The partition of organic compounds from water into the methyl isobutyl ketone extraction solvent with updated Abraham model equation

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Abstract

Experimental water-to-methyl isobutyl ketone partition coefficients have been determined for 27 different organic solutes based on gas chromatographic measurements. Updated Abraham model correlations were determined for describing solute transfer into methyl isobutyl ketone by combining the measured partition coefficient data determined in the present study with published experimental values taken from chemical and engineering literature. One hundred eighteen compounds were used in determining the revised Abraham model correlations. After calculations, the revised mathematical correlations were found to match the experimental data to within an overall average standard deviation of 0.21 log units.

Key Words and Phrases

Partition coefficient; Abraham model correlations; Extraction; Methyl isobutyl ketone extraction solvent

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1. Introduction

Sample preparation is an important step in analytical method development, particularly in the case of complex unknown samples containing low analyte concentrations. For such samples liquid-liquid extraction affords a convenient means both to concentrate the analyte and to isolate the analyte from chemical interferences that might prevent accurate quantification. Extractions involve the equilibrium partitioning of solute(s) between two immiscible (or partly miscible) liquid phases. Molecular interactions determine the solute's affinity for each of the liquid phases that comprise the two-phase extraction system. Ideally one would like to identify an extraction system that would completely remove the analyte using a small volume of liquid solvent, while leaving all chemical interferences in the other liquid phase. Extractions can generate considerable volumes of hazardous organic solvent that are harmful to the environment. To reduce environmental impact, workplace safety concerns and disposal costs the selection of an eco-friendly and benign extraction system is preferred. The more traditional petroleum-based organic solvents that are currently used in analytical chemistry are now slowly being replaced by ionic liquid solvents (ILs), deep eutectic solvents (DES) and natural deep eutectic solvents (NADES), and bio-derived solvents that are recyclable, exhibit lower toxicity and/or are more biodegradable [1].

Solvent selection depends to a large extent on the specific extraction method that will be utilized. Ionic liquid solvents are employed in vapor-phase headspace micro-drop extractions and in single-drop liquid-liquid micro-extractions [1]. The ionic liquid's high surface tension, high viscosity and low aqueous solubility helps to maintain the drop stability, and in the case of dispersive liquid-phase micro-extractions, the IL properties facilitate rapid drop reformation once the dispersing influence is removed. Bio-derived organic solvents have been used in traditional extraction processes for the removal of phenolic compounds and pollutants from waste water samples, for removal of natural products from biomass feedstocks, and for isolation of synthesized medicinal and pharmaceutical compounds from undesired reaction byproducts. Published papers have discussed in greater detail solvent selection guidelines [2-7] and the utilization of green, environmentally friendly organic solvents in practical liquid-liquid extractions [1, 8-11].

Our contribution to solvent selection for chemical separation processes has been two-fold. First we have experimentally determined gas chromatographic retention factors and infinite dilution activity coefficients, γ_i^∞, of organic solutes dissolved in numerous IL stationary phase solvents [12-32]. The measured chromatographic data have been used to solve several practical chemical separation problems and to develop Abraham model correlations that analytical chemists can use to estimate separation factors and γ_i^∞ values for additional organic solutes. To date, we have reported Abraham model correlations for more than 80 different IL solvents [12-32]. Second, we have used published water-to-organic solvent partition coefficients, P, and molar solubility ratios to develop predictive Abraham model correlations that describe solute transfer into more than 100 different organic mono-solvents of varying polarity and hydrogen-bonding character [33-47]. The different partition/extraction systems studied include many of the organic mono-solvents currently used in industrial manufacturing processes, as well as several compounds found on lists of recommended environmentally friendly solvents. Knowledge of the solubilizing properties of both solvent types is required in order to identify suitable replacement solvents.

