Determination of Abraham Model Correlations for Describing Solute Transfer into the Methyl Butyrate Mono-solvent at 298 K

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Abstract

Experimental mole fraction solubilities have been determined for 26 crystalline nonelectrolyte organic compounds and for one organometallic compound (ferrocene) dissolved in methyl butyrate at 298.15 K. The crystalline compounds cover a wide range of polarity and hydrogen-bonding character. Abraham model correlations were derived by combing the solubility data measured in the current study with published values retrieved from the chemical and engineering literature. The mathematical correlations determined in the current study were found to back-calculate the observed solubility data to within standard deviations of 0.10 log units (or less).

Key Words and Phrases

Methyl butyrate solvent; Solubility; Crystalline organic compounds; Abraham model

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1. Introduction

Organic solvents are routinely used in many industrial manufacturing processes ranging from the synthesis of chemical compounds, to the preparation of cosmetic and skincare consumer products, to the development of new medical compounds and drug formulations, and to the solubilization of dyes and pigments in oil-based paints and varnishes. Several million tons of organic solvents are consumed each year by the manufacturing sector [1]. Annual solvent consumption will likely increase in future years as the world population grows. Several common organic solvents, like N,N-dimethylformamide, N,N-dimethylacetamide, 1,4-dioxane and N-methyl-2-pyrrolidone, currently used in manufacturing processes are classified as “hazardous” and “substitution recommended” in solvent selection guidelines [2,3] because of their volatility and/or heat issues associated with human exposure. Replacement of hazardous compounds with safer solvent alternatives is a highly desired, though not easily achievable, goal for the industrial manufacturing sector. Many factors must be considered in selecting an appropriate solvent for a specific application, including the solvent’s physical and chemical properties, as well as purchase and disposal costs, environmental impact and the health/safety issues associated with both short-term and prolonged human exposure.

Solubilizing ability of the solvent is probably the physical property for which the least amount of information is readily available. Solubility depends upon molecular interactions between the dissolved solute and surrounding molecules, as well as breaking of solvent-solvent interactions needed to create the solvent cavity wherein the dissolved solute would reside. The breaking of solute-solute interactions, while important in determining the actual solubility of given solute, is not a major consideration in solvent selection considerations as these interactions will be same irrespective which solvent is chosen. Molecular interactions are solute and solvent specific, and depend upon molecular shape and size considerations, and the functional groups and their placement within both the solute and solvent molecules. Ideally experimental solubility data should be used in the solvent selection process. From a practical standpoint this is not always feasible as there are several million different solute-solvent combinations. Solubility determinations are time-consuming and expensive, and one cannot perform measurements for every possible combination.

During the last 20 years we [4-12] and other research groups [13-26] have performed solubility measurements for crystalline organic compounds in a wide range of organic mono-solvents and binary aqueous-organic solvent mixtures of varying polarity and hydrogen-bonding character. Solubilities have been reported for drug molecules, pesticides, insecticides, polycyclic aromatic hydrocarbons and chemical reagents used in industrial manufacturing processes. Experimental determinations have been limited in scope to a narrow range of temperatures (generally 298.15 K to 323.15 K) and to a select handful of organic mono-solvents and solvent mixtures. Except for our papers [4-12, 27-29], the published solubility studies include little information regarding how the measured solubility data could be used to predict the solubility of the solute in additional organic mono-solvents or solvent mixtures outside of the handful of specific solvents studied by the reporting authors. From a solvent selection standpoint the ability to predict the solubility of solutes in many different mono-solvents and solvent mixtures is what is really needed.

Our studies [4-12, 27-29] have interpreted the measured solubility data in terms of the Abraham solvation model which describes solute transfer between two phases in terms of:

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

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

the product of solute properties (called solute descriptors) and the complimentary solvent properties. Solute properties are denoted by the capitalized alphabetic characters in Eqns. 1 and 2 and are defined as follows: the solute excess molar refractivity expressed in units of (cm^3 mol^{-1})/10 (**E**); the solute dipolarity/polarizability (**S**); the overall or summation hydrogen-bond acidity and basicity (**A** and **B**, respectively); the McGowan volume given in units of (cm^3 mol^{-1})/100 (**V**); and the logarithm of the gas-to-hexadecane partition coefficient at 298 K (**L**). The complimentary solvent properties denoted by the lowercase alphabetic characters on the right-hand side of Eqns. 1 and 2 are determined by regressing the logarithm of the solute's water-to-organic solvent partition coefficient, log *P*, the logarithm of the solute's gas-to-organic solvent partition coefficient, log *K*, or the logarithm of the two molar solubility ratios, log ($C_{S,organic}/C_{S,water}$) and log ($C_{S,organic}/C_{S,gas}$), in accordance with the Abraham model equations. The subscripts in the two molar solubility ratios indicate the phase to which the solute molar concentrations pertain. Equations 1 and 2 will be discussed in greater detail in a later section that describes the calculation of the solvent coefficients of the methyl butyrate solvent from measured solubility data of crystalline organic compounds dissolved in methyl butyrate. The solubility data was measured as part of the current study.

