Fluid Phase Equilibria 270 (2008) 30–44

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

Correlation and prediction of partition coefficient between the gas phase and water, and the solvents dry methyl acetate, dry and wet ethyl acetate, and dry and wet butyl acetate

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ARTICLE INFO

Article history:
Received 24 April 2008
Received in revised form 31 May 2008
Accepted 8 June 2008
Available online 17 June 2008

Keywords:
Partition coefficient
Butyl acetate
Methyl acetate
Ethyl acetate
Linear free energy relationship

ABSTRACT

Experimental partition coefficient data have been compiled from the published literature for the water/methyl acetate, water/ethyl acetate and water/butyl acetate partition systems, log *P* data, and for the gas/methyl acetate, gas/ethyl acetate and gas/butyl acetate partition systems, log *K* data. Application of the Abraham solvation parameter model to the sets of partition coefficients leads to equations that correlate the log *P* data and log *K* data to 0.18 log units for the three dry alkyl acetate solvents. Slightly larger deviations were noted for solute partition into both wet ethyl acetate and wet butyl acetate. The derived correlations were validated using training set and test set analyses.

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1. Introduction

Knowledge of vapor–liquid equilibria in systems involving organic compounds is important in many commercial manufacturing processes. Practical applications include the design of distillation processes for separating synthesized compounds from reaction solvent mixtures, and the removal of trace impurities from organic solvents using gas stripping methods. Distillation and gas stripping processes are governed by the partitioning of solute and solvent molecules between the vapor and liquid phases. This partitioning is related to the thermodynamic properties of the mixtures, and is described by gas-to-liquid partition coefficients.

In recent years numerous thermodynamic models have been developed for estimating vapor–liquid equilibria and activity coefficients of compounds in binary, ternary and higher-order multi-component liquid mixtures. Predictive methods include equation-of-state models, group contribution approaches, semi-theoretical and strictly empirical activity coefficient models and linear free energy relationship (lfer) correlations. Of the published lfer methods the general solvation parameter model of Abraham [1,2] is one of the most useful approaches for the analysis and prediction of free energies of partition in chemical and biological systems. The method relies on two linear free energy relationships (lfers), one for processes within condensed phases

$$\mathrm{SP} = c + e \cdot \mathbf{E} + s \cdot \mathbf{S} + a \cdot \mathbf{A} + b \cdot \mathbf{B} + v \cdot \mathbf{V} \tag{1}$$

and one for processes involving gas-to-condensed phase transfer

$$\mathrm{SP} = c + e \cdot \mathbf{E} + s \cdot \mathbf{S} + a \cdot \mathbf{A} + b \cdot \mathbf{B} + l \cdot \mathbf{L} \tag{2}$$

The dependent variable, SP, is some property of a series of solutes in a fixed phase. The independent variables, or descriptors, are solute properties as follows: **E** and **S** refer to the excess molar refraction and dipolarity/polarizability descriptors of the solute, respectively, **A** and **B** are measures of the solute hydrogen-bond acidity and basicity, **V** is the McGowan volume of the solute and **L** is the logarithm of the solute

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doi:10.1016/j.fluid.2008.06.001

gas phase dimensionless Ostwald partition coefficient into hexadecane at 298 K. The first four descriptors can be regarded as measures of the tendency of the given solute to undergo various solute–solvent interactions. The latter two descriptors, **V** and **L**, are both measures of solute size, and so will be measures of the solvent cavity term that will accommodate the dissolved solute. General dispersion interactions are also related to solute size, hence, both **V** and **L** will also describe the general solute–solvent interactions. The regression coefficients and constants (*c*, *e*, *s*, *a*, *b*, *v*, and *l*) are obtained by regression analysis of experimental data for a specific process (i.e., a given partitioning process, a given stationary phase and mobile phase combination, *etc.*). In the case of water-to-condensed phase partition coefficients, *P*, where two solvent phases are involved, the *c*, *e*, *s*, *a*, *b*, *v*, and *l* coefficients represent differences in solvent phase properties. For any fully characterized system/process (those with calculated values for the equation coefficients) further values of SP can be estimated for solutes with known values for the solute descriptors. This is the major advantage in using Eqs. (1) and (2) to correlate solute properties having chemical, environmental and pharmaceutical importance.

