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Vapor-Liquid Equilibrium in the 2-Butanol–Water System and the Effect of Uranyl Nitrate

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Synopsis. Vapor-liquid equilibrium have been investigated by a modified Randall's method. The activities of solvents showed positive deviation from Raoult's law. There was a sign of salting effect on 2-butanol by addition of uranyl nitrate hexahydrate.

When the solute is non-volatile, the activity of the solvent or the behavior of the solute can be obtained from measurements of the change in the vapor pressure caused by the presence of the solute. Therefore, vapor-liquid equilibrium data for both 2-butanol–water and 2-butanol–water–uranyl nitrate systems have been determined at atmospheric pressure and 25 °C by a modification of Randall's method.

Experimental

Reagents: 2-Butanol and Uranyl Nitrate Hexahydrate. Reagent-grade chemicals were used without further purification. The conductivity water was prepared by the passage of the distilled water through mixed-bed ion-exchange resins.

Procedure. The vapor pressures of the 2-butanol and water system have been determined by a modification of Randall's method, as is shown in Fig. 1.[1,6)]

Analysis. The condensates in the high butanol range remaining in a single phase and the aqueous solution containing a large proportion of water were analyzed by means of an Abbe refractometer. Most of the condensates separated into two phases upon standing at room temperature. They were diluted with sufficient *tert*-butyl alcohol to produce a homogeneous solution, and then the solutions were analyzed by gas chromatography.[6)]

Results and Discussion

2-Butanol–Water System. The results of the experimental vapor-liquid equilibrium measurements are given in Fig. 2. The experimental value is the mean of two or three runs determined in each experiment. Assuming that the vapor phase obeys the ideal gas law over the complete concentration range, then the activity in the solution is given by p/p°. The saturated vapor pressure of a solvent at 25 °C was taken from Ref. 6 (p°_1: 23.7, p°_2: 17.1 mmHg). Activities are shown in Fig. 3. A positive deviation from Raoult's law, which is represented by the straight line, occurs as predicted. A discontinuous portion of the curve is not realized except in the two-phase region. The activity of the solvent must be the same in the two phases, which are in equilibrium with each other, because the chemical potential of the solvent is the same in each phase. Therefore, the dashed line, which indicates the region of the two phases, parallels the abscissa in the figures. However, in Fig. 3 the axes in water-rich region are magnified so as to be observed easily, and so the discontinuous portion is not shown clearly.

The values are comparable to those of the isomeric butanols.[1,2)] Palit has attributed the difference in the solubility of isomeric alcohol in water to the difference in the effects of the hydroxyl group upon electron displacement in the hydrocarbon chain.[3)] Paterson reported that the rate of proton exchange increased linearly with the water concentration, and that the τ (s) value for the attachment of the proton in the alcoholic OH group increased in this sequence; *n*-<

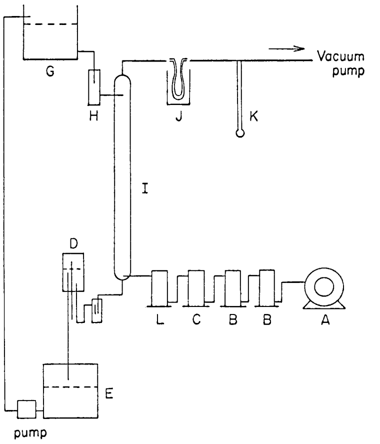

Fig. 1. Apparatus for measuring vapor pressure.
A: wet gas meter, B: $CaCl_2$ tube, C: soda lime tube D, H: flow regulator, E: lower sample tank, G: upper sample tank, I: packing tower, J: trap (Dewar vessel), K: manometer, L: bubbling tube

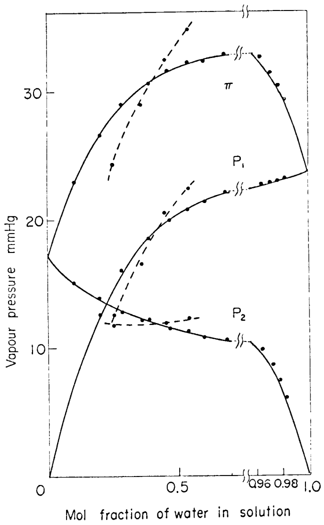

Fig. 2. Partial and total vapor pressures of 2-butanol–water system at 25 °C.
p_1: water, p_2: 2-butanol, slant dotted lines denote the effect of uranyl nitrate on the system of 2-butanol–water