A major benefit of using the Abraham model to describe solute transfer process is that once the solute descriptors are known for a given solute the numerical values can be used to predict the solubility of the given compound in any organic solvent for which the complimentary solvent properties have been determined. More than 100 different organic mono-solvents have been characterized by the Abraham model [4-7, 27-32]. Similarly once the solvent properties (lowercase alphabetical characters) have been determined the numerical values can be used to predict the solubility of many additional solutes dissolved in the given organic mono-solvent or solvent mixture. Abraham model solute descriptors are currently available for more than 8,000 chemical compounds [33]. In the case that the solute descriptor is not available in the published database it can be estimated by entering the SMILES code [33].

From the standpoint of solvent selection, the limitation to our approach is not the availability of solute descriptors as these values can often be reasonably estimated if the solute contained in the list of 8,000 compounds for which solute descriptors are known. Rather, our method is limited to the 100 or specific mono-solvents and two aqueous-alcohol solvent systems for which Abraham model correlations have been derived. This represents only a very small fraction of the solvents used in industrial manufacturing processes. In the current study we expand our solvent list to include methyl butyrate. Solubilities have been measured for phenothiazine, 1-chloroanthraquinone, *trans*-stilbene, fluoranthene, xanthene, benzil, benzoic acid, 4-*tert*-butylbenzoic acid, 4-chlorobenzoic acid, 2-methoxybenzoic acid, 4-methoxybenzoic acid, 2-methylbenzoic acid, 3-methylbenzoic acid, 3-methyl-4-nitrobenzoic acid, 4-methyl-3-nitrobenzoic acid, 2-chloro-5-nitrobenzoic acid, 3-nitrobenzoic acid, 4-nitrobenzoic acid, 3,5-dinitro-2-methylbenzoic acid, diphenylsulfone, ferrocene, salicylamide, 2-ethylanthraquinone, 3,5-dinitrobenzoic acid, 2-hydroxybenzoic acid, 2-chloro-5-nitrobenzoic acid, and 3-hydroxybenzoic acid dissolved in methyl butyrate at 298.15 K. In total solubilities were measured for 27 different crystalline nonelectrolyte compounds. Abraham model correlations were derived by combining our experimental values with published solubility data for anthracene [34], pyrene [34], 4-chloro-3-nitrobenzoic acid [34, 35], acetylsalicylic acid [34, 36], thioxanthen-9-one [34], 3,4-dimethoxybenzoic acid [12], 3,4,5-trimethoxybenzoic acid [8], 3,4-dichlorobenzoic acid [37] and o-acetoacetanisidide [9] taken from the published chemical literature.

2. Chemical Materials and Experimental Methodology

In assembling the crystalline organic compounds for the solubility determinations we selected compounds that exhibit a chemical diversity and that span a wide range of solute descriptors values. All chemicals used in the solubility measurements were purchased from commercial sources. The sample of methyl butyrate was dried over activated molecular sieves and distilled shortly before use. Samples of 2-ethylanthraquinone, *trans*-stilbene, 1-chloroanthraquinone, benzil, fluoranthene, diphenylsulfone, salicylamide, xanthene, and ferrocene were recrystallized three times from anhydrous methanol and dried for two days at 333 K prior to use. The carboxylic acid solutes were dried for two days at 333 K prior to use. Gas chromatographic analysis (flame ionization detector) indicated that the purities of purified samples of methyl butyrate, 2-ethylanthraquinone, *trans*-stilbene, 1-chloroanthraquinone, benzil, fluoranthene, diphenylsulfone, xanthene, and salicylamide were 0.997 mass fraction. The purities of the fifteen carboxylic acid samples were determined by a non-aqueous titrimetric method based on the published method of Fritz and Lisicki [38]. The method was modified for health reasons in that benzene was replaced by toluene in preparing the titration solvent. Acid-base titrations with freshly standardized sodium methoxide (thymol blue indicator) indicated that the purities of benzoic acid, 4-*tert*-butylbenzoic acid, 2-chloro-5-nitrobenzoic acid, 4-chlorobenzoic acid, 3,5-dinitrobenzoic acid, 3,5-dinitro-2-methylbenzoic acid, 2-hydroxybenzoic acid, 3-hydroxybenzoic acid, 2-methoxybenzoic acid, 4-methoxybenzoic acid, 2-methylbenzoic acid, 3-methyl-4-nitrobenzoic acid, 4-methyl-3-nitrobenzoic acid, 3-nitrobenzoic acid, and 4-nitrobenzoic acid were 0.998 (±0.003) mass fraction. The commercial suppliers and chemical purities of the chemicals used in the solubility measurements are summarized in Table 1.