At present we are developing/updating correlations for additional/existing systems [3–10] and are developing new computation methodologies for calculating solute descriptors from available experimental data and/or structural information [2,11–15]. To date we have published Abraham model correlations for describing the gas-to-solvent, *K*,

$$\log K = \frac{\text{solute concentration in solution}}{\text{solute concentration in the gas phase}} \tag{3}$$

where *K* is the dimensionless gas-to-solvent partition coefficient (with concentrations in each phase defined in terms of mol dm^{-3}), and water-to-solvent partition coefficients, *P*, for more than 50 common organic solvents. For several solvents, the published correlations include both the "practical" log *P* correlation where the solute is distributed between the equilibrium organic phase saturated with water and the aqueous phase that has been saturated with the organic solvent, as well as the "hypothetical" log *P* correlation that is calculated as the molar solubility ratio of the solute in the anhydrous organic solvent divided by the solute's molar solubility in water. Even though hypothetical, these latter log *P* correlations are still quite useful in that calculated log *P* values can be used to predict the solute's infinite dilution activity coefficient or molar solubility in the anhydrous (dry) solvent for those solutes for which the solute descriptors are known.

In the present study we report Abraham model correlations for the partitioning of solutes into anhydrous methyl acetate and into both anhydrous and wet ethyl acetate and butyl acetate both from the gas phase (log *K* data) and from water (log *P* data). As part of the present study we have updated the log *P* and log *K* correlations that we had previously reported for ethyl acetate. The updated correlations are based on much larger databases that include recently published experimental solubility data for several polycyclic aromatic hydrocarbons and substituted benzoic acid derivatives, plus other crystalline organic solutes.

2. Data sets and computation methodology

Most of the experimental data that we were able to retrieve from the published literature [17–78] pertained either to the infinite dilution activity coefficient, γ_{solute}, or Henry's law constants, K_{Henry}, for solutes dissolved in anhydrous methyl acetate and butyl acetate. In order to apply the Abraham model the infinite dilution activity coefficients needed to be converted to log *K* values for gas-to-organic solvent partition through Eqs. (3) and (4)

$$\log K = \log\left(\frac{RT}{\gamma^{\infty}_{\text{solute}} P^{\text{o}}_{\text{solute}} V_{\text{solvent}}}\right) \tag{4}$$

$$\log K = \log\left(\frac{RT}{K_{\text{Henry}} V_{\text{solvent}}}\right) \tag{5}$$

or for partition from water to the anhydrous organic solvent through Eq. (6)

$$\log P = \log K - \log K_{\text{w}} \tag{6}$$

Here *R* is the universal gas constant, *T* is the system temperature, $P^{\text{o}}_{\text{solute}}$ is the vapor pressure of the solute at *T*, and V_{solvent} is the molar volume of the solvent. The calculation of log *P* requires knowledge of the solute's gas phase partition coefficient into water, K_{w}, which is available for most of the solutes being studied. The experimental log *K* and log *P* values at 298.15 K for anhydrous methyl acetate and anhydrous butyl acetate are listed in Tables 1 and 2, respectively.

Our experimental databases also contain measured solubility data [79–109] for several crystalline solutes dissolved in both neat methyl acetate and neat butyl acetate. The solubility data were taken largely from our previously published solubility studies. At the time that our solubility studies were performed we included solvents for which we planned to derive correlation equations in the future. In the case of crystalline solutes, the partition coefficient between water and the anhydrous organic solvent is calculated as a solubility ratio

$$P = \frac{C_{\text{S}}}{C_{\text{W}}} \tag{7}$$

of the solute's molar solubilities in the organic solvent, C_{S}, and in water, C_{W}. Molar solubilities can also be used to calculate log *K* values, provided that the solid saturated vapor pressure, $P^{\text{o}}_{\text{solute}}$, at 298 K is also available. $P^{\text{o}}_{\text{solute}}$ can be transformed into the gas phase concentration, C_{G}, and the gas-to-water and gas-to-solvent partitions, K_{w} and *K*, can be obtained through

$$K_{\text{w}} = \frac{C_{\text{W}}}{C_{\text{G}}} \quad \text{or} \quad K_{\text{S}} = \frac{C_{\text{S}}}{C_{\text{G}}} \tag{8}$$

In Eq. (8), the vapor pressure and aqueous solubility data needed for these calculations are reported in our previous publications.

Molecular descriptors for all of the compounds considered in the present study are also tabulated in Tables 1 and 2. The tabulated values came from our solute descriptor database, which now contains values for more than 3500 different organic and organometallic compounds. The descriptors were obtained exactly as described before, using various types of experimental data, including water to

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