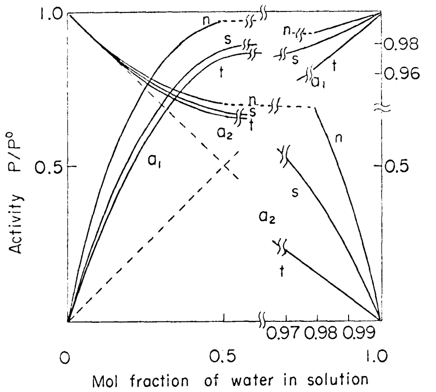

Fig. 3. Activities of components in isomeric butanol–water system at 25 °C. n, s, and t denote *n*-, *sec*-, and *tert*-butanol, respectively

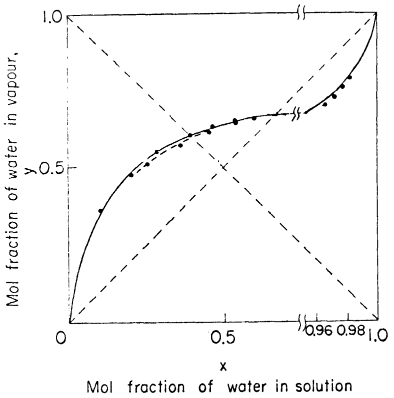

Fig. 4. Vapor-liquid equilibrium (*x*–*y* plot)
Solid line: 2-butanol–water
Slant dotted line: 2-butanol–water–uranyl nitrate

iso-<*sec*-<*tert*-butyl alcohol.[4,5] This is the same order as those of the increasing proton-accepting facility and of the deviation from Raoult's law. Positive deviations from Raoult's law are favored differences in the internal pressure or in the molecular-attractive forces, and therefore the activity coefficient, γ, yields much information on the nature of the latter. The increase in γ can bring about a separation into two liquid phases because the two components have their own attractive forces, dissimilar to one another.

The van Laar equation was found to fit the data for the system more closely than the Margules equation, much as in the case of the 1-butanol–water system.[6] The separation of γ into the enthalpy and entropy terms is quite general; they can not be exactly separated. In general, the contribution of the entropy term to γ is larger than that of the enthalpy. Isomeric butanols have almost equal molal volumes. Therefore, the entropy terms may not be so different. Consequently, it seems that the difference in γ of the isomeric butanols must be due to the enthalpy term.

Effect of Uranyl Nitrate on the Vapor-Liquid Equilibrium. The effect of the addition of $UO_2(NO_3)_2 \cdot 6H_2O$ on the 2-butanol–water system was determined, also the behavior of the distribution of the salt in the region of the liquid-liquid distribution was discussed. The addition of a salt to an aqueous solution of a non-electrolyte has a marked effect upon the vapor-liquid equilibrium; may either raise or lower the relative volatility of the non-electrolyte, or in an extreme case, cause the formation of two liquid phases. Various experimental studies of the salt effect on the vapor-liquid equilibrium have been reported.[7] However, these investigations have dealt almost exclusively with the equilibrium either at the boiling point or with a saturated salt concentration. On the other hand, only a few investigations at 25 °C have been performed. The knowledge of the vapor-liquid equilibrium accounts for the behavior of the salt in the range of the two liquid distribution. Each solvent for the liquid sample was determined by means of a refractometer after the salt has been removed by distillation.

The experimental data are shown graphically in Fig. 2 (slant dotted line). The liquid compositions were plotted on a salt-free basis. The addition of uranyl nitrate to the system resulted in an increase in the partial pressures of both water and 2-butanol above *ca.* a 0.5 mol fraction of water, while below that fraction it resulted in a decrease in both. As is shown in Fig. 4, there is a considerable salting-out of 2-butanol. This may be interpreted as being due to a breaking up or a loosening of the interaction between 2-butanol and water molecules. Consequently, the salting-out should largely be due to a preferential attraction between water molecules and uranyl nitrate. Whether uranyl nitrate with a net hydration of six water molecules appears in the butanol phase must depend largely on the competitive strength of the butanol and water molecules with respect to coordination with the uranyl nitrate. However, in this case, 2-butanol may not replace the water molecules as other solvents do.[8] Katzin *et al.* inspected the phase diagram in the region of the liquid-liquid distribution and found that the uranyl nitrate was extracted into the 2-methylpropanol phase with four water molecules coordinated.[6] Considering this result, in the 2-butanol phase it probably takes either UO_2^{2+}-$(NO_3^-)_2 \cdot (H_2O)_4 \cdot 2H_2O$ form just as in the aqueous phase, or $UO_2^{2+}(NO_3^-)_2 \cdot (H_2O)_4 \cdot x$BuOH form and the former joins the water molecules by hydrogen bonding, thus forming the second solvation shell. This can also be suggested on the basis of spectrophotometric measurements with IR and UV.

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