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Entropy of Transfer of Molecular Benzoic Acid from a Pure Liquid to an Aqueous Solution

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Abstract □ The solubility of benzoic acid in distilled, deionized water was determined over a limited temperature range. The entropy of transfer of molecular benzoic acid from a pure liquid to an aqueous solution was calculated. Data also were analyzed in terms of the hypothetical partial molal entropy of transfer of molecular benzoic acid from an ideal or a regular solution to an aqueous solution. Interpretation of the data indicates that solute-solvent interactions result in a reduction of the number of independent molecules relative to an ideal or a regular solution.

Keyphrases □ Benzoic acid—transfer entropy from pure liquid to aqueous solution, calculation of partial molal entropy □ Solutes, semipolar nonelectrolyte (benzoic acid)—transfer entropy from pure liquid to aqueous solution, equations □ Entropy of transfer from pure liquid to aqueous solution—benzoic acid, calculation of partial molal entropy

Molecular interactions involving solute (nonelectrolyte)–solvent (water) components have attracted considerable research interest (1–10). Solute substances nearly insoluble in water have provided several hypotheses about the structure of water and interactions occurring in this condensed liquid phase (1–4). To date, no one hypothesis has gained universal acceptance (8, 11–13).

Bulk properties of water, such as surface tension and the dielectric constant, have been useful for interpreting solution behavior (14, 15). The importance of the entropy of solution as an interpretive quantity also has been discussed (16, 17).

This study was undertaken to investigate the behavior of a semipolar nonelectrolyte solute, benzoic acid, in aqueous systems. Chertkoff and Martin (18) mentioned that benzoic acid serves as a prototype of relatively polar pharmaceutical solids. Solubility data at several temperatures were analyzed in terms of the entropy consequence of transferring molecular benzoic acid from a pure liquid to an aqueous solution. Equations were used which allow the calculation of the partial molal entropy of transfer from an ideal or a regular solution to an aqueous solution.

THEORETICAL

The partial molal entropy of solution, ΔS_2, developed by Hilde-

brand (19) has proved useful for interpreting solute-solvent interactions (20, 21). The $\Delta \bar{S}_2$ represents the entropy change of a solid forming a solution in a liquid, $(\bar{S}_2 - S_2{}^s)$, and may be written as:

$$R[(\partial \ln X_2/\partial \ln T)(\partial \ln a_2/\partial \ln X_2)] = \Delta \bar{S}_2 = (\bar{S}_2 - S_2{}^s) \quad \text{(Eq. 1)}$$

where X_2 is the mole fraction solubility of the solute, T is the temperature (Kelvin), a_2 is the activity of the solute, and the superscript s refers to the solid state of the solute. At constant temperature and pressure:

$$\Delta \bar{S}_2 = (\bar{S}_2 - S_2{}^\circ)_{P,T} + (S_2{}^\circ - S_2{}^s)_{P,T} \quad \text{(Eq. 2)}$$

and the superscript $\circ$ refers to the pure liquid solute. This equation may be rearranged to:

$$(\bar{S}_2 - S_2{}^\circ)_{P,T} = \Delta \bar{S}_2 - (S_2{}^\circ - S_2{}^s)_{P,T} \quad \text{(Eq. 3)}$$

where $(\bar{S}_2 - S_2{}^\circ)$ represents the partial molal entropy of transfer from the pure liquid to a solution.

The partial molal entropy of transfer from a pure liquid to a solution $(\bar{S}_2 - S_2{}^\circ)$, according to ideal or regular solution theory is equal to $(-R \ln X_2)$ (22), indicating molecular randomness. For systems that do not obey ideal solution behavior:

$$(\bar{S}_2 - S_2{}^\circ)_{P,T} - (\bar{S}_2{}' - S_2{}^\circ)_{P,T} = (\bar{S}_2 - \bar{S}_2{}')_{P,T} \quad \text{(Eq. 4)}$$

and $(\bar{S}_2 - \bar{S}_2{}')$ may be regarded as the partial molal entropy of transfer from an ideal solution to one that does not exhibit ideal solution behavior. By definition:

$$(\bar{S}_2{}' - S_2{}^\circ)_{P,T} = (-R \ln X_2)_{P,T} \quad \text{(Eq. 5)}$$

and Eq. 4 may be rewritten as:

$$(\bar{S}_2 - S_2{}^\circ)_{P,T} - (-R \ln X_2)_{P,T} = (\bar{S}_2 - \bar{S}_2{}')_{P,T} \quad \text{(Eq. 6)}$$

EXPERIMENTAL

Reagents—Benzoic acid[1] USP was recrystallized from chloroform.