Table 1. Chemical Sources and Mass Fraction Purities of Chemicals Used in the Solubility Studies

Chemical	Supplier	Purification Method	Purity (Mass Fraction)
Methyl butyrate	Acros Organics, Morris Plains, New Jersey, USA	Stored over molecular and distilled	0.997
1-Chloroanthraquinone	Aldrich Chemical Company, Milwaukee, Wisconsin, USA	Recrystallization from anhydrous methanol	0.997
Phenothiazine	Acros Organics	Dried for two days at 333 K	0.99
trans-Stilbene	Aldrich Chemical Company	Recrystallization from anhydrous methanol	0.997
Benzil	Aldrich Chemical Company	Recrystallization from anhydrous methanol	0.997
Fluoroanthene	Aldrich Chemical Company	Recrystallization from anhydrous methanol	0.997
Xanthene	Aldrich Chemical Company	Recrystallization from anhydrous methanol	0.997
2-Ethylanthraquinone	Aldrich Chemical Company	Recrystallization from anhydrous methanol	0.997
Diphenylsulfone	Aldrich Chemical Company	Recrystallization from anhydrous methanol	0.997
Salicylamide	Aldrich Chemical Company	Recrystallization from anhydrous methanol	0.997
Benzoin	Aldrich Chemical Company	Recrystallization from anhydrous methanol	0.997
Ferrocene	Aldrich Chemical Company	Dried for two days at 333 K	0.98
Benzoic acid	Aldrich Chemical Company	Dried for two days at 333 K	0..998
4-*tert*-Butylbenzoic acid	TCI America Chemical Company, Portland, Oregon, USA	Dried for two days at 333 K	0..998
2-Chloro-5-nitrobenzoic acid	Acros Organics	Dried for two days at 333 K	0..998
4-Chlorobenzoic acid	Acros Organics	Dried for two days at 333 K	0..998
3,5-Dinitrobenzoic acid	Aldrich Chemical Company	Dried for two days at 333 K	0..998

3,5-Dinitro-2-methylbenzoic acid	Aldrich Chemical Company	Dried for two days at 333 K	0..998
2-Hydroxybenzoic acid	Aldrich Chemical Company	Dried for two days at 333 K	0..998
3-Hydroxybenzoic acid	Acros Organics	Dried for two days at 333 K	0..998
2-Methoxybenzoic acid	Aldrich Chemical Company	Dried for two days at 333 K	0..998
4-Methoxybenzoic acid	Aldrich Chemical Company	Dried for two days at 333 K	0..998
2-Methylbenzoic acid	Aldrich Chemical Company	Dried for two days at 333 K	0.998
3-Methylbenzoic acid	Aldrich Chemical Company	Dried for two days at 333 K	0..998
3-Methyl-4-nitrobenzoic acid	Aldrich Chemical Company	Dried for two days at 333 K	0.998
4-Methyl-3-nitrobenzoic acid	Aldrich Chemical Company	Dried for two days at 333 K	0..998
3-Nitrobenzoic acid	Aldrich Chemical Company	Dried for two days at 333 K	0..998
4-Nitrobenzoic acid	Acros Organics	Dried for two days at 333 K	0..998
Toluene	Aldrich Chemical Company	None	0.998, anhydrous
Sodium methoxide, 25 mass % solution in methanol	Aldrich Chemical Company	None	
2-Propanol	Aldrich Chemical Company	None	0.99

Solubilities of the crystalline organic compounds in methyl butyrate were determined using a static, spectrophotometric method. The experimental methodology that we use has been given in many of our earlier publications [8-12], and to conserve journal space will only be briefly described in this communication. Clear aliquots of the saturated solutions were transferred by syringe into weighed volumetric flasks after the samples had equilibrated in a constant temperature water bath at 298.15 ± 0.05 K for at least three days with periodic agitation to facilitate dissolution and mixing. The volumetric flasks containing the transferred aliquots were weighed on an electronic analytical balance. The transferred solutions were diluted quantitatively with 2-propanol. Absorbances of the diluted solutions and of the nine standard solutions of known solute concentrations were recorded on a Milton Roy Spectronic 1000 Plus spectrophotometer (Milton Roy, Rochester, NY, USA). The concentration of each diluted solution was calculated from a Beer-Lambert law graph of absorbance versus concentration curve obtained from the measured absorbances of nine standard solutions. The analysis wavelengths and concentration ranges used for each solute have been given in our earlier publications [10, 35, 39-60].

