Solution Calorimetry Studies of Hydrogen Bonding in Aliphatic Alcohols

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Introduction

Alcohols in the pure state exist in a high degree of association (polymerized). This association results from hydrogen bonding at the hydroxyl site. If alcohols are placed in a nonhydrogen bonding solvent, such as heptane, the extent of alcohol association is concentration dependent. At low concentrations the alcohol will exist as unassociated (single) molecules, whereas at high concentration the molecules of alcohol will be associated. At intermediate concentrations, an equilibrium between single and associated molecules will exist (2,4).

If a pure alcohol is dissolved in a nonhydrogen bonding (inert) solvent such that the concentration of the resulting solution is low, the alcohol will be converted from the associated hydrogen bonded form to the unassociated nonhydrogen bonded form. The major contribution to the heat of this dissolving process, the enthalpy of solution, will then be the energy to break the hydrogen bonds for the associated alcohol. Studies reported in the literature indicate tha the enthalpies of solvation are minor in inert solvents (1). Since the dissolving process is primarily a hydrogen bond breaking process, the enthalpy of solution will be endothermic and will reflect the strength of the hydrogen bond between the alcohol molecules.

Experimental

Measurements of heats of solution were made in a Parr 1451 solution calorimeter by mixing neat alcohol with 100 mL of heptane solvent and recording the temperature change with a recorder thermistor system. The amount of alcohol used in each of the heat of solution experiments was chosen such that the concentration of the resulting alcohol-heptane solution was in the concentration range where unassociated (single) molecules exist. This concentration range for each alcohol was determined from concentration-dependent nmr data (2,4). Rapid exchange in the equilibrium between unassociated and associated alcohol molecules causes only one hydroxyl proton nmr line to be observed. The chemical shift of the hydroxyl nmr line is alcohol-concentration dependent. A plot of chemical shift versus concentration yields a sigmoid curve. The concentration range over which the alcohol exists as unassociated molecules was assumed to be that portion of the sigmoid curve parallel to the concentration axis at the low concentration limit.

Temperature measurements are the major source of uncertainty in the heat of solution values. In order for the resulting heptane-alcohol solution to be in the concentration range where unassociated alcohol molecules predominate, a small amount of alcohol (0.4 to 0.07 g) is mixed with the heptane, resulting in a small temperature change. All determinations were carried out at a 0.5 °C (50 mv range) full-scale expansion on the recorder. At a 0.5 °C recorder scale-expansion, one millimeter on the recorder paper which is near the lower limit of measurement is equal to 0.002 °C. Calculation of $\triangle T$ from a temperature versus time curve by a standard Parr method (3) generated two significant digits.

The heat capacity of the calorimeter was determined by heat transfer from hot copper metal to the calorimeter. Hot copper metal was dropped into the calorimeter loaded with a 100-mL sample of heptane.

$$q_{copper} = - q_{calorimeter}$$

By knowing the specific heat of the copper, mass of the copper, initial and final temperatures of the copper, and initial and final temperatures of the calorimeter, one can calculate the heat capacity of the calorimeter.

$$q_{copper} = mass_{Cu} \, C_{Cu} \, (T_f \, (Cu) - T_i \, (Cu))$$

$$q_{calorimeter} = {}^C calorimeter \, (T_f \, (Cal) - T_i \, (Cal))$$

$$C_{calorimeter} = \frac{- \, mass_{Cu} \, C_{Cu} \, (T_f \, (Cu) - T_i \, (Cu))}{(T_f \, (Cal) - T_i \, (Cal))}$$

Table I summarizes the calibration data and calculations. Using C_{Cu} as 0.09305 cal/g deg (5), the average value for the heat capacity of the calorimeter was determined to be 67.6 cal/deg.

TABLE I. (Calorimeter Calibration)

Trial	mass of	$T_{i(Cu)}$	$T_f(Cu), T_f(Cal)$	$T_i(Cal)$	$C_{calorimeter}$
1	9.9944 g	74.89 °C	22.25 °C	21.52 °C	67.25 $\frac{cal}{deg}$
2	9.9948 g	74.89 °C	22.16 °C	22.45 °C	67.98 $\frac{cal}{deg}$

Results and Discussion

The strength of a hydrogen bond depends on the polarity of the molecules at the hydrogen-bonding site, on electrostatic effects, and on the ability of the molecules to approach each other (steric effects). In the series of alcohols chosen for this study (Table II), the polarity at the hydrogen-bonding site is nearly constant. The general form of

