Fluid Phase Equilibria 431 (2017) 66–74

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Abraham model linear free energy relationships for describing the partitioning and solubility behavior of nonelectrolyte organic solutes dissolved in pyridine at 298.15 K

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ARTICLE INFO

Article history:
Received 11 July 2016
Received in revised form
10 October 2016
Accepted 11 October 2016
Available online 12 October 2016

Keywords:
Activity coefficients
Partition coefficients
Solubility ratios
Solute transfer processes
Pyridine solvent

ABSTRACT

A headspace gas chromatographic method is used to measure infinite dilution activity coefficients of 20 liquid organic solutes dissolved in pyridine at 298.15 K. The measured infinite dilution activity coefficients are used to calculate air-to-pyridine and water-to-pyridine partition coefficients. The calculated partition coefficients, combined with published experimental data for an additional 52 inorganic and organic solutes taken from the chemical literature, are used to derive Abraham model correlations for describing the transfer of nonelectrolyte solutes into pyridine from both water and the gas phase. The derived mathematical described the air-to-pyridine and water-to-pyridine partition coefficients to within 0.13 log units.

1. Introduction

Selection of the most suitable organic solvent for an industrial manufacturing process is a critical task as one must consider not only the physical and chemical properties of the potential solvent candidates, but economical and safety issues as well. Physical properties, such as density and viscosity, have been measured for most of the commonly used organic solvents. For mixed solvent systems predictive methods have been developed for estimating densities and viscosities using group contribution methods if actual experimental values are not available. Experimental data is less abundant for solvent properties involving the solubilization of organic and inorganic solute molecules. There are several millions of known organic and inorganic compounds, and it is not feasible to perform solubility measurements for every possible solute-solvent pair. Fortunately predictive methods are also available for estimating the solubility of gaseous, liquid and crystalline nonelectrolyte solutes dissolved in neat organic solvents and multicomponent organic solvent mixtures. The “quality” of the predicted values ranges anywhere from “very good” to “marginal” depending upon the complexity of the solute and solvent molecules being considered. Very good predictions are often obtained for very simple solute-solvent systems containing only nonspecific interactions. The more complex systems involving multi-functional solute and solvent molecules, however, present greater challenges. These latter systems may involve formation of solute-solute, solvent-solvent and/or solute-solvent association complexes through the formation of hydrogen-bonds.

Our contribution in the area of solvent selection has been twofold. First we have experimentally determined infinite dilution activity coefficients [1–9], air-to-liquid partition coefficients [1–9] and solubility data [3–6] for solutes dissolved in wide range of organic solvents of varying polarity and hydrogen-bonding character. The published experimental data is available to the scientific community for utilization in the development of better predictive models. Concurrent with our experimental endeavors we have been very active in developing mathematical expressions for predicting the fore-mentioned solute transfer properties in more than 100 neat organic solvents [3–6,10], in more than 70 different

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http://dx.doi.org/10.1016/j.fluid.2016.10.009
0378-3812/

anhydrous ionic liquid solvents [11,12], and in both binary aqueous-methanol [13] and aqueous-ethanol [14,15] solvent mixtures. To date the list of organic solvents studied have included several saturated and aromatic hydrocarbons, haloalkanes and haloaromatic compounds, linear and branched alcohols, alkyl alkanoates, monofunctional and polyfunctional linear and cyclic ethers, alkoxyalcohols, secondary and tertiary alkylamides, linear and cyclic ketones, and a wide range of miscellaneous organic solvents (dimethyl sulfoxide, propylene carbonate, tributyl phosphate, aniline, acetic acid).

In the present communication we extend our considerations to include pyridine, which is an organic solvent used in manufacturing processes involving the production of dyes and rubbers. Pyridine is a good polar solvent for titrations involving weakly acidic compounds, and can be used in the titrant solvent for Karl Fischer titrations for the determination of trace moisture in organic samples. A headspace gas chromatographic method was used to measure infinite dilution activity coefficients (γ_∞) and air-to-liquid partition coefficients (K) for 8 different aliphatic hydrocarbons (alkanes, alkenes, alkynes), 4 different aromatic compounds (benzene, alkylbenzenes, halobenzenes), 3 different chloroalkanes (1-chlorobutane, 1,2-dichloropropane, isopropylbromide), acetone, tetrahydrofuran, butyl acetate, pentyl acetate and acetonitrile dissolved in pyridine at 298.15 K. In total measurements were made for 20 different organic solutes. The measured experimental values, combined with published activity coefficients [16–29], and solubility data for both gaseous [30–36] and crystalline [37–42] organic and inorganic compounds, were used to derive Abraham model linear free energy relationships (LFERs) for solute transfer into neat pyridine from both water and from air. The literature data is discussed in greater in a later section of the manuscript titled Construction of Partition Coefficient Data Sets. The derived LFERs described the observed molar solubility data, water-to-pyridine partition coefficients, and air-to-pyridine partition coefficients to within 0.13 log units.