Molar concentrations of the diluted samples deduced from the Beer-Law law graph were converted into mole fraction solubilities using the mass of the sample analyzed, molar masses of the solvent and the respective solutes, volume of the volumetric flasks, and any dilutions that were needed in order to place the measured absorbances on the Beer-Lambert law curve. We checked for possible solvate formation by determining the melting point temperature of the equilibrated solid phases recovered from the saturated solutions after the solubility measurements of each solute were completed. The melting point temperature of each equilibrated solid phase was within ± 0.5 K of the melting point temperature of the commercial sample or recrystallized compound prior to being in contact with the methyl butyrate solvent.

The experimental mole fraction solubilities, $X_{S,\mathrm{organic}}^{\mathrm{exp}}$, of the crystalline organic solutes in methyl butyrate are tabulated in the second and fourth columns of Table 2. The numerical values represent the average of 4 to 10 independent experimental determinations, which were reproducible to within ± 2 % (relative error). To the best of our knowledge there are no published solubility data for these organic solutes in methyl butyrate that we can compare our experimental values against. The only published solubility data that we were able to find for organic compounds dissolved in methyl butyrate were values previously published by Acree and coworkers [8, 9, 12, 34-37].

Table 2. Mole Fraction Solubilities, $X_{S,organic}^{exp}$, of 27 Crystalline Organic Compounds Dissolved in Methyl Butyrate at a Temperature of 298.15 K

Crystalline Organic Compound	$X_{S,organic}^{exp}$
1-Chloroanthraquinone	0.007890
Phenothiazine	0.05399
trans-Stilbene	0.05369
Benzil	0.1476
Fluoroanthene	0.1017
Xanthene	0.1192
2-Ethylanthraquinone	0.05008
Diphenylsulfone	0.04092
Salicylamide	0.06269
Benzoin	0.01183
Ferrocene	0.04560
Benzoic acid	0.1574
4-*tert*-Butylbenzoic acid	0.05604
2-Chloro-5-nitrobenzoic acid	0.05518
4-Chlorobenzoic acid	0.009674
3,5-Dinitrobenzoic acid	0.03143
3,5-Dinitro-2-methylbenzoic acid	0.02532
2-Hydroxybenzoic acid	0.1122
3-Hydroxybenzoic acid	0.04003
2-Methoxybenzoic acid	0.04882
4-Methoxybenzoic acid	0.009874
2-Methylbenzoic acid	0.1389
3-Methylbenzoic acid	0.1254
3-Methyl-4-nitrobenzoic acid	0.01391
4-Methyl-3-nitrobenzoic acid	0.02683
3-Nitrobenzoic acid	0.08759
4-Nitrobenzoic acid	0.008404

3. Development of Abraham Model Correlations for Solute Transfer into Methyl Butyrate

The Abraham solvation parameter model describes solute transfer in terms of molarity-based partition coefficients and molar solubility ratios. The experimental solubility data that is tabulated in Table 2 are given in terms of mole fractions and must be converted to molar solubilities in order to be used in our subsequent regression analyses. Mole fraction based solubilities are converted into molar solubilities by dividing $X_{\mathrm{S,organic}}^{\mathrm{exp}}$ by the ideal molar volume of the saturated solution:

$$C_{\mathrm{S,organic}}^{\mathrm{exp}} \approx X_{\mathrm{S,organic}}^{\mathrm{exp}}/[X_{\mathrm{S,organic}}^{\mathrm{exp}}\, \mathrm{V}_{\mathrm{Solute}} + (1 - X_{\mathrm{S,organic}}^{\mathrm{exp}})\, \mathrm{V}_{\mathrm{Solvent}}] \qquad (3)$$

The numerical values used for the molar volumes of the hypothetical subcooled liquid solutes are given in our earlier publications [10, 31, 32, 35, 39-66], along with the aqueous molar solubilities, $C_{\mathrm{S,water}}$, and solute molar gas concentrations, $C_{\mathrm{S,gas}}$, needed in calculating the two molar solubility ratios. The mole fraction solubilities of anthracene [34], pyrene [34], 4-chloro-3-nitrobenzoic acid [34, 35], acetylsalicylic acid [34, 36], thioxanthen-9-one [34], 3,4-dimethoxybenzoic acid [12], 3,4,5-trimethoxybenzoic acid [8], 3,4-dichlorobenzoic acid [37] and o-acetoacetanisidide [9]that were retrieved from the published literature were similarly converted to molar solubilities and molar solubility ratios.

