# Thermodynamics of Association for Benzene-Benzyl Alcohol, Benzene-Phenethyl Alcohol, and Fluorobenzene-Benzyl Alcohol in Dilute Aqueous Solution

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Vapor pressure measurements have been made on dilute aqueous solutions of benzene-benzyl alcohol (BZOH), benzene-phenethyl alcohol (PEOH), and fluorobenzene-BZOH at 15, 25, 35, and  $45^{\circ}$ C. The benzene results have been interpreted with a mass action model which attributes deviations from ideality to the formation of benzene dimers and heterodimers with BZOH and PEOH. The benzene heterodimers form endothermically at  $25^{\circ}$ C with large and negative heat capacity changes. The dimerization constant for the benzene-BZOH dimer reaches a maximum of  $0.57 M^{-1}$  at about  $37^{\circ}$ C, while the benzene results have been interpreted with a mass action model which, in addition to fluorobenzene dimers and heterodimers, includes the formation of a fluorobenzene-BZOH trimer. Thermodynamic properties for these aggregates are reported and compared with results obtained in previous studies.

KEY WORDS: Vapor pressure; dimerization constant; hydrophobic association; benzene; fluorobenzene; benzyl alcohol; phenethyl alcohol; dilute aqueous solutions.

## 1. INTRODUCTION

Previous vapor pressure studies from this laboratory have produced thermodynamic information about the association of hydrocarbons and polar hydrocarbon derivatives in dilute aqueous solutions.<sup>(1-7)</sup> From these studies, reliable estimates of the association

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constants, enthalpies, and in some cases heat capacity changes for dimerization have been obtained.<sup>(5)</sup> The results support the prevailing view that water molecules in contact with a hydrocarbon are more ordered than those in the bulk liquid water<sup>(8-10)</sup> and that hydrophobic association between hydrocarbons occurs with loss of part of the ordered region as the nonpolar moieties come into contact.<sup>(2,4,5)</sup>

In earlier communications, we reported on the self-association of benzene<sup>(1,2)</sup> and fluorobenzene,<sup>(7)</sup> the association of cyclohexane with cyclohexanol<sup>(2)</sup> and of benzene with phenol.<sup>(4)</sup> A comparison of the benzene-benzene and benzene-phenol systems provided information about the effect of hydroxyl addition on the thermodynamic quantities of interest, namely  $K_{11}$ ,  $\Delta H$ , and  $\Delta C_p$ . We thought it important to study the interaction of benzene with benzyl and phenethyl alcohol to assess the effect of successive additions of -CH<sub>2</sub> groups on the relevant thermodynamic quantities. The interaction of fluorobenzene with benzyl alcohol is also of interest because it gives information about the effect of fluorine substitution and about the behavior of fluorocarbons in aqueous solution. In this paper, all of the interaction of benzene with BZOH and PEOH is accounted for by assuming that only a simple heteroassociation reaction

benzene(aq) + BZOH(aq) or PEOH(aq)  $\rightarrow$  heterodimer(aq)

contributes to deviations from ideality. Both of these dimers form endothermically with a large and negative heat capacity change. This behavior is consistent with that of other hydrophobic association reactions previously investigated.<sup>(5)</sup>

The interaction of fluorobenzene with BZOH cannot be satisfactorily accounted for by a mass action model considering only heterodimer formation. In order to account for the vapor pressure results at the larger fluorobenzene fugacities, one more reaction has to be included

2-fluorobenzene(aq) + BZOH(aq)  $\rightarrow$  2-fluorobenzene BZOH(aq)

The thermodynamic constants characterizing these interactions are given in the discussion.

#### 2. EXPERIMENTAL

The vapor pressure apparatus used to obtain vapor pressure - composition data and the methods of purifying water and benzene have been described previously.<sup>(2,11)</sup> Gold label benzyl and phenethyl al-



Fig. 1. Pressure of benzene vs. molar concentration of benzene in solutions of benzene in  $H_2O$ , ---; in 0.08*M* benzyl alcohol (aq), \*; and in 0.18*M* benzyl alcohol (aq),  $\triangle$ ; all at 25°C.

cohol (Aldrich) were distilled under reduced pressure prior to use.

