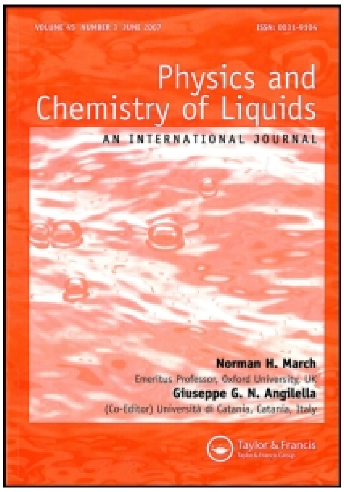

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SOLUBILITY OF BENZILIC ACID IN SELECT ORGANIC SOLVENTS AT 298.15 K

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Experimental solubilities are reported for benzilic acid dissolved in ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 2-propanol, 2-butanol, 2-methyl-1-propanol, diethyl ether and methyl *tert*-butyl ether at 298.15 K. Results of these measurements reveal that the observed solubilities in the nine alcohol solvents fall within a fairly narrow mole fraction range of each other. Benzilic acid is also very soluble in the two ether solvents studied.

Keywords: Benzilic acid solubilities; Alcohol solvents

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 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 scarce. To address this need, researches have developed predictive methods for generating desired quantities.

Of the predictive expressions that have been suggested in recent years, linear solvation energy relationships (LSERs) offers 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. One such LSER is the

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Abraham general solvation model that enables one to describe the partition of solutes between water and a given solvent [1–8]

$$\log P = c + r \cdot R_2 + s \cdot \pi_2^{\mathrm{H}} + a \cdot \Sigma\alpha_2^{\mathrm{H}} + b \cdot \Sigma\beta_2^{\mathrm{H}} + v \cdot V_x \tag{1}$$

and between the gas phase and a given solvent

$$\log L = c + r \cdot R_2 + s \cdot \pi_2^{\mathrm{H}} + a \cdot \Sigma\alpha_2^{\mathrm{H}} + b \cdot \Sigma\beta_2^{\mathrm{H}} + l \cdot \log L^{(16)} \tag{2}$$

The dependent variables in Eqs. (1) and (2) are the $\log P$ (the partition coefficient of solute(s) between water and a given solvent) and $\log L$ (Ostwald solubility coefficient). The independent variables are the solute descriptors as follows: R_2 and V_x refer to the excess molar refraction and McGowan volume of the solute, respectively, $\Sigma\alpha_2^{\mathrm{H}}$ and $\Sigma\beta_2^{\mathrm{H}}$ are measures of the solute hydrogen-bond acidity and hydrogen-bond basicity, π_2^{H} denotes the solute dipolarity/polarizability descriptor, and $L^{(16)}$ is the solute gas phase dimensionless Ostwald partition coefficient into hexadecane at 298 K. The Ostwald partition coefficient, L, is the inverse of the Henry's law constant (Pa m^3 mole^{-1}). It should be noted that the various c, r, s, a, b, v and l coefficients depend on the solvent phase under consideration. The r-coefficient gives the tendency of the phase to interact with solutes through polarizability-type interactions, mostly *via* electron pairs. The s-coefficient is a measure of the solvent phase dipolarity/polarity, while the a- and b-coefficients represent the solvent phase hydrogen-bond basicity and hydrogen-bond acidity, respectively. The l- and v-coefficients are a combination of the work needed to create a solvent cavity wherein the solute will reside, and the general dispersion interaction energy between the solute and solvent phase. In the case of partition coefficients, where two solvent phases are involved, the c, r, s, a, b, v and l coefficients represent differences in the solvent phase properties.

To date mathematical expressions have been deduced for approximately 50 or so dry solvents. The derived mathematical expressions allow one to predict the partitioning and solubility behavior of organic and organometallic solutes, provided that one knows the numerical values of the various solute descriptors. Development of a single correlation equation requires experimental data for at least 50 or so different solutes. It is important that the data set contain solutes that span as wide of a range of solute descriptors as possible in order to derive meaningful correlations. Partition coefficients of volatile solutes can be measured directly as the solute gas-liquid chromatographic retention volumes on the given organic solvent stationary phase, or calculated from infinite dilution activity coefficients. This latter information is available in the published literature in the form of binary liquid–vapor equilibria data. Solubility measurements provide a very convenient means for including nonvolatile solutes in the regressional analysis. Here, the partition coefficient is calculated as the ratio of the solute molar solubility in the organic solvent under consideration and water (or saturated vapor concentration in the case of the gas/liquid partition).

We, in collaboration with the Abraham research group, are in the process of developing/updating correlation equations for additional/existing solvent systems. The very early correlations for "dry" solvents were based upon data sets that contained very few carboxylic acid solutes. Many of the early correlations have been updated; however, we still find ourselves in need of additional carboxylic acid solubility data for several fairly common alcohol and ether solvents. For this reason, benzilic acid solubilities were measured in 11 organic solvents. Results of these measurements, combined with published solubility data and infinite dilution activity coefficient data, will be used in subsequent studies to develop water/organic solvent partition and gas/liquid partition correlations based upon Eqs. (1) and (2). The subsequent studies will also use the measured solubility data to check the numerical values of the solute descriptors (R_2, π_2^H, $\Sigma\alpha_2^H$, $\Sigma\beta_2^H$, and V_x) that have been calculated previously for benzilic acid.

