation. The symbols used are as follows and for all symbols suffixes 1 and 2 denote water and isobutyl alcohol, respectively; x : mole fraction of water in solution, y : mole fraction of water in the vapor, π : total pressure, p : partial pressure, γ : activity coefficient of solvent, a : activity of solvent.

By assuming that the vapor phase obey the ideal

Fig. 2 Partial and total vapor pressures at 25°C
 p_1 : Water, p_2 : Isobutyl alcohol
The open circle denotes the effect of $\text{Co}(\text{NO}_3)_2$

gas law over the whole concentration range, then the activity in the solution is given by p/p° (p°_1 : 23.7 mmHg⁹⁾, p°_2 : 12.6 mmHg⁹⁾). Activity coefficients are calculated using the equation $\gamma = y \cdot \pi / x \cdot p^\circ$. Total and partial pressures are given in Fig. 2. The x - y plot is shown in Fig. 3. The open circle denotes the effect of cobalt nitrate. A plot of activity vs. mole fraction is shown in Fig. 4. Positive deviation from Raoult's law which is represented by the straight dotted line occurs, as predicted from the regular solution theory. The discontinuous portion of the curve can not be determined, where the solution consists of two phases. Each isomer other than tert-butyl alcohol is partly miscible with water and forms a two phase system.

x , mole fraction of water in solution

Fig. 3 The x - y plot for water at 25°C
The open circle denotes the effect of $\text{Co}(\text{NO}_3)_2$.

x , mole fraction of water in solution

Fig. 4 Activities of isobutyl alcohol and water at 25°C

a_1 : Water, a_2 : Isobutyl alcohol

On the other hand, tert-butyl alcohol is completely miscible with water at 25°C. The order of deviation from Raoult's law is the same as that of solubility of butyl alcohols in water, which is influenced absolutely, mainly by its ability to form hydrogen bonds. Palit has attributed the different solubility of isomeric butyl alcohol in water to the difference of effects of the hydroxyl group upon electron displacement in the hydrocarbon chain⁹⁾. Paterson et al. recently reported that the rate of proton exchange increased linearly with water concentration, and that τ (sec) for attachment of the proton in the alcoholic OH group increased in the sequence n -<iso-<sec-<tert-butyl alcohol¹⁰⁾. This is the same order as that of increasing proton-accepting facility. Positive deviations from Raoult's law would result from the difference in the internal pressure or molecular attractive forces, and therefore activity coefficient γ yields much information on the nature of the latter. The increase of γ bring about separation into two liquid phases because the attractive force between the same species becomes larger than that between the different species. The separation of γ into the entropy and enthalpy terms is general, though it can not so exactly separated. In general, the contribution of entropy term to γ is larger than that of enthalpy¹¹⁾. Isomeric butyl alcohols have almost equal molar volumes. Therefore, based on the regular solution theory, the entropy term may not be so different for each isomeric butyl alcohol. Consequently, it seems that the difference in γ of each isomeric butyl alcohol should be due to enthalpy term.

3.2 The effect of cobalt nitrate hexahydrate on isobutyl alcohol-water system

The effect of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ on the vapor-solution equilibrium of isobutyl alcohol-water system was determined at 25°C and also the behavior of distribution of the cobalt nitrate between two phases was discussed. The addition of a salt to an aqueous solution of a non-electrolyte has a marked effect upon the vapor-solution equilibrium and may raise or lower the relative volatility of the non-electrolyte or, in the extreme case, cause the formation of two liquid phases. Various experimental studies of the salt effect on vapor-solution equilibria have been reported¹²⁾. However, previous investigations have dealt almost exclusively with the equilibrium at boiling point or with the saturated salt solution, and only a few investigations at 25°C have been performed. The knowledge of vapor-solution equilibrium accounts for the behavior of the solute in the region of a two liquid phase.

Determination of solvent composition in solution was carried out after cobalt nitrate was removed by

distillation. The concentration of cobalt nitrate ranged from 0.02 to 0.1 mol/l and was determined by EDTA titration method. The experimental data are shown in Fig. 2 (open circle). Liquid composition are plotted on a salt free basis, in order that the effect of the cobalt nitrate on the composition of the equilibrium vapor phase is compared with the equilibrium curve of the binary isobutyl alcohol-water system. The addition of cobalt nitrate to the system resulted in the decrease of partial pressures of both components. This is interpreted as being due to fastening the interaction between the cobalt nitrate and solvent. As shown in Fig. 3, there is a considerable amount of salting-out of isobutyl alcohol. This salting-out effect should be due to a preferential attraction between water and cobalt nitrate. Whether cobalt nitrate with a net hydration of six water molecules appears in the isobutyl alcohol phase, must largely depend on the competitive strength of isobutyl alcohol and water molecules with respect to coordination with the cobalt nitrate. However, in this case, isobutyl alcohol may not replace the water molecules as other solvents do¹³.

Katzin et al. investigated the phase diagram in the region of liquid-liquid distribution and obtained the result that uranyl nitrate (the same coordination structure as cobalt nitrate) was extracted into the isobutyl alcohol phase with four water molecules coordinated¹³. Considering this result and salting-out of isobutyl alcohol, in isobutyl alcohol phase cobalt nitrate takes probably either the form $[\text{Co}^{++}(\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_4] \cdot 2 \text{H}_2\text{O}$ just as in the aqueous phase, or the form $[\text{Co}^{++}(\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_4] \cdot \text{BuOH}$ and the former combines the water molecules by hydrogen bonding and thus forming the second solvation shell¹⁴. Distribution ratio of cobalt nitrate (molarity of cobalt nitrate in the aqueous phase/that in the isobutyl alcohol phase) vs. its molarity in the aqueous phase C_a is shown in Fig. 5. The ratios show almost constant values. This indic-

Fig. 5 Distribution ratio of cobalt nitrate vs. its concentration in the aqueous phase C_a

ates that the species distributed are the same over the concentration range investigated. In conclusion, it seems that hexahydrated water molecules in cobalt nitrate are not readily substituted by isobutyl alcohol molecules. <E 313> (Received Sept. 25, 1972)

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