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Vapor-Liquid Equilibria for NH_3 and H_2O in the 100 to 150°C Region: Effect of Low Levels of Phenol on Partial Pressure of Ammonia

Experimental results are reported for the partial pressure of ammonia in water solutions containing low concentrations of phenol. Experiments were performed in 0.6 molal phenol at 100 and 150°C. Results at 150°C indicate that the very small effect of phenol on the partial pressure of ammonia is within the limit of experimental error, 3%, and therefore could not be established from the data. However, at 100°C, the partial pressure of ammonia was decreased by nearly 10%. Computer program TIDES—a computerized thermodynamic framework for calculating vapor-liquid equilibria for volatile weak electrolytes and other common gases—has been revised to account for the effect of low concentrations of phenol.

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INTRODUCTION

Chemical and related industries frequently use water to cool and wash process streams. For example, in coal-gasification processing, water absorbs not only small quantities of nitrogen, carbon monoxide, hydrogen, argon, lower hydrocarbons, and phenolics, but also sizable quantities of ammonia, carbon dioxide, hydrogen sulfide, hydrogen cyanide, and sulfur dioxide. Describing phase equilibria for aqueous solutions of volatile, weak electrolytes have been the subject of several recent studies (Edwards et al., 1978; Renon and Beutier, 1978); however, these studies do not account for the presence of phenol, which is nearly nonvolatile but partially dissociates in water. Growing interest in coal gasification has motivated questions regarding the effect of phenol on the degree of dissociation of volatile, weak electroytes. We have performed some experiments on ammonia-phase equilibria in water containing low levels of phenol. The temperature range of 100 to 150°C was chosen to correspond to industrial coal-gasification operating conditions. For typical coal-gasification processes, concentrations of 0.07 to 0.2 molal phenol have been reported for wastewater streams (Div. of the Bureau of Mines, 1974). Our experiments were performed with 0.6 molal phenol solutions to amplify the phenol's effect.

REVISION OF PROGRAM TIDES

To calculate the effect of phenol on ammonia partial pressure, Program TIDES (a computerized molecular thermodynamic correlation for phase equilibria of aqueous volatile, weak electrolytes as described by Pawlikowski, 1981) has been revised to account for phenol dissociation. Phase-equilibrium and chemical-equilibrium expressions for phenol are incorporated into the solution schemes for bubblepoint, dewpoint, and flash calculations. Table 1 provides the phenol dissociation constant and its temperature dependence as reported by Tsonopoulos (1976). Henry's constant for phenol is also given as a function of temperature. Because there are no data available, all binary interaction parameters for phenol and phenolate ion and all other species were set equal to zero.

To examine Program TIDES' capability to predict phase equilibria for solutions containing phenol, some experiments for NH_3 and phenol in water were performed.

EQUIPMENT AND PROCEDURE

A static experimental apparatus was used for measurements on both liquid- and vapor-phase compositions. Details of the experimental apparatus are described elsewhere (Pawlikowski, 1981). Gas-liquid chromatography was used for sample analysis.

After the equilibrium cell was thoroughly cleaned, it was filled with 0.6 molal phenol solution. The solution was degassed by pulling a vacuum for several hours. The cell is then pressurized with NH_3, and the solution was allowed to equilibrate overnight. Samples of both liquid and vapor phases were taken using the technique outlined by Pawlikowski. Phenol levels in the vapor phase were below the detection limit of the chromatograph. After sampling was completed, the pressure in the cell was adjusted by the addition of more ammonia vapor.

Anhydrous ammonia (purity better than 99.99%) was obtained from Matheson Gas Co. Water was obtained from a reverse-osmosis

TABLE 1. PROPERTIES OF PHENOL IN WATER*

Dissociation Equilibrium:

$$C_6H_5OH \overset{K_{EQ}}{\rightleftharpoons} C_6H_5O^- + H^+$$

$$ln\ K_{EQ} = -00669.42/T \qquad -27.7262\ ln\ (T) + 174.133$$

K_{EQ} is mol/kg H_2O
for a temperature range of 25 to 250°C

Henry's Constant

$$ln\ H\ (\text{bar kg/mol}) = -58.808 + 0.26613T - 0.31628E - 3T^2$$

for a temperature range of 0 to 100°C

Phenol-Phenol Interaction Parameter, β_{tt} in kg H_2O/mol

$$\beta_{tt} = 42.979 - 0.25389T + 0.3698E - 3T^2$$

for a temperature range of 0 to 100°C

Henry's constants and β_{tt} parameters obtained from data of Good and Millay (1956) and Hirata (1975).

* Temperature T in K.