TABLE II (Alcohol Series)

Alcohol	R′	R′′	R′′′
Benzyl alcohol	phenyl	hydrogen	hydrogen
4-methyl-2-pentanol	isobutyl	methyl	hydrogen
2-methyl-3-pentanol	isopropyl	ethyl	hydrogen
t-butyl alcohol	methyl	methyl	methyl
t-amyl alcohol	ethyl	methyl	methyl
2,4-dimethyl-3-pentanol	isopropyl	isopropyl	hydrogen
4-heptanol	n-propyl	n-propyl	hydrogen
3-methyl-3-pentanol	ethyl	ethyl	methyl
3-ethyl-3-pentanol	ethyl	ethyl	ethyl

the alcohol series is given by the formula in Figure 1. The variation of R′, R′′, and R′′′ for the series is listed in Table II.

Steric effects at the hydroxyl site clearly determine the strength of the molecular association in this series of compounds (2). As the size of the hydroxyl neighboring groups increases, the ability of the molecules to approach each other will decrease, and the strength

FIGURE 1. (general formula)

$$R' - \underset{\underset{H}{\overset{\overset{R''}{\mid}}{O}}}{\overset{\mid}{C}} - R'''$$
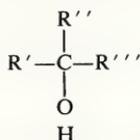
of the hydrogen bond will decrease. This decrease in hydrogen-bond strength with increase in steric hindrance at the hydroxyl site will result in a decrease in the heat of solution.

The alcohols are arranged into two groups for discussion, tertiary and secondary-primary. As expected, the heats of solution for the tertiary alcohols are generally lower (6.5 to 5.1 Kcal/mole) than those of the secondary-primary group (7.1 to 5.9 Kcal/mole). Tables III and IV summarize results of measurements of heats of solution for these groups. The alcohols are arranged in each table from high to low heats of solution.

The four tertiary alcohols listed in Table III have neighboring groups that vary from

TABLE III. (Enthalpies of Solution of Tertiary Alcohols)

Alcohol	Moles of alcohol per 100 mL of heptane	$\triangle T$	$\triangle H$*
t-butyl alcohol	.000928	− .089	6.5
t-amyl alcohol	.000849	− .080	6.4
3-methyl-3-pentanol	.00200	− .17	5.7
3-ethyl-3-pentanol	.00264	− .20	5.1

* heat of solution in Kcal/mole of alcohol

methyl, methyl, and methyl to ethyl, ethyl, and ethyl. The enthalpies of solution vary systematically with expected steric hindrance for this series of alcohols. It should be noted, however, that t-amyl and t-butyl alcohols have nearly the same heats of solution indicating that they have similar steric hindrance at the hydroxyl site (2,4).

The first member of the group in Table IV (highest heat of solution, strongest

Table IV. (Enthaplies of Solution of Primary and Secondary Alcohols)

Alcohol	Moles of Alcohol per 100 mL of heptane	$\triangle T$	$\triangle H$*
Benzyl alcohol	.00142	− .15	7.1
4-methyl-2-pentanol	.00297	− .30	6.8
2-methyl-3-pentanol	.00154	− .15	6.6
2,4-dimethyl-3-pentanol	.00348	− .32	6.2
4-heptanol	.00346	− .30	5.9

* heat of solution in Kcal/mole of alcohol

hydrogen bond, and lowest steric hindrance at the hydroxyl site) is a primary alcohol with neighboring groups of phenyl, hydrogen, and hydrogen. The large phenyl group is compensated for by the two very small hydrogen atoms. The remaining members of this group are secondary alcohols with neighboring groups varying from methyl, isobutyl, and hydrogen to two n-propyl groups and a hydrogen atom. The order seems to be what is expected except possibly for 4-heptanol and 2,4-dimethyl-3-pentanol. One might expect neighboring isopropyl groups to hinder sterically the hydroxyl site more thatn the n-propyl groups because of branching next to the hydroxyl site. This does not, however, agree

with the calorimetry results or some unpublished nmr hydrogen-bonding studies (4). One might argue that the longer n-propyl group hinders the hydroxyl site more than the branched isopropyl group because of its ability to reach the hydrogen-bonding site.

This study clearly shows that the heat of solution of a alcohol in a nonhydrogen-bonding solvent reflects the nature of the steric hindrance by neighboring groups at the hydroxyl site.

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