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Development of Abraham model correlations for solute transfer into both 2-propoxyethanol and 2-isopropoxyethanol at 298.15 K

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ABSTRACT

Infinite dilution activity coefficients (γ_∞) were measured at 298 K for 9 different aliphatic hydrocarbons (alkanes, cycloalkanes, alkenes), 7 different aromatic compounds (benzene, alkylbenzenes, halobenzenes), and for 1,2-dichloropropane, dichloromethane, acetone, acetonitrile, tetrahydrofuran, 1,4-dioxane and 2-propanol dissolved in both 2-propoxyethanol and 2-isopropoxyethanol at 298 K using a headspace gas chromatographic method. As part of the experimental study solubilities of 18 and 20 crystalline organic nonelectrolyte solutes were determined in 2-propoxyethanol and 2-isopropoxyethanol, respectively, at 298 K using a UV/visible spectrophotometric method. The experimental values were converted to gas-to-alkoxyethanol partition coefficients, water-to-alkoxyethanol partition coefficients, and molar solubility ratios using standard thermodynamic relationships. Abraham model correlations for solute transfer into both alkoxyethanols were derived from the calculated solubility ratios and partition coefficients. The derived Abraham model describes the observed solubility ratios and partition coefficients to within 0.12 log units (or less).

1. Introduction

Organic solvents represent a significant quantity of the chemicals used in industrial manufacturing processes. Increased chemical and disposal costs, coupled with environmental concerns and governmental regulations controlling the release of hazardous materials into the environment, have prompted the manufacturing sector to find ways reduce organic solvent consumption. Implementation of solvent-free processes provides one solution to the problem; however, from a practical standpoint it is not feasible to completely eliminate organic solvents from all synthetic methods and chemical separations. Organic solvents provide a critical role in dissolving organic starting materials, in facilitating heat and mass transfer, and serve as mobile phases for chemical separations involving high-performance liquid chromatography. A more viable and more practical solution to the problem is to replace expensive solvents derived from petroleum with solvents made from renewable resources, and to replace hazardous solvents with ones that exhibit better environmental, health and safety properties.

Solvent selection includes economical, toxicological and chemical considerations. Our contributions in the area of solvent selection have focused on chemical considerations and specifically on the solubilizing properties of potential solvent candidates. For organic synthesis the solvent must be able to dissolve the starting material(s) and provide for the convenient isolation of the synthesized product from the reaction solvent media. This can either be accomplished by selecting a solvent in which the product is not soluble or by evaporation of the solvent once the reaction is complete. In the case of purification by extraction one needs to find a two-phase partitioning system (usually water and an organic solvent) where the compounds to be separated have vastly different relative solubilities in the respective immiscible liquid phases. Purification by recrystallization is also based on solubility differences of the compound in the hot versus cold solvent, or in the dissolving solvent versus precipitating anti-solvent. The solubility of a dissolved solute in different solvents is controlled by molecular interactions between the solute and surrounding solvent molecules, as well as by solvent–solvent and solute–solute interactions.

In the past several years we have reported mathematical correlations for describing measured partition coefficient and solubility data for solutes dissolved in both traditional organic solvents and in ionic liquid solvents based on the Abraham solvation parameter model [1–7]. Solute partitioning can be between two condensed phases (a biphasic aqueous-organic or organic–organic system):

$$\log(P \text{ or } C_{\mathrm{S,organic}}/C_{\mathrm{S,water}}) = \mathrm{c_p} + \mathrm{e_p}\cdot\mathbf{E} + s_p\cdot\mathbf{S} + \mathrm{a_p}\cdot\mathbf{A} + \mathrm{b_p}\cdot\mathbf{B} + \mathrm{v_p}\cdot\mathbf{V} \quad (1)$$