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TABLE 2. MEASURED VAPOR-LIQUID EQUILIBRIA FOR NH_3 IN AQUEOUS MIXTURES CONTAINING 0.6 MOLAL PHENOL

	Molality of NH_3 mol/kg H_2O	Partial Pres. of NH_3 bar
$m_{phenol} = 0.61$ 100°C		
	5.13	1.26
	13.68	3.70
	23.71	8.01
	32.28	12.18
$m_{phenol} = 0.59$ 150°C		
	1.30	1.02
	4.20	3.64
	4.80	4.04
	9.35	7.72
	11.27	9.33
	19.29	16.15

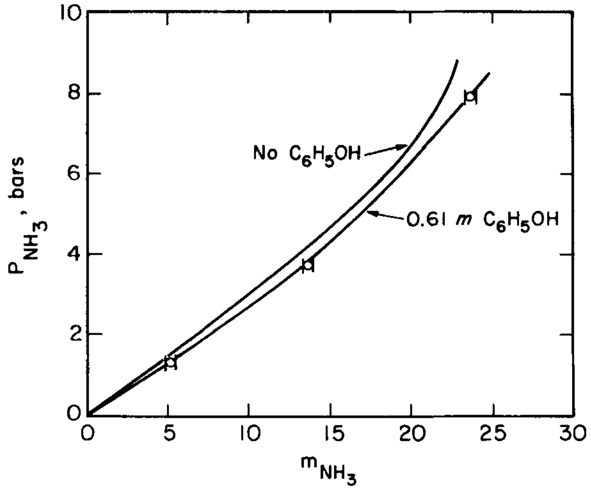

Figure 1. Vapor-liquid equilibria for NH_3 in 0.61 m C_6H_5OH at 373 K (Points experimental; lines calculated with TIDES).

unit and further purified by deionization and filtration. Phenol (purity better than 99.5%) was obtained from Mallinckrodt, Inc.

RESULTS AND DISCUSSION

Table 2 gives experimental results. Figures 1 and 2 provide a comparison between the partial pressure of ammonia in water and the partial pressure over the phenol solution. At 100°C, the effect of phenol is larger than 3% and is therefore detectable from the experimental error of 3%. At 150°C, the experimental data lie within 3% of the curve calculated for NH_3 in phenol-free water; therefore, the small effect of phenol cannot be established.

The lower curves in Figures 1 and 2 are calculated with program TIDES after revision to include phenol dissociation. Figure 1 indicates that Program TIDES, without any further modifications, can be used to calculate phase equilibria for ammonia with phenol present. Figure 3 provides TIDES prediction for phenol and NH_3 in H_2O at 25°C. Because the phenol-dissociation constant increases with decreasing temperature, a larger effect of phenol of P_{NH_3} is detected at 25 than at 100°C. Unfortunately, we have no experimental data at 25° for comparison.

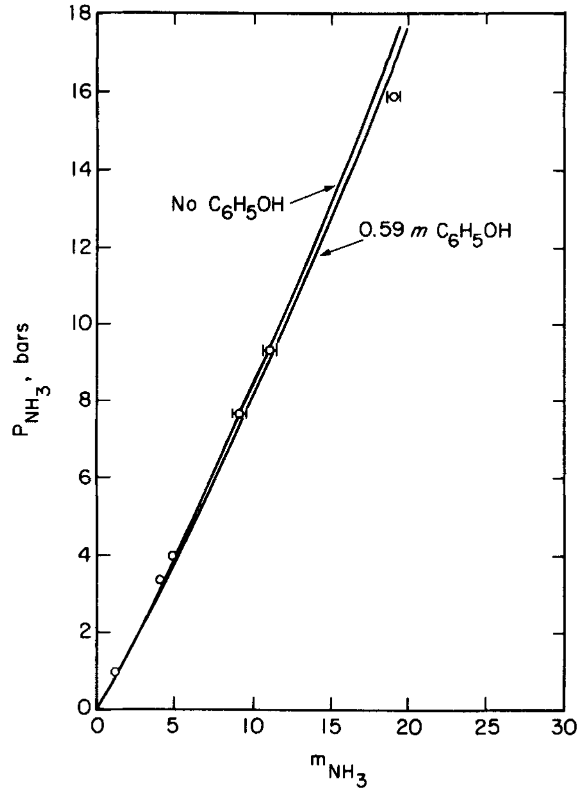

Figure 2. Vapor-liquid equilibria for NH_3 in 0.59 m Phenol at 423 K (Points experimental; lines calculated with TIDES).