Approximately 300, 150, and 50 vapor pressure vs. composition data sets were obtained for benzene-BZOH, benzene-PEOH, and fluorobenzene-BZOH, respectively, at 15, 25, 35, and 45 °C. The concentrations of benzyl alcohol solutions were 0.09 and 0.18M, while those of phenethyl alcohol were 0.06 and 0.08M. The concentration of benzyl alcohol used in the fluorobenzene experiments was 0.1M. Figure 1 shows typical results at 25 °C, plotted as the partial pressure of benzene vs. the formal benzene concentrations. For comparison, a similar plot for the systems with no added fixed solute is included in the figure. The decrease in pressure at a given concentration is attributed to the formation of molecular aggregates.<sup>(1.4)</sup>

## 3. RESULTS AND DISCUSSION

As has already been stated, in this investigation all deviations from ideal solution behavior are attributed to the formation of molecular aggregates. The dimerization of benzene and fluorobenzene is assumed to occur simultaneously with the formation of heterodimers and, in the case of fluorobenzene, with the formation of larger aggregates. Although one might expect both BZOH and PEOH to selfassociate to a small extent in dilute aqueous solution, the introduction of an interaction term to account for the formation of alcohol dimers

$K_{11}$ (L-mol <sup>-1</sup> )	10 <sup>-6</sup> RMSD <sup><i>a</i></sup>	M <sup>b</sup>	$K_{11}$ (L-mol <sup>-1</sup> )	$10^{-6}$ RMSD <sup><i>a</i></sup>	M <sup>b</sup>
Benz	ene-Benzyl Alco	hol	Benzene	e-Phenethyl Alc	ohol
			15°C		
$0.475 \pm 0.002^{c}$	6.87	0.09	$0.521 \pm 0.002$	4.49	0.06
$0.517 \pm 0.002$	5.95	0.09	$0.552 \pm 0.003$	9.77	0.08
$0.487 \pm 0.002$	12.4	0.18			
$0.536 \pm 0.003$	16.6	0.18			
			25°C		
$0.520 \pm 0.003$	10.1	0.09	$0.615 \pm 0.006$	14.2	0.06
$0.592 \pm 0.002$	6.26	0.09	$0.608 \pm 0.009$	32.2	0.08
$0.508 \pm 0.001$	9.36	0.18			
$0.554 \pm 0.002$	13.7	0.18			
			35°C		
$0.547 \pm 0.001$	2.45	0.09	$0.561 \pm 0.002$	4.02	0.06
$0.611 \pm 0.001$	2.51	0.09	$0.592 \pm 0.001$	4.74	0.08
$0.563 \pm 0.001$	5.01	0.18			
$0.615 \pm 0.001$	12.9	0.18			
		4	45°C		
$0.492 \pm 0.001$	4.7 <b>4</b>	0.09	$0.540 \pm 0.002$	4.32	0.06
$0.581 \pm 0.001$	5.97	0.09	$0.580 \pm 0.002$	9.34	0.08
$0.564 \pm 0.002$	13.7	0.18			
$0.618 \pm 0.003$	23.5	0.18			

Table I. Equilibrium Constants for the Formation of the Benzene-<br/>Benzyl Alcohol and Benzene-Phenethyl Alcohol Dimers in<br/>Dilute Aqueous Solutions

<sup>a</sup> Root mean square deviation in formal benzene concentration (M). <sup>b</sup> Formal or analytical concentration of the alcohol. <sup>c</sup> Standard or  $1\sigma$  error in  $K_{11}$ .

does not significantly improve the data correlation.