2. Materials and experimental methodology

All chemicals used in this study were purchased from commercial suppliers, and with the exception of pyridine, were used without further purification. Pyridine was stored with potassium hydroxide pellets and distilled in the presence of calcium hydride. Other compounds were used without further purification. Purity of the substances was confirmed by the gas chromatography. No peaks with the area more than 0.5% of that of the main compound was observed. A list of chemicals used, the names of the chemical suppliers and chemical purities (in mass fractions) are given in Table 1.

Limiting activity coefficients in pyridine were determined by gas chromatographic headspace analysis technique. Equilibrium vapor phase was sampled from thermostated vials (total volume 22 ml) containing 5 ml of solution with concentration of a solute lying in the range 0.1–0.5 vol % or containing 5 ml of a pure compound. The area S of the chromatographic peak of a solute is proportional to its vapor pressure p_{solute} over a solution. The area S_0 of the chromatographic peak for the same compound sampled from the saturated vapor over its neat liquid phase at the same conditions is proportional to its saturated vapor pressure p^o_{solute}. Thus, the activity coefficient γ given by

$$\gamma = p_{solute}/(p^o_{solute}\cdot x) \tag{1}$$

can be determined from the peak area values using a formula:

$$\gamma = S/(S_0\cdot x) \tag{2}$$

where x is the equilibrium molar fraction of a solute in the liquid phase. In the case of volatile and/or poorly soluble compounds, the value of x changes significantly due to partial evaporation of a solute, so that a correction is required [4]. The measurements were repeated for 3 different concentrations and 2 times for each particular concentration. No significant concentration dependence of the activity coefficients was observed, which means that the activity coefficients can be considered as corresponding to infinite dilution (denoted as γ^∞).

Logarithms of the dimensionless air-to-liquid partition coefficients, log K, were calculated using the following mathematical formula:

$$\log K = \log\left(\frac{RT}{\gamma^\infty p^o_{solute} V_{solvent}}\right) \tag{3}$$

The values of p^o_{solute} were taken from literature [43]. The molar volume of pyridine $V_{solvent}$ is 0.0806 L mol^{-1}, based on the experimental density reported by Gokavi et al. [44]. The results are reported in Table 2.

3. Construction of partition coefficient data sets

The experimental data in Table 2 gives log K values for 20 different liquid organic solutes. Our search of published chemical and engineering literature found experimental activity coefficient and solubility data for an additional 52 solutes of varying polarity and hydrogen-bonding character. Gorbachuk and coworkers [18.19] determined the infinite dilution activity coefficients of several halogenated benzene (fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, 1,2-dichlorobenzene), alcohol (methanol, ethanol, 1-propanol, 1-butanol), and alkanone (acetone, 2-octanone) solutes in pyridine. Park et al. [17] measured the infinite dilution activity coefficients and air-to-liquid partition coefficients of octane, toluene ethanol, nitromethane, butanone and 1,4-dioxane in 68 organic solvents using a headspace analyzer. The list of solvents studied by the authors included pyridine. Eikens [16] reported infinite dilution activity coefficients of several linear and branched alkane dissolved in pyridine. Our measured activity coefficient data for heptane, octane and nonane are approximately 8–10% smaller than the published literature values of $\gamma^\infty = 7.43$ (heptane), $\gamma^\infty = 8.52$ (octane), and $\gamma^\infty = 9.69$ (nonane) determined by Eikens. The log K values differ by much less: log $K = 2.829$ (ours) versus log $K = 2.830$ (Eikens) for heptane; log $K = 3.283$ (ours) versus log $K = 3.285$ (Eikens) for octane; and log $K = 3.728$ (ours) versus log $K = 3.745$ (Eikens) for nonane. Solubility data for several gaseous solutes (hydrogen [34], nitrogen [31], oxygen [30], nitrous oxide [32], carbon monoxide [36], carbon dioxide [33] and methane [35]) were retrieved from volumes of the IUPAC Solubility Series. Several studies reported solubility data for crystalline nonelectrolyte solutes. Choi et al. [37] and Coon et al. [38] determined the solubility of polycyclic aromatic hydrocarbons (acenaphthene, anthracene, biphenyl, fluoranthene, fluorene, phenanthrene, pyrene) and polycyclic aromatic hetero-atom compounds (carbazole, xanthene) in pyridine and thiophene from ambient room temperature up to near the melting point temperature of the solutes. Solubility data were also found for ferrocene [39], azathioprine [40], N-[(4-bromo-3,5-difluoro)phenyl]acrylamide [41] and N-[(4-bromo-3,5-difluoro)phenyl]maleimide [42].

The retrieved activity coefficients and mole fraction solubilities have been converted to logarithms of air-to-pyridine partition coefficients, log K, and logarithms of molar solubility ratios, log