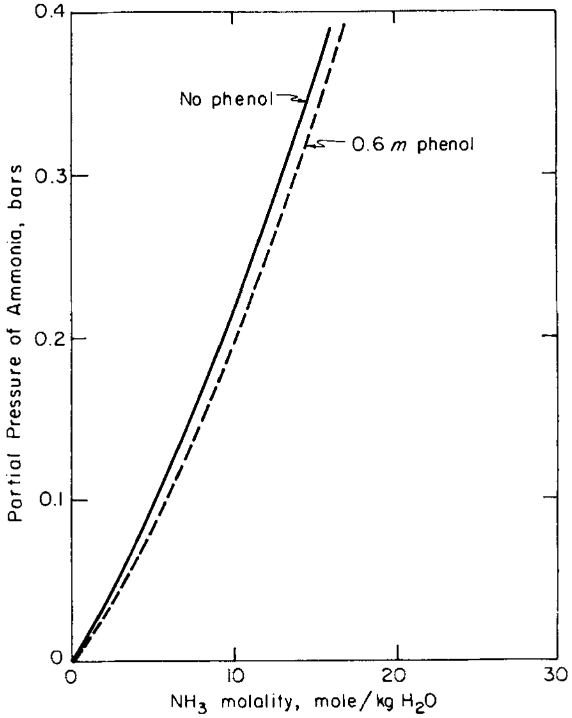

Figure 3. Effect of phenol on NH_3 partial pressure in aqueous solutions at 298 K.

CONCLUSION

Concern over the effect of phenol on weak, volatile electrolyte dissociation reactions has motivated us to perform some experiments on the partial pressure of ammonia in water containing low concentrations of phenol. Our results indicate that at typical levels found in coal-gasification processing waste streams, phenol has only a small effect on the partial pressure of ammonia at 100°C and an undetectable effect of 150°C. By accounting for phenol dissociation while neglecting any binary interactions between phenol and other solutes, Program TIDES can adequately calculate the small correction to ammonia partial pressure.

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Improved Successive Quadratic Programming Optimization Algorithm for Engineering Design Problems

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INTRODUCTION

We present an algorithm for optimizing structured engineering processes which is computationally more efficient and conceptually cleaner than an earlier one described in Berna et al. (Bern80, 1980). The algorithm is based on sequential quadratic programming. It is a special case of a broader a class of algorithms developed by Edahl (Edah82, 1982).

THEORY

The optimization problem can be stated as follows:

$$\begin{gathered} \min \Phi(z) \\ s.t.\ g(z) = 0 \\ z_{\min} \le z \le z_{\max} \\ z \in E^{n+r} \\ g: E^{n+r} \to E^n \\ \Phi: E^{n+r} \to E^1 \end{gathered} \tag{P1}$$

The Lagrangian of this problem is:

$$L(z,\tau,\kappa_{\min},\kappa_{\max}) = \Phi(z) - \tau^T g(z) - \kappa_{\min}^T(z_{\min} - z) + \kappa_{\max}^T(z_{\max} - z),$$

with τ the Lagrange multipliers on the equality constraints and $\kappa_{\min}$ and $\kappa_{\max}$ the Kuhn-Tucker multipliers on the lower and upper bounds of z, respectively.

The Kuhn-Tucker conditions for this problem are:

$$\begin{gathered} \kappa_{\min}[z_{\min} - z] = 0 \\ \kappa_{\max}[z_{\max} - z] = 0 \\ \kappa_{\min}, \kappa_{\max} \le 0 \end{gathered}$$

For a typical flowsheet calculation of the type we are considering, n may be on the order of 10,000, with r on the order of 10. This formulation is quite general as general inequality constraints can be converted to equality constraints through the use of bounded slack variables.

Powell's (Powe77, 1977) approach to solving this problem is to linearize the equality constraints, assume a quadratic approximation to the objective function, and solve the resulting QPP. Variables are then updated by taking the step

$$\Delta z = \alpha d$$

where d is the step calculated by the QPP.

The disadvantage of using Powell's method is the size of the Hessian Matrix for the QPP. For a problem with 10,000 variables, the Hessian contains 100 million elements, far too many for even the most advanced machines to handle. By partitioning the variables into two sets, the independent or decision variables, u, and the dependent or pivoted variables, x, we now show how a QPP can be set up on the decision variables only.

Let x_k and u_k be the values of the dependent and independent variables respectively at the present iteration. Linearizing the equality constraints about this point gives:

$$g(x_{k+1},u_{k+1}) \sim g(x_k,u_k) + (\partial g/\partial x^T)_k \Delta x_k + (\partial g/\partial u^T)_k \Delta u_k$$

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