Procedure—The solubility of benzoic acid in distilled, deionized water was determined using a previously published method (23). Temperatures were maintained within $\pm 0.05°$ throughout the equilibration period. Prior to analysis, all solutions were filtered using a filter holder[2] and filters[3] with a pore size of 0.22 μm. Benzoic acid concentrations were determined by spectrophotometric assay[4] at 227 nm and/or the USP method of assay for benzoic acid (24). Comparable assay results were observed with either method.

RESULTS

Calculation of Concentration of Molecular Benzoic Acid—The total molar concentration of dissolved benzoic acid $[C]$ is equal to the sum of the unionized $[U]$ and ionized $[I]$ species:

$$[C] = [U] + [I] \quad \text{(Eq. 7)}$$

According to the equilibrium expression for the dissociation of a weak acid:

$$Ka = [I]^2/[U] \quad \text{(Eq. 8)}$$

where Ka is 6.31×10^{-5} (25). When $[I]$ is small in comparison to

[1] Lot RK556, Ruger Chemical Co.
[2] Swinny, Millipore Corp., Bedford, Mass.
[3] Millipore filter, Catalog No. GSWP 013 00.
[4] Perkin-Elmer 124 spectrophotometer.

Table I—Mole Fraction Solubility of Molecular Benzoic Acid in Distilled, Deionized Water

Temperature (Kelvin)	$X_2, \times 10^4$
293.3°	3.97
298.2°	4.73
303.2°	5.62
308.2°	6.71
313.2°	7.92
318.2°	9.57

$[C]$, then:

$$[I]^2 \cong Ka \times [C] \quad \text{(Eq. 9)}$$

$$[I] \cong (Ka \times [C])^{1/2} \quad \text{(Eq. 10)}$$

and:

$$[U] = [C] - (Ka \times [C])^{1/2} \quad \text{(Eq. 11)}$$

where $[U]$ is the molar concentration of dissolved molecular benzoic acid.

Calculation of ΔS_2—Mole fraction solubilities for molecular benzoic acid at several temperatures are presented in Table I. The entropy of solution, $\Delta \bar{S}_2$, was calculated from the slope of the solubility curve, $\ln X_2$ versus $\ln T$, according to the relationship:

$$\Delta \bar{S}_2 = R(d \ln X_2/d \ln T)_{\text{sat}, P} \quad \text{(Eq. 12)}$$

The correlation coefficient for this linear relationship is 1.00, and $\Delta \bar{S}_2$ is 21.2 eu (sat = saturated).

The limited solubility of molecular benzoic acid placed the solution within the range of dilute solution behavior such that it could be assumed that the Henry's law factor $(\partial \ln a_2/\partial \ln X_2)$ approaches unity. The limited temperature range over which the solubilities were determined allows the assumption that $(d \ln X_2/d \ln T)$ is independent of temperature.

Calculation of $(S_2{}^\circ - S_2{}^s)_{P,T}$—The quantity $(S_2{}^\circ - S_2{}^s)$ may be approximated by the relationship given by Hildebrand and Scott (26):

$$(S_2{}^\circ - S_2{}^s)_{P,T} \cong \Delta S_m{}^F - \Delta C_p \times \ln (T_m/T) \quad \text{(Eq. 13)}$$

where $\Delta S_m{}^F$ is the entropy of fusion at the melting point, $\Delta C_p = (C_p{}^1 - C_p{}^s)$ where $C_p{}^1$ and $C_p{}^s$ are the molal heat capacities of the liquid and solid forms, respectively, T_m is the melting point, and T is the temperature at which the process takes place. The values for $\Delta S_m{}^F$, ΔC_p, and T_m were taken from previously published data (27).