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or involve partitioning between a condensed phase and the gas phase:

$$\log\left(K \text{ or } C_{\mathrm{S,organic}}/C_{\mathrm{S,gas}}\right) = \mathrm{c_k} + \mathrm{e_k}\cdot\mathbf{E} + \mathrm{s_k}\cdot\mathbf{S} + \mathrm{a_k}\cdot\mathbf{A} + \mathrm{b_k}\cdot\mathbf{B} + \mathrm{l_k}\cdot\mathbf{L} \tag{2}$$

where P and K denote the respective partition coefficients. Eqs. 1 and 2 have also been used to describe the logarithm of molar solubility ratios, log ($C_{\mathrm{S,organic}}/C_{\mathrm{S,water}}$) and log ($C_{\mathrm{S,organic}}/C_{\mathrm{S,gas}}$), with the subscripts “organic”, “water” and “gas” indicating the phase to which the solute molar concentrations pertain. The independent variables in Eqs. (1) and (2), or descriptors, are solute properties as follows: **E** and **S** correspond 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** refers to the McGowan volume of the solute and **L** is the logarithm of the solute gas phase dimensionless gas to hexadecane partition coefficient at 298 K. The complementary solvent (or process) properties are indicated by the lower case letters in Eqs. (1) and (2). The numerical values of the solvent coefficients (c_p, e_p, s_p, a_p, b_p, v_p, c_k, e_k, s_k, a_k, b_k, and l_k) are determined by regression analysis of partition coefficients and solubility ratios for a series of solutes dissolved in the given solvent or two-phase partitioning system.

Specific solvents studied in the past five years include diisopropyl ether [8], 2-hexadecene [9,10], 1,9-decadiene [9,10], benzonitrile [2], 2-methoxyethanol [11], 2-ethoxyethanol [12], 2-butoxyethanol [13], 1,2-propylene glycol [14], acetophenone [15], aniline [15] and acetic acid [16]. All of the solvents listed above contain a single type of functional group attached to either an alkyl chain or aromatic benzene ring, except for the three 2-alkoxyalcohols. We are particularly interested in developing Abraham model correlations for organic solvents possessing multiple functional groups as our goal is to one day be able to predict the five equation coefficients in Eqs. (1) and (2) from only structural considerations. This will require an extensive database of equation coefficients for a chemically diverse set of solvents possessing different types of functional groups and hydrogen-bonding capabilities. In the present study we extend our earlier considerations to include two additional 2-alkoxyethanol solvents, namely 2-propoxyethanol and 2-isoproxyethanol. Alkoxyalcohols contain both an ether functional group (—O—) and a hydroxyl functional group (—OH). This will allow us to search for possible synergistic effects between adjacent ether and hydroxyl groups once we begin our search for methods to predict the solvent/process coefficients.

Infinite dilution activity coefficients (γ_∞) were measured at 298 K for a series of organic solutes containing up to 9 different aliphatic hydrocarbons (alkanes, cycloalkanes, alkenes), up to 9 different aromatic compounds (benzene, alkylbenzenes, halobenzenes), two cyclic ethers (tetrahydrofuran, 1,4-dioxane), chloroalkanes (dichloromethane, 1,2-dichloropropane), acetone, acetonitrile, 2-propanol, and butyl acetate (in 2-isopropoxyethanol only) dissolved in both 2-propoxyethanol and 2-isopropoxyethanol using a gas chromatographic headspace analysis method. Gas-to-liquid partition coefficients (K) were calculated using these results and saturated vapor pressures of solutes taken from the published literature. As part of this study solubilities were measured at 298 K for acetylsalicylic acid, acenaphthene, benzil, benzoic acid, 1-chloroanthraquione, 4-chloro-3-nitrobenzoic acid, 3,5-dinitrobenzoic acid, 3,5-dinitro-2-methylbenzoic acid, diphenyl sulfone, fluorene, 2-hydroxybenzoic acid, 3-hydroxybenzoic acid, 2-methylbenzoic acid, phenothiazine, *trans*-stilbene, thioxanthen-9-one, and xanthene dissolved in the two 2-alkoxyethanol solvents as well. Solubilities were also determined for 3-chlorobenzoic acid, 2-ethylanthraquinone and pyrene dissolved in 2-isopropoxyethanol and for 3,4-dimethoxybenzoic acid dissolved in 2-propoxyethanol. The measured gas-to-liquid partition coefficient and solubility data, combined with published solubility data for anthracene [17,18], benzoin [19], pyrene [20], 4-nitrobenzoic acid [21], 2-methoxybenzoic acid [21], 4-methoxybenzoic acid [21], 4-hydroxyacetanilide [21], 4-chlorobenzoic acid [21], 3-methylbenzoic acid [21], 3,4-dimethoxybenzoic acid [22], 3,4-dichlorobenzoic acid [23], biphenyl [21], and salicylamide [21], were used to derive Abraham model log (P or $C_{\mathrm{S,organic}}/C_{\mathrm{S,water}}$) and log ($K$ or $C_{\mathrm{S,organic}}/C_{\mathrm{S,gas}}$) correlations for describing solute transfer into 2-propoxyethanol and 2-isopropoxyethanol both from water and from the gas phase.

