

Solubility of 2-Hydroxybenzoic Acid in Select Organic Solvents at 298.15 K

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Experimental solubilities are reported for 2-hydroxybenzoic acid dissolved in 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol, 1-pentanol, 1-octanol, dibutyl ether, 1,4-dioxane, tetrahydrofuran, ethyl acetate, butyl acetate, 2-propanone, 2-butanone, and cyclohexanone at 298.15 K. Results of these measurements reveal that the observed solubilities in the eight alcohol solvents fall within a fairly narrow mole fraction range of each other. 2-Hydroxybenzoic acid is more soluble in both 1,4-dioxane and tetrahydrofuran than in any of the other alcohol, ester, or ketone solvents studied.

Introduction

Partition coefficients describing the distribution of a solute between two completely immiscible and/or partly miscible gas/liquid and liquid/liquid phases are often needed in chemical engineering computations involving chromatographic separations and selection of suitable organic solvents for extracting organic compounds from aqueous solutions. For many organic solutes, experimentally determined 1-octanol/water partition coefficients are readily available in the published chemical, pharmaceutical, and engineering literature. Measured partition coefficient data for other immiscible liquid/liquid systems are more scarce. To address this need, researchers have developed predictive methods for generating desired quantities.

Of the predictive expressions that have been suggested in recent years, linear solvation energy relationships (LSERs) offer perhaps the most general method in that the derived correlations enable not only estimation of partition coefficients but also estimation of other physicochemical and biochemical properties as well. Proposed LSERs have taken several different mathematical forms, depending upon whether one wishes to predict gas/organic solvent partition coefficients (as $\log L$) (Abraham et al., 1990)

$$\log L = c + rR_2 + s\pi_2^H + a\sum\alpha_2^H + b\sum\beta_2^H + l\log L^{16} \quad (1)$$

$$\log L = c + d\delta_2 + s\pi_2^H + a\sum\alpha_2^H + b\sum\beta_2^H + l\log L^{16} \quad (2)$$

$$\log L = c + rR_2 + q\mu_2^2 + a\sum\alpha_2^H + b\sum\beta_2^H + l\log L^{16} \quad (3)$$

or water/organic solvent partition coefficients (as $\log P$) (Abraham et al., 1990; Meyer and Maurer, 1993 and 1995)

$$\log P = c + rR_2 + s\pi_2^H + a\sum\alpha_2^H + b\sum\beta_2^H + vV_x \quad (4)$$

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$$\log P = c + d\delta_2 + s\pi_2 + a\alpha_2 + b\beta_2 + vV_x \quad (5)$$

where R_2 and V_x refer to the excess molar refraction and the McGowan volume of the solute, respectively, π_2^H (and π_2) is the solute dipolarity/polarizability descriptor, and $\sum\alpha_2^H$ (and α_2) and $\sum\beta_2^H$ (and β_2) are measures of the solute's hydrogen-bond acidity and hydrogen-bond basicity, respectively. δ_2 is a polarizability parameter which was preset by Kamlet et al. (1988) to 0.0 in the case of nonpolychlorinated aliphatic solutes, to 0.5 for polychlorinated aliphatic solutes, and to 1.0 for aromatic solutes. Numerical values of the solute descriptors are available in several published tabulations for 500+ common organic molecules and inorganic gas solutes (Abraham 1993a,b; Kamlet et al., 1988; Meyer and Maurer, 1995). For any given solvent, numerical values of the various curve-fit coefficients (c , r , s , a , b , d , l , q , and v) are deduced by regressing experimental partition coefficient data in accordance with eqs 1–5. At the present time coefficients are available for only 50 or so different water/organic solvent and gas/solvent systems (Meyer and Maurer, 1993 and 1995; Abraham et al., 1998).

We, in collaboration with the Abraham research group, are in the process of developing correlational equations for additional solvent systems and new methodologies for calculating solute descriptors. 1-Propanol was the first solvent for which we (Abraham et al., 1999) reported LSER solvent coefficients. It should be noted that 1-propanol is completely miscible with water at 298.15 K, and the $\log P$ and $\log L$ values used in developing the correlation equations were deduced from measured infinite dilution activity and solubility data for solutes dissolved in neat 1-propanol.

Continued development of LSERs for describing the partitioning behavior of solutes requires that a large database be available for each of the different systems that is to be studied. For this reason, 2-hydroxybenzoic acid solubilities were measured in 16 organic solvents. Results of these measurements, combined with our previously published solubility data for polycyclic aromatic hydrocarbon solutes, will be used in subsequent studies to develop gas/liquid partition and water/organic solvent partition correlations based upon eqs 1–5.

Experimental Methods

2-Hydroxybenzoic acid (Aldrich 99+%, ACS Reagent Grade) was dried in an oven for several hours at 80 °C and

Table 1. Experimental Mole Fraction Solubilities x_A^{sat} of 2-Hydroxybenzoic Acid, 4-Hydroxybenzoic Acid, and Benzoic Acid in Select Organic Solvents at 298.15 K

solvent	mole fraction solubility		
	2-HOC ₆ H ₄ COOH	4-HOC ₆ H ₄ COOH	C ₆ H ₅ COOH
1-propanol	0.1636	0.1084 ^a	0.1791 ^b 0.1743 ^c
2-propanol	0.1789	0.1297 ^a	0.1937 ^b
1-butanol	0.1646	0.1154 ^a	0.2016 ^b
2-butanol	0.1869	0.0901 ^a	0.1524 ^b
2-methyl-1-propanol	0.1430		
2-methyl-2-propanol	0.2193		
1-pentanol	0.1611	0.1145 ^a	0.1832 ^b
1-octanol	0.2143	0.1032 ^a	0.1987 ^b
dibutyl ether	0.09185		
1,4-dioxane	0.2945		0.2853 ^b
tetrahydrofuran	0.3642		0.3348 ^c
ethyl acetate	0.1425		0.1649 ^b 0.1637 ^c
butyl acetate	0.1363		0.1699 ^b
2-propanone	0.1817		
2-butanone	0.1852		
cyclohexanone	0.2301		