Thirty six Abraham model expressions can be constructed for solute transfer into methyl butyrate from the log ($C_{\mathrm{S,organic}}/C_{\mathrm{S,water}}$) values just calculated. An additional 36 Abraham model expressions can be constructed for solute transfer into methyl butyrate from the gas phase from the log ($C_{\mathrm{S,organic}}/C_{\mathrm{S,gas}}$) values. Each set of thirty six Abraham model equations contain the six respective methyl butyrate solvent coefficients. Two additional Abraham model equations can be generated from methyl butyrate's water-to-methyl butyrate partition coefficient, log P, and from methyl butyrate's gas-to-methyl butyrate partition coefficient, log K. These two partition coefficients are calculated from:

$$\text{Log } K = \log (\text{RT}/V_{\text{methyl butyrate}}\, P_{\text{methyl butyrate}}) \tag{4}$$

$$\text{Log } P = \log (\text{RT}/V_{\text{methyl butyrate}}\, P_{\text{methyl butyrate}}) - 2.08 \tag{5}$$

where R is the universal gas constant, $V_{\text{methyl butyrate}}$ is the molar volume of the methyl butyrate solvent, $P_{\text{methyl butyrate}}$ is the vapor pressure of neat methyl butyrate at 298.15 K, and the value of 2.08 is the logarithm of methyl butyrate's gas-to-water partition coefficient. The numerical values of log (K or $C_{\text{S,organic}}/C_{\text{S,gas}}$) and log ($P$ or $C_{\text{S,organic}}/C_{\text{S,water}}$) are listed in the eighth and ninth columns of Table 3. Also tabulated in Table 3 are the solute descriptors for the 37 organic compounds considered in the current study.

Table 3. Experimental log (K or $C_{\text{S,organic}}/C_{\text{S,gas}}$) and log ($P$ or $C_{\text{S,organic}}/C_{\text{S,water}}$) Data for Solutes Dissolved in Methyl Butyrate at 298.15 K

Solute	**E**	**S**	**A**	**B**	**L**	**V**	Log K^a	log P^b
Phenothiazine	1.890	1.560	0.310	0.300	8.389	1.4789	10.168	4.765
1-Chloroanthraquinone	1.900	1.790	0.000	0.570	9.171	1.6512	10.411	4.377
Anthracene	2.290	1.340	0.000	0.280	7.568	1.4544	8.174	5.144
trans-Stilbene	1.350	1.210	0.000	0.230	7.456	1.5630	8.230	5.815
Fluoranthene	2.377	1.550	0.000	0.240	8.827	1.5850	9.301	5.851
Pyrene	2.808	1.710	0.000	0.280	8.833	1.5850	9.313	5.813
Benzil	1.445	1.590	0.000	0.620	7.611	1.6374	8.994	4.124
Methyl butanoate	0.106	0.600	0.000	0.450	2.893	0.8880	3.703	1.623
Xanthene	1.502	1.070	0.000	0.230	7.153	1.4152	7.712	5.212
Benzoic acid	0.730	0.900	0.590	0.400	4.657	0.9317	6.834	1.694
Acetylsalicylic acid	0.781	1.690	0.710	0.670	6.279	1.2879	9.594	1.094
4-*tert*-Butylbenzoic acid	0.730	1.111	0.551	0.443	6.547	1.4953	8.801	3.578
4-Chlorobenzoic acid	0.840	1.020	0.630	0.270	4.947	1.0541	7.287	2.487
3,4-Dichlorobenzoic acid	0.950	0.920	0.670	0.260	5.623	1.1766	7.812	3.066
2-Chloro-5-nitrobenzoic acid	1.250	1.400	0.670	0.460	6.513	1.2283	9.218	2.268
4-Chloro-3-nitrobenzoic acid	1.250	1.470	0.700	0.440	6.685	1.2283	9.535	2.324
2-Methoxybenzoic acid	0.899	1.410	0.450	0.620	5.636	1.1313	7.982	1.182
4-Methoxybenzoic acid	0.899	1.250	0.620	0.520	5.741	1.1313	8.435	1.735
3,4-Dimethoxybenzoic acid	0.950	1.646	0.570	0.755	6.746	1.3309	9.714	1.267
3,4,5-Trimethoxybenzoic acid	1.001	1.760	0.603	0.850	7.711	1.5309	10.841	1.586
2-Methylbenzoic acid	0.730	0.840	0.420	0.440	4.677	1.0726	6.440	2.140