Using a model which only includes interaction parameters for benzene self-association and the formation of benzene-BZOH and benzene-PEOH heterodimers, one can write two mass balance equations to relate the concentration of chemical species in solution. These relations are

$$f_{\rm B} = C_{\rm B} + 2K_2C_{\rm B}^2 + K_{11}C_{\rm B}C_{\rm A} \tag{1}$$

$$f_{\rm A} = C_{\rm A} + K_{11}C_{\rm B}C_{\rm A} \tag{2}$$

For fluorobenzene, in order to account for the formation of a trimer composed of two fluorobenzene and one BZOH molecules, the mass balance relations become

$$f_{\rm B} = C_{\rm B} + 2K_2C_{\rm B}^2 + K_{11}C_{\rm B}C_{\rm A} + 2K_{21}C_{\rm B}^2C_{\rm A}$$
(3)

$$f_{\rm A} = C_{\rm A} + K_{11}C_{\rm B}C_{\rm A} + K_{21}C_{\rm B}^2C_{\rm A} \tag{4}$$

In Eqs. (1) to (4),  $f_{\rm B}$  and  $f_{\rm A}$  are the formal concentrations of volatile solute (benzene, fluorobenzene) and alcohol, respectively.  $C_{\rm B}$  and  $C_{\rm A}$  are the monomer concentrations and  $K_2$  and  $K_{11}$  are the formation constants for the aromatic dimer and heterodimers, in that order.  $K_{21}$  is the formation constant for the fluorobenzene-BZOH trimer. Because the dependence of  $K_2$  on temperature has been measured previously for both benzene<sup>(2)</sup> and fluorobenzene,<sup>(7)</sup> the model for the benzene systems requires the introduction of only a single parameter,  $K_{11}$ . For the fluorobenzene system two parameters are needed,  $K_{11}$  and  $K_{21}$ . The values of  $C_{\rm B}$  are calculated from the vapor pressures using the known values of the Henry's law constants for benzene,<sup>(2)</sup> fluorobenzene,<sup>(7)</sup> and small corrections for vapor phase nonideality.

Table I lists values of  $K_{11}$  at four temperatures for 16 and 8 separate runs of benzene with BZOH and PEOH, respectively. Table II contains values of  $K_{11}$  and  $K_{21}$  (at four temperatures) for four separate runs of fluorobenzene with BZOH. Tables I and II also include the root mean square deviation (RMSD) in benzene or fluorobenzene concentration as well as the molarity of the original solution. Because the data for the benzene systems are qualitatively different from those for fluorobenzene, we will discuss them separately.

#### 3.1. Benzene-BZOH and Benzene-PEOH

From the results shown in Table I, we can see that, for benzyl alcohol as for phenol,<sup>(4)</sup> the values of  $K_{11}$  are not significantly concentration dependent. There is, however, an apparent connection between the temperature dependence at the higher temperatures (above 35 °C) and the concentration of benzyl alcohol. We feel that the data presented here do not warrant a different fit for the results at each concentration. This difficulty results in a large uncertainty in the value of  $\Delta C_p$ . It is clear, nonetheless, that for benzyl alcohol  $K_{11}$  goes through a maximum around 37 °C. In the case of phenethyl alcohol, both sets of solutions are close in concentration, and the temperature depen-

T(°C)	K <sub>11</sub> (L-mol)	$K_{21}$ (L-mol) <sup>2</sup>	RMSD <sup>a</sup>	M <sup>b</sup>
15	$^{\circ}0.468 \pm 0.013^{\circ}$	$^{c}3.31 \pm 0.74^{c}$	$5.80 \times 10^{-6}$	0.10
25	$0.575 \pm 0.006$	$3.36 \pm 0.36$	$3.05 \times 10^{-6}$	0.10
35	$0.627 \pm 0.009$	$6.68 \pm 0.54$	$4.80 \times 10^{-6}$	0.10
45	$0.730 \pm 0.013$	$10.15 \pm 0.79$	6.90×10 <sup>-6</sup>	0.10

Table II. Equilibrium Constants for the Formation ofthe Fluorobenzene-Benzyl Alcohol Dimer and Trimer in DiluteAqueous Solutions

<sup>a</sup> Root mean square deviation in formal benzene concentration (M). <sup>b</sup> Formal or analytical concentration of benzyl alcohol. <sup>c</sup>Standard or  $1 \sigma$  error in parameter.

dence of both runs is very similar. For phenethyl alcohol,  $K_{11}$  goes through a maximum at about 30°C.