Calculation of $(\bar{S}_2 - S_2{}^\circ)_{P,T}$—The relationship among $\Delta \bar{S}_2$, $(\bar{S}_2 - S_2{}^\circ)_{P,T}$, and $(-R \ln X_2)_{P,T}$ was discussed previously (16, 28). For a series of regular solutions, a plot of $\Delta \bar{S}_2$ versus $(-R \ln X_2)_{P,T}$ yields a linear relationship with a y intercept of $(S_2{}^\circ - S_2{}^s)_{P,T}$.

Actually, it is found that the y intercept is greater than $(S_2{}^\circ - S_2{}^s)_{P,T}$ when the data are plotted in this manner. The discrepancy results because $\Delta \bar{S}_2$ also includes the value $(-R \ln a_2)_{P,T}$, where a_2 is the activity of the pure solute. Therefore, Eq. 2 must be modified to include the quantity $(-R \ln a_2)$ and:

$$\Delta \bar{S}_2 = (\bar{S}_2 - S_2{}^\circ)_{P,T} + (S_2{}^\circ - S_2{}^s)_{P,T} + (-R \ln a_2)_{P,T} \quad \text{(Eq. 14)}$$

and:

$$(\bar{S}_2 - S_2{}^\circ)_{P,T} = \Delta \bar{S}_2 - (S_2{}^\circ - S_2{}^s)_{P,T} - (-R \ln a_2)_{P,T} \quad \text{(Eq. 15)}$$

Finally:

$$(\bar{S}_2 - S_2{}^\circ) = 21.2 \text{ eu} - (S_2{}^\circ - S_2{}^s)_{P,T} - (-R \ln a_2)_{P,T} \quad \text{(Eq. 16)}$$

The data for the various thermodynamic functions are summarized in Table II.

Table II—Summary of Thermodynamic Data for Molecular Benzoic Acid Dissolved in Distilled, Deionized Water

Temper-ature (Kelvin)	$(-R \ln a_2)^a$, eu	$(-R \ln X_2)$, eu	$(S_2^\circ - S_2^s)$, eu	$(\bar{S}_2 - S_2^\circ)$, eu	$(\bar{S}_2 - \bar{S}_2^i)$, eu
293.2°	3.25	15.6	6.74	11.2	−4.40
298.2°	3.07	15.2	6.97	11.2	−4.00
303.2°	2.89	14.9	7.20	11.1	−3.80
308.2°	2.72	14.5	7.42	11.1	−3.40
313.2°	2.54	14.2	7.64	11.0	−3.20
318.2°	2.37	13.8	7.86	11.0	−2.80

^{a} J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott, "Regular and Related Solutions," Van Nostrand Reinhold, New York, N.Y., 1970, p. 22, Eq. 2.51 ($R \ln a_2 \simeq \Delta S_m{}^F \ln T/T_m$).

DISCUSSION

When a semipolar nonelectrolyte containing both an apolar substituent and a polar group that is capable of hydrogen bonding is introduced into an aqueous environment, two types of interaction might occur: (a) the polar substituent may interact with the water molecules by hydrogen bond formation, and (b) an interaction as a result of van der Waals' forces between water and the apolar portion of the solute may take place.

The data in Table II are somewhat uncertain in view of the approximate relationships used to calculate $(-R \ln a_2)$ and $(S_2^\circ - S_2^s)$. However, over the temperature range studied, all values for $(\bar{S}_2 - \bar{S}_2^i)$ are negative for molecular benzoic acid dissolved in distilled, deionized water. These thermodynamic data suggest that the experimental solution does not conform to a structure of maximum disorder or randomness, i.e., an ideal or a regular solution.