MATERIALS AND METHODS

Benzilic acid (Aldrich, 99+ %) was used as received. The purity of the commercial sample, as determined by titration with sodium hydroxide was 99.8% (±0.3%). Ethanol (Aaper Alcohol and Chemical Company, absolute), 1-propanol (Aldrich, 99+ %, anhydrous), 1-butanol (Aldrich, HPLC, 99.8+ %), 1-pentanol (Aldrich, 99+ %), 1-hexanol (Alfa Aesar, 99+ %), 1-heptanol (Alfa Aesar, 99+ %), 2-propanol (Aldrich, 99+ %, anhydrous), 2-butanol (Aldrich, 99+ %, anhydrous), 2-methyl-1-propanol (Aldrich, 99+ %, anhydrous), diethyl ether (Aldrich, 99+ %, anhydrous) and methyl *tert*-butyl ether (Arco, 99.9+ %) were stored over molecular sieves and distilled shortly before use. Gas chromatographic analysis showed solvent purities to be 99.7 mole 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) with periodic agitation. After equilibration, the samples stood unagitated for several hours in the constant temperature bath to allow any finely dispersed solid particles to settle. Attainment of equilibrium was verified both by repetitive measurements the following day (or sometimes after two days) and by approaching equilibrium from supersaturation by pre-equilibrating the solutions at a slightly higher temperature. Aliquots of saturated benzilic 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 258 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 calculated molar absorptivity varied slightly with concentration, from $\varepsilon \approx 406\,\mathrm{L\,mol^{-1}\,cm^{-1}}$ (8.82×10^{-4} Molar) to $\varepsilon \approx 375\,\mathrm{L\,mol^{-1}\,cm^{-1}}$ (4.41×10^{-3} Molar) over the concentration range studied.

Experimental molar concentrations were converted to (mass/mass) solubility fractions by multiplying by the molar mass of benzilic acid, volume(s) of 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 solubility mass fractions using the molar masses of the solute and solvent.

RESULTS AND DISCUSSION

Experimental mole fraction solubilities of benzilic acid, X_A^{sat}, in the 11 organic solvents studied are listed in Table I. Numerical values represent the average of between

TABLE I Experimental mole fraction solubilities, X_A^{sat}, of benzilic acid, 2-hydroxybenzoic acid, 4-hydroxybenzoic acid and benzoic acid in select organic solvents at 298.15 K

Solvent	*Benzilic acid*	*2-Hydroxybenzoic acid* [9,10]	*4-Hydroxybenzoic acid* [11]	*Benzoic acid* [12,13]
Ethanol	0.1667	0.1100	0.1213	0.1789
1-Propanol	0.1461	0.1636	0.1084	0.1791
1-Butanol	0.1403	0.1646	0.1154	0.2016
1-Pentanol	0.1326	0.1611	0.1145	0.1832
1-Hexanol	0.1199		0.1121	0.1905
1-Heptanol	0.1126			0.1699[a]
2-Propanol	0.1518	0.1789	0.1297	0.1937
2-Butanol	0.1411	0.1869	0.0901	0.1524
2-Methyl-1-propanol	0.1054	0.1430	0.09642[a]	0.1577[a]
Diethyl ether	0.1287	0.1521		0.1837
Methyl *tert*-butyl ether	0.1541	0.1833[a]	0.1074[a]	0.2251[a]

[a] Measured as part of this study.

four and eight independent determinations, with the measurements being reproducible to ± 2.5%. We were unable to find any published experimental benzilic acid solubility data in the chemical literature against which to compare directly our measured values. We did find experimental solubility data for 2-hydroxybenzoic acid [9,10], 4-hydroxybenzoic acid [11] and benzoic acid [12,13], and these values are tabulated in the third, fourth and five columns of Table I, respectively. We have also included in the table a few additional mole fraction solubilities that were measured as part of the present study. All four 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 four crystalline solutes are aromatic monofunctional carboxylic acids, and to a first approximation one would except that the molecular interactions between benzilic acid and a given solvent would be similar to the molecular interactions between 2-hydroxybenzoic acid and the specified organic solvent. These interactions, in turn should be similar to those between 4-hydroxybenzoic (or benzoic acid) and the organic solvent solvent under consideration. Naturally, there might be some slight differences/variations caused by the location of the hydroxyl functional group.

Examination of the numerical entries in Table I reveals that, in the case of benzilic acid, the experimental solubilites are fairly close together for the nine alcohol solvents. The mole fraction solubility of benzilic acid does decrease slightly with increasing 1-alkanol chain length. Carboxylic acids are known to hydrogen-bond with the hydroxyl functional group on the alcohol. Hydrogen-bond formation enhances the solubilization. It is not unreasonable to expect less hydrogen-bond formation with the larger alcohol molecules. The concentration of the hydroxyl group does decrease with increasing alkyl chain. For the small alcohols the effect may not be as pronounced because the saturation limit is never reached. There is always considerably more solvent hydroxyl groups than dissolved carboxylic acid solute molecules in the solution. Benzilic acid, 2-hydroxybenzoic acid, 4-hydroxybenzoic acid and benzoic acid are also quite soluble in diethyl ether and methyl *tert*-butyl ether. Here, the two lone electron pairs on the ether oxygen atom provide sites for possible hydrogen-bond formation.

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