Both the 16 sets of  $K_{11}$ , T values for BZOH and the 8 sets for PEOH were fitted to the equation

$$K_{11} = K_{11}(298) \exp[-\Delta H(1/T - 1/298.15)/R + \Delta C_{\rm p} \ln (T/298.15)/R + \Delta C_{\rm p}(298.15 - T)/RT]$$
(5)

where  $\Delta C_{\rm p}$  is the heat capacity change for forming the heterodimer (assumed independent of temperature),  $\Delta H$  is the enthalpy of dimerization at 25 °C, and  $K_{11}$  (298) is the dimerization constant at that reference temperature. The  $K_{11}$ , T values were correlated by Eq. (5) with an RMSD in  $K_{11}$  of 0.038 M<sup>-1</sup> for BZOH and 0.025 M<sup>-1</sup> for PEOH. The values of the least squares parameters for BZOH are

$$K_{11}(298) = 0.553 \pm 0.014 \text{ L-mol}^{-1}$$
  

$$\Delta H = 1.20 \pm 0.42 \text{ Kcal-mol}^{-1} = 5.02 \pm 1.76 \text{ KJ-mol}^{-1}$$
  

$$\Delta C_{p} = -98 \pm 64 \text{ cal-mol}^{-1} \text{-K}^{-1} = -410 \pm 267 \text{ J-mol}^{-1} \text{-K}^{-1}$$

and for PEOH

$$K_{11}(298) = 0.593 \pm 0.014 \text{ L-mol}^{-1}$$
  

$$\Delta H = 0.78 \pm 0.37 \text{ Kcal-mol}^{-1} = 3.26 \pm 1.54 \text{ KJ-mol}^{-1}$$
  

$$\Delta C_{n} = -148 \pm 58 \text{ cal-mol}^{-1} \text{-K}^{-1} = -619 \pm 242 \text{ J-mol} \text{-K}^{-1}$$

Figure 2 shows a plot of  $K_{11}$  vs. T for BZOH. Figure 3 is a similar plot for PEOH. The solid lines represent the optimum fit to Eq. (5) of the



**Fig. 2.** Equilibrium constants for the benzene-benzyl alcohol 1:1 complex in  $H_2O$  vs. temperature. Points are  $K_{11}$  values from Table I; line is the least squares curve obtained from the fit of Eq. (5) to the points. Results for 0.08*M* benzyl alcohol solutions (+,\*); results for 0.18*M* solutions  $(\Delta, \Box)$ .

# entire collection of $K_{11}$ , T values.

A general conclusion that emerged from comparing the benzenebenzene and benzene-phenol systems is that the addition of polar or highly polarizable groups to a hydrocarbon tends to lower  $\Delta H$  without significantly affecting the equilibrium constant for dimer formation.<sup>(4)</sup> This effect was attributed to the presence of dipole-induced dipole or dipole-dipole interactions which add an exothermic contribution to  $\Delta H$ not present in hydrocarbon self-association. Another factor which may be of importance is that the substitution of a hydrogen by an -OH group increases the electron density of the aromatic ring reducing its hydrophobicity because of favorable van der Waals interactions with water.<sup>(12)</sup> The results obtained for benzyl and phenethyl alcohol, both with large dipole moments (approximately 1.7 and 1.6 D. respectively), <sup>(13)</sup> are in agreement with our general conclusion. Ideally, to assess the effect of -OH addition, the  $\Delta H$  for the benzene-BZOH and benzene-PEOH systems should be compared with the  $\Delta H$  of interaction for the benzene-toluene and benzene-phenylethane systems, respectively. Unfortunately, these systems cannot be studied because Furthermore, and this is important, we of solubility limitations. believe that, because of the large and negative heat capacity changes observed in these systems, comparisons of  $\Delta H$  values at a single reference temperature, say 25 °C, are not necessarily meaningful.