^a Experimental data taken from Martin et al. (1984). ^b Experimental data taken from Beerbower et al. (1984). ^c Experimental data taken from Lin and Nash (1993).

used without further purification. The purity of 2-hydroxybenzoic acid was 99.86 ± 0.12 mass %, as determined by five volumetric titrations using a freshly standardized sodium hydroxide titrant and a phenolphthalein indicator. 1-Propanol (Aldrich, 99+%, anhydrous), 2-propanol (Aldrich, 99+%, anhydrous), 1-butanol (Aldrich, HPLC, 99.8+%), 2-butanol (Aldrich, 99+%, anhydrous), 2-methyl-1-propanol (Aldrich, 99.5%, anhydrous), 2-methyl-2-propanol (Arco Chemical Company, 99+%), 1-pentanol (Aldrich, 99+%), 1-octanol (Aldrich, 99+%, anhydrous), dibutyl ether (Aldrich, 99%), 1,4-dioxane (Aldrich, 99.8%, anhydrous), tetrahydrofuran (Aldrich, 99.9%, anhydrous), ethyl acetate (Aldrich, HPLC, 99.9%), butyl acetate (Aldrich HPLC, 99.7%), 2-propanone (Aldrich HPLC, 99.9+%), 2-butanone (Aldrich HPLC, 99.5+%), and cyclohexanone (Aldrich, 99.8%) were stored over molecular sieves before use. Gas chromatographic analysis showed solvent purities to be 99.7 mol % percent or better.

Excess solute and solvent were placed in amber glass bottles and allowed to equilibrate in a constant-temperature water bath at 25.0 ± 0.1 °C for at least 3 days (often longer). Attainment of equilibrium was verified both by repetitive measurements after several additional days and by approaching equilibrium from supersaturation by pre-equilibrating the solutions at a higher temperature. Aliquots of saturated 2-hydroxybenzoic acid solutions were transferred through a coarse filter into a tared volumetric flask to determine the amount of sample and diluted quantitatively with methanol for spectrophotometric analysis at 304 nm on a Bausch and Lomb Spectronic 2000. Concentrations of the dilute solutions were determined from a Beer–Lambert law absorbance versus concentration working curve for nine standard solutions. The concentration of 2-hydroxybenzoic acid in the standard solutions varied from 8.83×10^{-5} M to 4.42×10^{-4} M. The calculated molar absorptivity of $\epsilon \approx 3985$ L mol⁻¹ cm⁻¹ was constant over this concentration range.

Experimental molar concentrations were converted to (mass/mass) solubility fractions by multiplying by the molar mass of 2-hydroxybenzoic acid, the volume(s) of the volumetric flask(s) used, and any dilutions required to place the measured absorbances on the Beer–Lambert law absorbance versus concentration working curve and then dividing by the mass of the saturated solution analyzed.

Mole fraction solubilities were computed from (mass/mass) solubility fractions using the molar masses of the solute and solvent. 2-Propanone, 2-butanone, and cyclohexanone do absorb at the analysis wavelength. 2-Hydroxybenzoic acid was sufficiently soluble in these three solvents that by the time the saturated solutions were appropriately diluted for the measured absorbances to fall on the Beer–Lambert Law curve, the solvent background absorbances were negligible.

Results and Discussion

Experimental 2-hydroxybenzoic acid solubilities x_A^{sat} , in 16 organic solvents studied are listed in Table 1. Numerical values represent the average of between four and eight independent determinations, with the measurements being reproducible to $\pm 1.8\%$. We were unable to find any published solubility data in the chemical literature against which to compare directly our measured values. We did find experimental solubility data for benzoic acid (Beerbower et al., 1984; Lin and Nash, 1993) and 4-hydroxybenzoic acid (Martin et al., 1984), and these values have been tabulated in the third and fourth columns of Table 1. All three solutes are expected to have different solubilities in any given solvent because of differences in their respective melting point temperatures and enthalpies of fusion. The three crystalline solutes are benzoic acid derivatives, however, and to a first approximation one would expect that the molecular interactions between 2-hydroxybenzoic acid and a given solvent would be similar to the molecular interactions between benzoic acid and the specified organic solvent. These interactions, in turn, should be similar to those between 4-hydroxybenzoic acid and the organic solvent under consideration. Naturally, there might be some slight differences/variations caused by the location of the hydroxyl functional group.

Examination of Table 1 reveals that, in the case of benzoic acid, the published mole fraction solubilities are fairly close together for the alcohol solvents. Benzoic acid is more soluble in 2-propanol than in 1-propanol, and more soluble in 1-butanol than in 2-butanol. Many of the same trends are observed for both 2-hydroxybenzoic acid and 4-hydroxybenzoic acid. Both hydroxybenzoic acids are more soluble in 2-propanol than 1-propanol. A reversal in

solubility order is noted in the two butanol solvents. Measured solubilities in the alcohol solvents do fall within a narrow mole fraction range, particularly if 2-methyl-1-propanol is excluded. Benzoic acid and 2-hydroxybenzoic acid are more soluble in 1,4-dioxane and tetrahydrofuran than in any of the alcohol, ketone, and ester solvents studied.

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Acknowledgment

Received for review May 17, 1999. Accepted July 27, 1999. T.L.S. thanks the University of North Texas and the U.S. Department of Education for support provided under the Ronald E. McNair Postbaccalaureate Achievement Program.

JE990134W