Interpretation of the negative entropies of transfer from an ideal solution to an aqueous solution is a matter of controversy. Feldman and Gibaldi (6) discussed the thermodynamics of aqueous solutions of benzoic acid in keeping with the view of Nemethy and Scheraga (2-4). Nemethy and Scheraga (2-4) considered the negative entropy a consequence of increased water structure due to the introduction of a nonpolar molecule into the aqueous environment, a condition not thermodynamically favored. Related to this unfavorable state is the partial reversal of the solution process which is manifested by an association of the nonpolar side chains, the association being termed the hydrophobic bond. The low water solubility of hydrocarbons is said to be a consequence of this entropic relationship. Nemethy and Scheraga (2-4) also considered the influence of the polar side chains of proteins (4). It was their view that the nonpolar portion of a molecule carrying a polar group can still exert about the same influence on the energy states of water as in nonpolar solutes. They further pointed out that the exact local structure of water in the neighborhood of the polar group may differ from that found in solutions where the solute does not contain a polar portion.

In this connection, it is important to compare the aqueous solubilities of benzene and benzoic acid in order to discuss the role of the carboxyl group in the solution process. The mole fraction solubility of benzene in water (29) is reproduced in Table III, and certain comparisons are of interest.

1. The mole fraction solubilities of benzene and benzoic acid are 3.99×10^{-4} (299.2°K) and 4.73×10^{-4} (298.2°K), respectively. Therefore, at temperatures near 25°, the aqueous solubility of benzoic acid is only about 1.2 times greater than benzene. Since solubility expresses a summary of all solute–solvent interactions, it appears that the carboxyl group is not particularly influential at this temperature.

The lack of difference between the mole fraction[5] solubilities of benzene and benzoic acid is surprising based on their differing physicochemical properties: physical state at room temperature and standard pressure, molar volume, electronic characteristics, and relative polarity. Part of the answer relating to the magni-

Table III—Mole Fraction Solubility of Benzene in Water^a

Temperature (Kelvin)	X_2, $\times 10^4$
290.2°	3.95
295.2°	3.97
299.2°	3.99
302.2°	4.02
305.2°	4.12
308.2°	4.20
315.2°	4.40
317.2°	4.45
319.2°	4.57

^{a} Results from Ref. 29.

tude of aromatic hydrocarbon–water interactions concerns the uniqueness of water as a solvent, a topic summarized by other authors (10). Consideration must also be given to the strength of the solute–solute interaction and its relationship to solubility. The physical state of a molecule is an indication of intermolecular bonding. Benzene is a liquid and benzoic acid is a solid. Therefore, the presumed advantage of the carboxyl group in increasing the aqueous solubility of benzoic acid over benzene may be somewhat balanced by the propensity of benzoic acid molecules to attract each other rather than to interact with water. This argument is partly intuitive since the partial molal free energy of transfer from solid to solution contains two components: (a) the transfer from solid to liquid, and (b) the transfer from liquid to solution. On the other hand, a liquid needs only to be transferred from the liquid state to solution.

Limitations to the interpretation of solubility data for two compounds in water were outlined by Hildebrand and Scott (30). In particular, it is difficult to compare a solid and a liquid solute because the solubility of the latter relates to the vapor pressure at any given temperature[6, 7]. Furthermore, steric implications have not been considered which may influence solubility interpretation.

2. As temperature increases, the mole fraction solubility of benzoic acid in water increases more rapidly than benzene. At 318°K, benzoic acid solubility is approximately two times greater than that of benzene. Evidently, the effect of temperature on the water molecule and solute favors increased interactions between water and the polar carboxyl group of benzoic acid. Regardless of the model proposed for water structure, hydrogen bonding between water molecules diminishes as temperature is increased, making water molecules available for increased hydrogen bonding with the carboxyl group.