Fig. 3. Equilibrium constants for the benzene-phenethyl alcohol 1:1 complex in  $H_2O vs.$  temperature. Results for 0.06*M* phenethyl alcohol solutions (\*); results for 0.08*M* solutions ( $\Delta$ ).

A comparison of the benzene-phenol, benzene-BZOH, and benzene-PEOH systems also allows us to estimate the effect of successive additions of -CH<sub>2</sub> groups to the remaining thermodynamic quantities of interest, namely  $K_{11}$  and  $\Delta C_p$ . As in the case of -OH substitution, the addition of -CH<sub>2</sub> groups does not significantly affect the values of  $K_{11}$ . The values of  $\Delta C_p$ , on the other hand, appear to become more negative as the aliphatic chain length increases. This behavior is expected if hydrocarbon association is regarded as a partial reversal of hydrophobic hydration. The hydrophobic hydration process is characterized by an increase in the solute partial molar heat capacity. This increase, due to the formation of a more thermally labile water structure around the hydrocarbon, is found to be proportional to the number of -CH<sub>2</sub> groups in the chain.<sup>(9,12)</sup> Because of the large uncertainties in  $\Delta C_p$ , a quantitative determination of the dependence of  $\Delta C_{\rm p}$  on the number of -CH<sub>2</sub> groups cannot be made. In any event, it is clear that, in these systems, heat capacity effects are very important in causing the  $\Delta H$  of dimerization to become negative near room temperature. This, of course, is relevant because an endothermic  $\Delta H$  of interaction is often regarded as one of the thermodynamic parameters which characterizes hydrophobic association.

#### 3.2. Fluorobenzene/Benzyl Alcohol

The behavior of the fluorobenzene/BZOH system is very different from that of benzene-BZOH. In the fluorobenzene system, the presence of strong dipole-dipole interactions seems to cause the formation of larger associated species which complicate the determination of the thermodynamic parameters characteristic of dimer formation. As Table II shows, the dimerization constant for fluorobenzene-BZOH at 25 °C is similar in magnitude to those observed for benzene-BZOH and benzene-PEOH. The temperature dependence of  $K_{11}$ , however, is markedly different. The calculated dimerization constants can, in fact, be fitted with an RMSD of 0.017 M<sup>-1</sup> in  $K_{11}$  to an equation of the form

$$K_{11} = K_{11} (298) \exp[-\Delta H (1/T - 1/298.15)/R]$$
(6)

where  $K_{11}(298)$  is the dimerization constant at 298 K and  $\Delta H$  is the enthalpy of dimerization. The results are

$$K_{11}(298) = 0.555 \pm 0.010 \text{ L-mol}^{-1}$$
  
 $\Delta H = 2.56 \pm 0.25 \text{ kcal-mol}^{-1} = 10.71 \pm 1.04 \text{ kJ-mol}^{-1}$ 

Equation 6 implies that  $\Delta H$  is a constant within the temperature range studied. This behavior is in sharp contrast with that of the benzene systems, for which large and negative heat capacity changes were calculated in the same temperature range. The model we have chosen, because it gives an excellent fit of all the data, assumes that the only higher-order species formed is a trimer composed of two fluorobenzene molecules and one BZOH molecule. It is likely, however, that other larger aggregates also contribute to the observed vapor pressure effects. The values of  $K_{21}$  shown in Table II appear to indicate that the formation of larger species is highly endothermic. We hope to be able to document these important differences between the benzene and fluorobenzene systems in future work. Studies of the benzene and fluorobenzene interactions with phenylacetic acid have already been made and will be described in a subsequent paper in this series. Studies of the fluorobenzene-phenol and fluorobenzene-PEOH systems are also planned. At the conclusion of these investigations, a better understanding of the factors controlling hydrophobic association should emerge.

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