3-Methylbenzoic acid	0.730	0.890	0.600	0.400	4.819	1.0726	7.156	2.176
3-Methyl-4-nitrobenzoic acid	1.040	1.336	0.525	0.500	6.266	1.2468	8.678	2.314
4-Methyl-3-nitrobenzoic acid	1.040	1.461	0.659	0.521	6.434	1.2468	9.311	2.064
3-Nitrobenzoic acid	0.990	1.180	0.730	0.520	5.601	1.1059	8.493	1.563
4-Nitrobenzoic acid	0.990	1.520	0.680	0.400	5.770	1.1059	8.746	1.846
3,5-Dinitro-2-methylbenzoic acid	1.310	2.120	0.750	0.650	8.040	1.4210	11.898	1.942
Thioxanthen-9-one	1.940	1.441	0.000	0.557	8.436	1.5357	9.152	4.084
Benzoin	1.585	2.115	0.196	0.841	9.159	1.6804	11.412	2.681
Diphenylsulfone	1.570	2.150	0.000	0.700	8.902	1.6051	10.576	3.186
Ferrocene	1.394	0.900	0.000	0.230	6.003	1.2043	6.337	4.217
o-Acetoacetanisidide	1.190	2.333	0.264	1.025	8.563	1.6108	11.505	1.271
Salicylamide	1.160	1.650	0.630	0.480	5.910	1.0315	9.173	1.488
2-Ethylanthraquinone	1.410	1.545	0.000	0.557	8.781	1.8106	9.972	5.158
3,5-Dinitrobenzoic acid	1.250	1.630	0.700	0.590	6.984	1.2801	10.154	1.854
2-Hydroxybenzoic acid	0.900	0.850	0.730	0.370	4.732	0.9904	7.270	1.910
3-Hydroxybenzoic acid	0.910	0.880	0.860	0.580	4.860	0.9904	7.808	0.808

[a] For the crystalline solutes the experimental value is log ($C_{S,organic}/C_{S,gas}$).

[b] For the crystalline solutes the experimental value is log ($C_{S,organic}/C_{S,water}$).

The solutes included in the log (P or $C_{S,organic}/C_{S,water}$) and log ($K$ or $C_{S,organic}/C_{S,gas}$) data sets are crystalline compounds, except for methyl butyrate. We were not able to find any solubility data for gaseous solutes dissolved in methyl butyrate or any infinite dilution activity coefficient data for liquid solutes dissolved in methyl butyrate that could be used calculate partition coefficients. Despite this minor shortcoming the solutes included in the two data sets do cover a wide range of solute polarities and hydrogen-bonding capability, including several fairly strong H-bond donors (3-hydroxybenzoic acid, **A** = 0.860; 3,5-dinitro-2-methylbenzoic acid, **A** = 0.750; 3-nitrobenzoic acid, **A** = 0.730; 2-hydroxbenzoic acid, **A** = 0.730) and several fairly strong H-bond acceptors (o-acetoacetanisidide, **B** = 1.025; 3,4,5-trimethoxybenzoic acid, **B** = 0.850; benzoin, **B** = 0.841).

Regression analysis of the experimental values yielded the following two Abraham model expressions:

$$\log (P \text{ or } C_{S,organic}/C_{S,water}) = 0.238(0.141) + 0.368(0.060)\,\mathbf{E} - 0.538(0.090)\,\mathbf{S} - 1.031(0.079)\,\mathbf{A} - 4.623(0.163)\,\mathbf{B} + 4.253(0.131)\,\mathbf{V} \quad (6)$$

(with N = 37, SD = 0.088, R^2 = 0.997, F = 1868)

$$\log (K \text{ or } C_{S,organic}/C_{S,gas}) = 0.201(0.118) - 0.502(0.063)\,\mathbf{E} + 1.290(0.089)\,\mathbf{S} + 2.469(0.078)\,\mathbf{A} + 0.958(0.034)\,\mathbf{L} \quad (7)$$

(with N = 37, SD = 0.099, R^2 = 0.996, F = 2148)

where the standard error (at the 95 % level) in each calculated equation coefficients is reported within the parenthesis immediately following the respective equation coefficient. Each regression analysis was performed using the commercial IBM SPSS Statistical 22 software. The statistical information associated with each correlation includes the number of experimental data points used in the regression analysis (N), the standard deviation (SD), the squared correlation coefficient (R^2) and the Fisher F-statistic (F). As an informational note the $b_k \cdot \mathbf{B}$ was removed from Eqn. 7 because methyl butyrate lacks an acidic hydrogen and therefore cannot act as a hydrogen-bond donor. The $b_k \cdot \mathbf{B}$ term was retained in Eqn. 6, however, as the expression pertains to solute transfer into methyl butyrate from water. Here the b_k equation coefficient represents the difference in the acidity of methyl butyrate and water, which does possess two acidic hydrogens.