The views of Nemethy and Scheraga (2-4) are not shared by Hildebrand (12) who criticized the term hydrophobic bond. Hildebrand's criticism centers about the idea that hydrocarbons prefer a nonpolar environment rather than be surrounded by water. He contended that: "molecules of water prefer to be hydrogen bonded together rather than separate to admit alkanes." Hildebrand (11) also questioned the iceberg concept of water, based on the relative diffusivities of methane in water and carbon tetrachloride. At 25°, methane diffuses 0.6 times as fast in water as it does in carbon tetrachloride. Diffusivity is mainly dependent upon temperature, viscosity of the solvent, and molecular cross section of the diffusant. Since the viscosities of water and carbon tetrachloride are nearly identical, it is suggested that the molecules of methane are only retarded by the hydrogen bonds in water and not by an ice-like structure. According to Hildebrand's argument, the low water solubility of molecular benzoic acid is due in large part to the difference in internal pressures between

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[5] Interpretation of solubility data depends on the concentration unit utilized. For example, the aqueous solubilities of benzene and benzoic acid are different if the data are expressed as grams per milliliter. The mole fraction unit is preferred for theoretical discussions, however, because the molecular ratios of solute and solvent are immediately evident.

[6] This limitation also relates to interpretation of solubility data using thermodynamic parameters. For example, a plot of ln X_2 versus ln T for the benzene data implies the choice of the pure liquid hydrocarbon as the standard state (29). This standard state may be criticized from two standpoints: (a) liquid aromatic hydrocarbons are said to have some structure of their own (29); and (b) Franks et al. (29) showed that this choice of standard state for benzene masks certain solution characteristics, such as heat capacity change, as compared with a different standard state.

[7] A comment made by the reviewer is important to a discussion of solubility and vapor pressure. The vapor pressure of benzoic acid is expected to be much lower than that of benzene at 298°K. Hence, if solubilities were compared at equal vapor pressures, the benzoic acid solubility would be much higher than that of benzene.

the solute and solvent. He noted (12) that: "Ice is wet by octane. The fact that octane is nearly insoluble in water is merely the result of the fact that this attraction is not strong enough to penetrate the high cohesion of water."

Application of regular solution theory to the molecular benzoic acid solution provides an alternative method of data interpretation. The thermodynamic consequences of the regular solution postulate (22) are as follows:

$$(\overline{F}_2 - \overline{F}_2{}') = RT \ln (a_2/X_2) = (\overline{H}_2 - \overline{H}_2{}') - T(\overline{S}_2 - \overline{S}_2{}')$$
(Eq. 17)

$$(\overline{S}_2 - \overline{S}_2{}') = 0 \qquad\qquad\text{(Eq. 18)}$$

and:

$$(\overline{F}_2 - \overline{F}_2{}') = RT \ln (a_2/X_2) = (\overline{H}_2 - \overline{H}_2{}') \quad \text{(Eq. 19)}$$

Thus, a regular solution has a positive "excess" free energy and enthalpy and the excess free energy is essentially temperature independent. The excess free energy is a function of composition[8]. Although the data in Table II indicate positive excess free energies at all temperatures (i.e., a_2 is greater than X_2), the excess entropies are less than what would be expected for a regular solution. Regular solutions of iodine are violet and those in which a specific solute–solvent interaction has occurred are brown. In the latter solutions, there is also evidence of negative excess entropies (16, 17). For solutions of molecular benzoic acid in water, an analogy would suggest that a specific interaction has occurred between the solute and solvent. The temperature effect on the excess entropies is also of interest to this suggestion. At higher temperatures, the excess entropies diminish.

The suggestion of a specific interaction does not absolutely require that the interaction of molecular benzoic acid and water is of a magnitude such that a_2 is less than X_2. Furthermore, it is even possible that the interaction is equal to or less than that of a geometric mean. Shinoda and Hildebrand (31) reported data showing that iodine forms a weak complex with 1,1-dichloroethane and 1,2-dichloroethane. Data are also reported which show that the solute–solvent interactions are less than that of a geometric mean, while at the same time the entropies are nearly regular for solutions of iodine and 1,2-dichloroethane and are slightly negative for solutions of iodine and 1,1-dichloroethane. An explanation for this situation concerns the polarity of the solvents. It is reasoned that the high polarity contributes to an increase in the energies of vaporization of the solvent without a corresponding increase in solvent power for the solute. This argument may be applied to the case at hand. Among the unusual properties of water are its high polarity, relatively large energy of vaporization, and degree of hydrogen bonding. These factors would diminish solute–solvent interactions, as evidenced by the small solubilities of molecular benzoic acid in water, and at the same time permit zero or even negative entropies to be evidenced.

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