2. Experimental methodology

2.1. Gas chromatographic headspace measurements

2-Propoxyethanol (Acros Organics, 98%), 2-isopropoxyethanol (Aldrich, 99%), n-hexane (Sigma-Aldrich, 99%), n-heptane (Acros Organics, 99%), n-octane (Sigma-Aldrich, 99%), n-nonane (Acros Organics, 99%), cyclohexane (Acros Organics, 99.5%), methylcyclohexane (Aldrich, 99%), 1,7-octadiene (Acros Organics, 99%), 1-heptyne (Acros Organics, 99%), 1-octyne (Alfa Aesar, 98%), benzene (Sigma-Aldrich, 99%), fluorobenzene (Acros Organics, 99%), chlorobenzene (Acros Organics, 99.6%), bromobenzene (Acros Organics, 99%), toluene (Sigma-Aldrich, 99.8%), ethylbenzene (Fluka, 99%), *o*-xylene (Sigma-Aldrich, 99%), *m*-xylene (Sigma-Aldrich, 99%), *p*-xylene (Sigma-Aldrich, 99%), dichloromethane (Kupavnareaktiv, 99.9%), 1,2-dichloropropane (Fluka, 98.5%), acetone (Ecos-1, 99.8%), acetonitrile (J.T.Baker, 99.9%), butyl acetate (Ecos-1, 99.5%), 1,4-dioxane (Komponent-Reaktiv, 99.5%), 2-propanol (Ecos-1, 99.8%), tetrahydrofuran (Ecos-1, 99.5%) were purchased. Most of the compounds were used in the experiments without further purification except tetrahydrofuran and 1,4-dioxane which were distilled over sodium, and 2-propanol which was dried with calcium hydride and distilled. Gas chromatograms of all the substances show no peaks with the area exceeding 0.5% of that of the peak corresponding to the main substance.

In a typical experiment, for each solute–solvent pair we prepared 6 solutions containing different concentrations of a solute in the range 0.1–0.8 volume percents. At such concentrations, solutions are thought to behave as infinitely diluted ones, which was confirmed by the absence of dependence of the results from concentration. The activity coefficient of a solute at infinite dilution γ_∞ is given by $\gamma_\infty = p/(p_{solute}{}^o \cdot x)$, where x is the equilibrium molar fraction of a solute in the liquid phase, p is the saturated vapor pressure of a solute over the solution, and $p_{solute}{}^o$ is the saturated vapor pressure of the same solute over its pure liquid phase. The ratio $p/p_{solute}{}^o$ was determined by means of gas chromatographic headspace technique using PerkinElmer Clarus 580 chromatograph with a headspace autosampler.

The samples (5 ml) of solutions and pure solutes are placed into sealed 22 ml vials and thermostated at 298.15 K. Portions of equilibrium vapor phase are taken from these vials by autosampler and transferred into the chromatographic column, and the areas of chromatographic peaks that are proportional to the vapor pressure of each compound inside the vial are calculated. We also take into account that the actual value of x due to partial evaporation of a solute into the headspace can be different from the initial molar fraction of a solute by introducing a correction.

Gas-to-liquid partition coefficients K can be calculated using a formula $\log K = \log\left(\frac{RT}{\gamma_\infty p_{solute}{}^o V_{solvent}}\right)$, where $V_{solvent}$ is the molar volume of a solvent. The values of $p_{solute}{}^o$ were taken from literature [24]. The Gibbs energy of solvation with the standard states defined as a hypothetical ideal solution at unit mole fraction and a gas at 1 bar fugacity is given by $\Delta_{solv}G = RT\ \ln\left(\gamma_\infty p_{solute}{}^o\right)$. Results are presented in Tables 1 and 2.

2.2. Solubility measurements

Acenaphthene (Aldrich, 98%), acetylsalicylic acid (Aldrich, 99%), benzil (Aldrich, 97%), benzoic acid (Aldrich, 99+%), 1-chloroanthraquinone (Aldrich, 99%), 3-chlorobenzoic acid (Aldrich, 99%), 4-chloro-3-nitrobenzoic acid (Acros Organics, 99.5%), 3,4-dimethoxybenzoic acid (Acros Organics, 99+ %), 3,5-dinitrobenzoic