Examination of the associated statistical information reveals that both Abraham model expressions provide a reasonably accurate mathematical description of the observed solubility data as evidenced by near-unity squared correlation coefficients and small standard deviations on the order of SD = 0.099 log units or less. Figures 1 and 2 provide a visual summary of the descriptive ability of our derived Abraham model correlations for solute transfer into the methyl butyrate solvent. In the case of the log (K or $C_{S,organic}/C_{S,gas}$) data the numerical values span a range of approximately 8.2 log units, from log (K or $C_{S,organic}/C_{S,gas}$) = 3.703 for methyl butyrate to log (K

or $C_{\mathrm{S,organic}}/C_{\mathrm{S,gas}}$) = 11.898 for 3,5-dinitro-2-methylbenzoic acid. A slightly smaller range of 5.0 log units was noted for the log (P or $C_{\mathrm{S,organic}}/C_{\mathrm{S,water}}$) data.

4. Conclusion

Correlations based on the Abraham solvation parameter model have been found to provide reasonably accurate mathematical descriptions of solute transfer into methyl butyrate. Standard deviations between the experimental solubility ratios, log ($C_{\mathrm{S,organic}}/C_{\mathrm{S,water}}$) and log ($C_{\mathrm{S,organic}}/C_{\mathrm{S,gas}}$), of the 37 compounds considered in the current study and back-calculated values based on the Abraham model were SD = 0.088 and SD = 0.099 log units for Eqns. 6 and 7, respectively. Based on our more than 15 years of experience using the Abraham model we fully expect that Eqns. 6 and 7 will permit researchers to obtain good estimates of the solubility of additional organic compounds dissolved in methyl butyrate, provided that the solute descriptors of the range of values used in deriving the two predictive expressions. As a cautionary note we remind readers only a single liquid solute and no gaseous solutes were included in developing our Abraham model correlations. The correlations will likely need to be updated in future years when solubility data and activity coefficient data becomes available for gaseous and liquid solutes dissolved in methyl butyrate. The dataset given in the current communication will provide a good starting for any future updating of the methyl butyrate Abraham model correlations.

Acknowledgements

The authors acknowledge the National Science Foundation's Research Experiences for Undergraduates (REU) program (CHE-1757946) for supporting Estefania Garcia's participation in this research. Ellen Qian, Anisha Wadawadigi, Olivia Zha, Kelly Liu, Jingyi Dai, Shrika Eddula and Carina Jiang thank the University of North Texas Texas Academy of Mathematics and Science (TAMS) program for providing a summer research scholarship to each student.

Disclosure statement

No potential conflict of interest was reported by the authors.

