Enthalpy of Nonideal Binary Solutions: *T*-Butanol-Benzene, *T*-Butanol-Water

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This investigation continues the study of the thermodynamic properties of paraffinic alcohols, which exhibit considerable hydrogen bonding, and their nonideal mixtures with nonpolar and polar compounds. Previously benzene (*6*), *n*-hexane (*6*), methanol (*6*), ethanol (*10, 11*), *n*-pentane (*10, 11*), *n*-butanol (*9*), *t*-butanol (*4, 14*), and binary mixtures of benzene-methanol (*6*), methanol-*n*-hexane (*6*), benzene-ethanol (*10, 11*), benzene-*n*-pentane (*10, 11*), and *n*-butanol-benzene (*9*) have been studied. In this investigation enthalpies of binary mixtures of 50 mole % *t*-butanol in benzene and 75 mole % *t*-butanol in water were measured in a adiabatic flow calorimeter at temperatures from 250° to 550°F. and pressures from 20 to 1,000 lb./sq. in. abs. This range of temperature and pressure covered the vapor, liquid, and two-phase regions for all the systems studied. All enthalpy values reported (British thermal units per pound of solution) are based on the reference state of the pure liquid components at 77°F. and their vapor pressure in which state the enthalpy was arbitrarily taken to be zero.

In constructing the pressure-enthalpy diagrams presented the results of McCracken (*6*) for benzene, Krone and Johnson (*4*) for *t*-butanol, and Keenan (*2*) for water were used. No previous enthalpy measurements have been reported for the *t*-butanol-benzene system. Timmermans (*12*) tabulates most of the available mixture data. Heats of mixing have been measured by Wolf (*13*) at 77°F. The heat of mixing for the 50% mixture was taken as 6.02 B.t.u./lb. of solution.

Mixture enthalpy data for the *t*-butanol-water system are also nonexistent. Vapor pressures and vapor-liquid equilibrium data have been determined by Ewert (*1*) at temperatures below the boiling point. Lange (*5*) and Kenttamaa (*3*) have both measured heats of dilution for this system over different ranges of composition. Lange reports a heat of mixing for the 75 mole % *t*-butanol mixture of —4.90 B.t.u./lb. of solution which was used in this work.

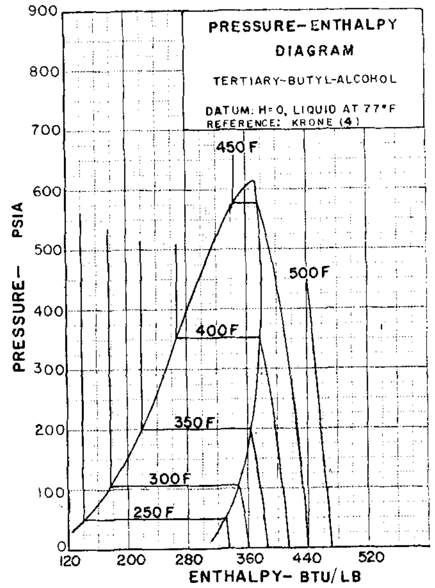

Fig. 1. Pressure-enthalpy diagram for t-butanol.

EXPERIMENTAL RESULTS

The *t*-butanol was guaranteed to contain 99.9% *t*-butanol. Ordinary distilled water was used. Throughout this investigation the material in the calorimeter was checked for evidence of thermal degradation with a refractometer and vapor-phase chromatograph. No evidence of any change in fluid composition could be detected.

The experimental method and procedure for calculating the experimental enthalpy of the mixture relative to the reference state was essentially the same as that reported by McCracken (*6, 7*) and Storvick (*10, 11*). The original data and all pertinent details are given by O'Neill (*8*). The method of constructing the pressure-enthalpy diagrams was essentially that reported by Shannon, Gustafson, and O'Neill (*9*). The pressure and enthalpy values have an estimated accuracy of ± 1%. The estimated critical points have an estimated uncertainty of ± 5°F. and ± 7 lb./sq. in. abs.

The pressure-enthalpy charts for pure *t*-butanol, and the binary mixtures with benzene and water are shown in Figures 1, 2, and 3. The saturated and super-heated properties of the *t*-butanol systems are given in Tables 1 to 6*. The original data are given by O'Neill (*8*). All of the mixture data on *t*-butanol were obtained exclusively in this work, while the diagram for pure *t*-butanol was produced from the data of Krone (*4*). Maslan (*14*) also has presented a pressure-enthalpy diagram for *t*-butanol. Sup-