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Figure 1

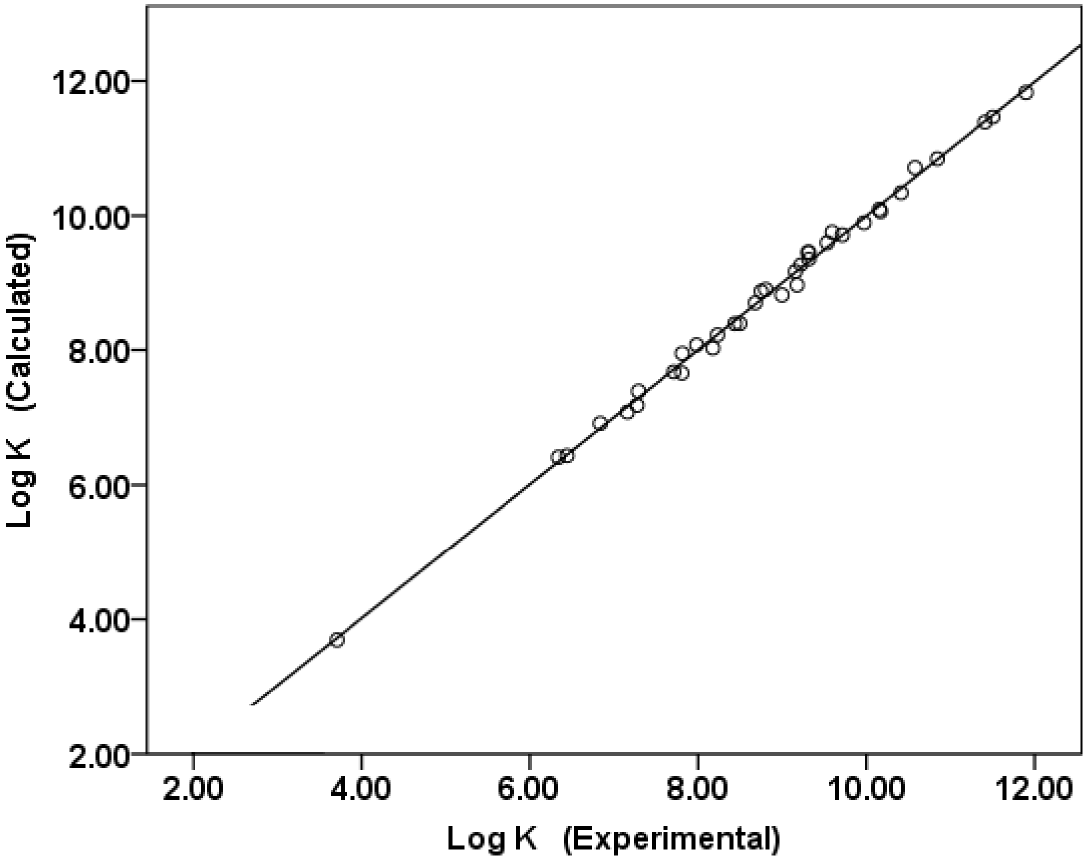

Figure 1. Graphical comparison of experimental log (*K* or $C_{S,organic}/C_{S,gas}$) data for nonelectrolyte organic solutes dissolved in methyl butyrate and back-calculated values based on Eqn. 7.

Figure 2

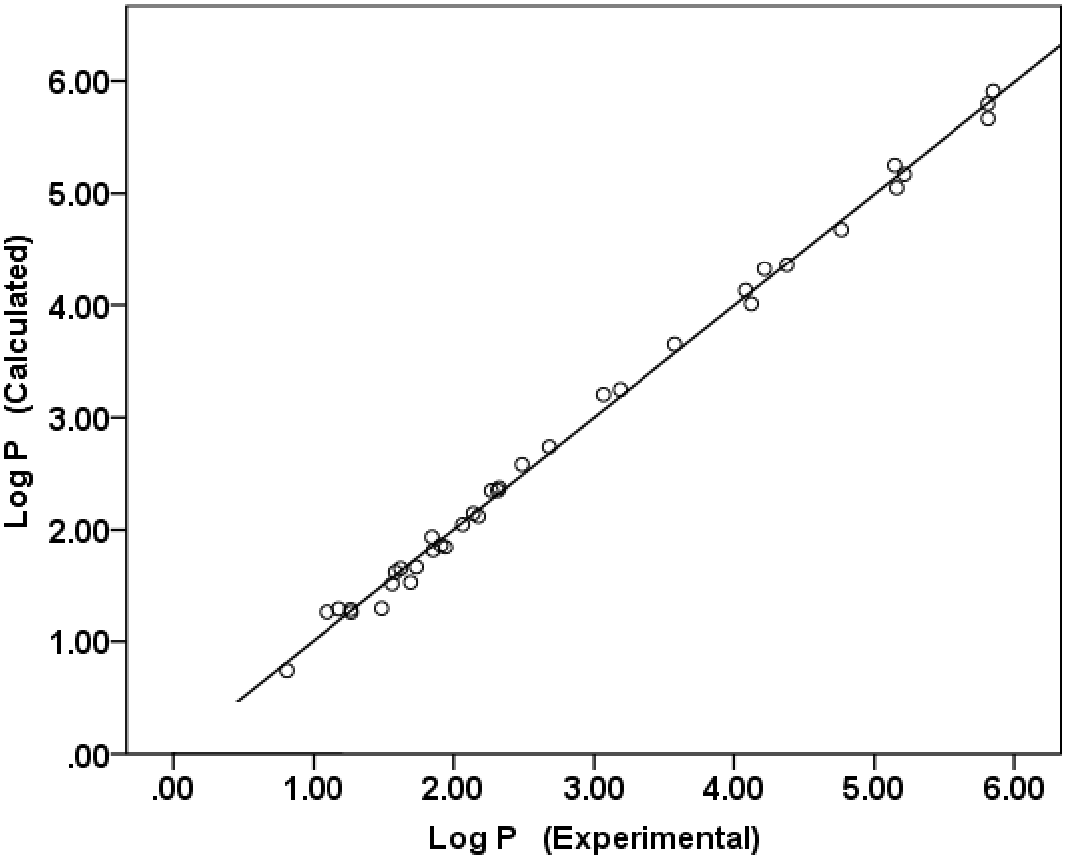

Figure 2. Graphical comparison of experimental log (*P* or $C_{\mathrm{S,organic}}/C_{\mathrm{S,water}}$) data for nonelectrolyte organic solutes dissolved in methyl butyrate and back-calculated values based on Eqn. 6.