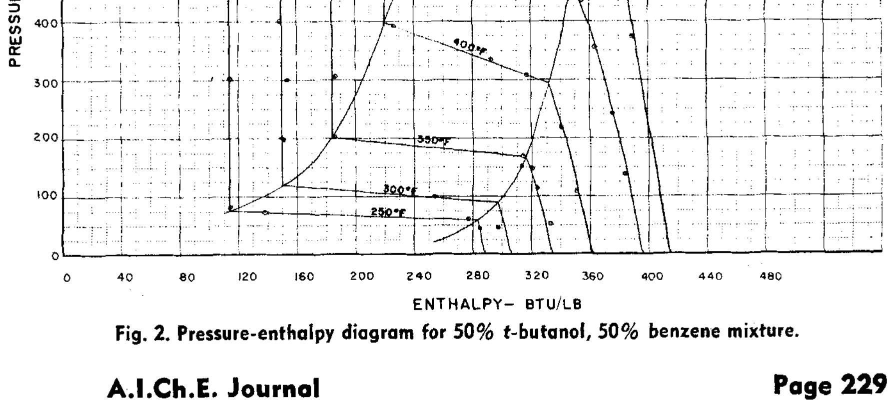

Fig. 2. Pressure-enthalpy diagram for 50% t-butanol, 50% benzene mixture.

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* Tabular material has been deposited as document 7420 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or for 35-mm. microfilm.

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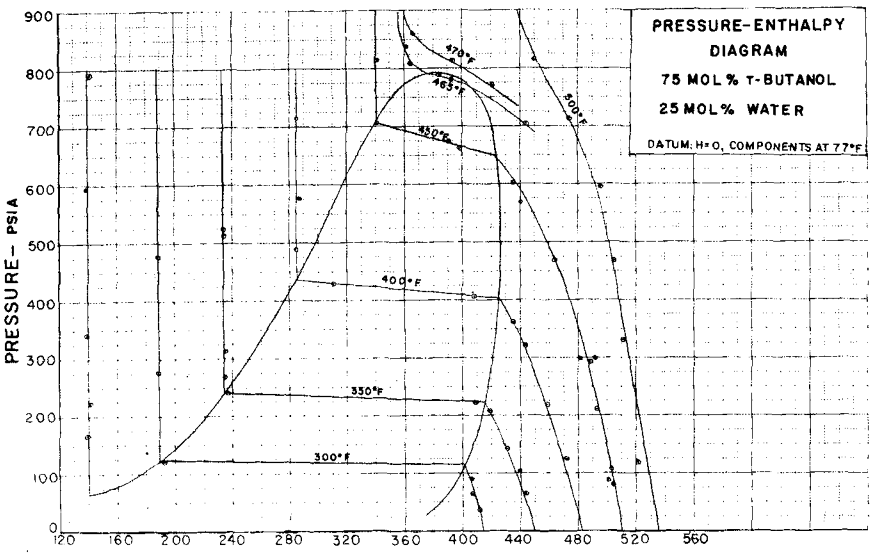

Fig. 3. Pressure-enthalpy diagram for 75% *t*-butanol, 25% water mixture.

plementary enthalpy-temperature and latent heat temperature diagrams for these systems are given by O'Neill.

DISCUSSION

It was found that the methods of McCracken (*6, 7*) and Storvick (*10, 11*) did not accurately predict the effect of pressure on the vapor-phase mixture enthalpies at constant temperature for the normal and *t*-butanol-benzene systems but are adequate in predicting the deviation encountered in the pure alcohols and in dilute solutions of polar-nonpolar mixtures. For the *t*-butanol-water mixture a modification of Storvick's method was found to accurately predict the mixture enthalpies. Since water does not have a homomorph, the values for pressure deviation in enthalpy were obtained directly from the steam tables (*2*) which include the hydrogen bonding effects of the pure water for use in Storvick's equations. The excellent correlation over the complete temperature and pressure range may be due to the fact that the solution was dilute (7.5 wt. % water). A detailed discussion of these results, methods for correlating the pure component data, and methods for predicting the enthalpies of the mixtures from the properties of the pure components is given by O'Neill (*8*).

The calculated heats of association for the *t*-butanol were found to be considerably less than those found for *n*-butanol, especially at the higher temperatures and pressures. The differences in these heats of association indicate that molecular structure does have a pronounced effect on the degree of hydrogen bonding of the alcohols in the vapor phase. It is postulated that molecules which contain highly branched chains, such as *t*-butanol, are incapable of forming large polymolecules owing to the effect of steric hinderance. Since the heat of association is a measure of the degree of hydrogen bonding, it was expected that *n*-butanol would have higher values than the tertiary isomer.

ACKNOWLEDGMENT

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Time Optimal Control of Nonlinear Systems with Constraints

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The work of Amundson et al. (*1*) has served to hasten the chemical engineer into the application of feedback control theory to chemical systems. The feasibility of a computer as a process controller was demonstrated by Tierney et al. (*12*) and as a process optimizer by Eckman and Lefkowitz (*10*). The recent papers of Kalman et al. (*7*) and Lapidus et al. (*8*) have dealt with the optimum dynamic control of a chemical process or plant using a general purpose digital computer. As shown the concept of dynamic programming may be applied to linearized systems directly to generate the optimum dynamic control strategy or law.

Since chemical systems are usually nonlinear and may not always be approximated by a linearized model, a strategy for generating the optimum dynamic control strategy in the stationary nonlinear case must be developed. While theoretically this can still

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