Our recent publication [42] reported the Abraham model correlation for the water-to-2,2,5,5-tetramethyloxolane partition system based on direct experimental partition coefficient data for 59 organic solutes. Unlike other greener ether solvents (such as 2,5-dimethyltetrahydrofuran and methyl cyclopentyl ether) 2,2,5,5-tetramethyloxolane is inherently resistant to peroxide formation due to the lack of any alpha-hydrogen atoms adjacent to ether oxygen moiety. Principle

Component Analysis based on the Abraham model solvent coefficients revealed that the general solvation properties of 2,2,5,5-tetramethyloxolane were very close to those of both toluene and chlorobenzene. The green solvent 2,2,5,5-tetramethyloxolane can replace the solvents toluene and/or chlorobenzene, certainly as far as partition-related processes are concerned.

In the present study we have measured water-to-methyl isobutyl ketone (MIBK) partition coefficients of 27 different organic compounds at an ambient room temperature of T = 293 K using a gas chromatographic method of analysis. Methyl isobutyl ketone is often used as an extraction solvent for the removal and pre-concentration of metal ions as metal chelates from aqueous solutions prior to spectroscopic analysis [48-51]. Results of our partition coefficient measurements, combined with published values taken from the chemical literature [52-61], are used to update our existing Abraham model correlations for the water-MIBK partition system. Our existing correlation [52] was reported ten years ago and was based on the partition coefficient data available at that time. The revised Abraham model correlations are based on a much larger database that includes an additional 28 experimental values. A total of 119 partition coefficients were used in developing our updated Abraham model correlation for solute transfer into the water-saturated MIBK extraction solvent.

2. Experimental Section

Methyl isobutyl ketone (Sigma-Aldrich Chemical Company, Saint Louis, Missouri, USA, ≥0.995 purity, HPLC grade) was used without further purification. The 27 organic solutes were purchased from commercial sources. The chemical suppliers and mass fraction chemical purities are listed in Table 1.

The concentration of solute partitioned between MIBK and water was determined using gas chromatography. A small amount of solute was added to equal volumes of MIBK:water in sealed glass vials. Samples were vortexed and allowed to equilibrate for at least 2 hours at ambient room temperature of 293 ± 1.0 K. After equilibration was established, the partitioned layers were quantitatively analyzed for the solute's peak area in triplicate for gas chromatographic analysis with a flame ionization detector.

Three gas chromatograph systems were used for data collection as following: Agilent Intuvo 9000 Gas Chromatograph System (Agilent, Santa Clara, California, USA), Shimadzu GC-2010 Plus (Shimadzu Scientific Instruments, Columbia, Maryland, USA) and Shimadzu Nexis GC-2030 (Shimadzu Scientific Instrments). A non-polar stationary phase of 5% phenyl methylpolysiloxane of varying manufactures and dimensions was used in each gas chromatograph system. The Agilent Intuvo 9000 Gas Chromatograph System used a HP-5ms (Agilent) with dimensions (length, column I.D. and film thickness) of 30 m, 0.32 mm and 0.25 µm, respectively. The Shimadzu GC-2010 Plus and Nexis GC-2030 used a SH-Rtx-5 (Shimadzu Scientific Instruments) with dimensions (length, column I.D. and film thickness) of 30 m, 0.32 mm and 1.00 µm, respectively. Chromatographic analysis of the partitioned layers for each partitioned solute was performed using the same experimental conditions. All chromatographic methods had the inlet and detector temperature set at 240 °C and used helium as the carrier gas. The oven temperature varied since it was optimized for chromatographic separation for each solute. Experimental logarithms of partition coefficients of the 27 solutes in this study, tabulated in Table 2, were obtained by taking the logarithm of the average individual partition coefficients that were calculated by dividing the solute peak area in MIBK by the solute peak area in water.

Table 1: Tabulation of chemical solutes and their suppliers and mass fraction purities.

Solute	Supplier	Mass fraction purity

2-Methyl-2-propanol	Sigma-Aldrich Chemical Company, Milwaukee, Wisconsin, USA	0.995+
2-Propanol	Fisher Chemical	0.999+, HPLC grade
1-Propanol	Alfa Aesar, Ward Hill, Massachusetts, USA	0.999
2-Butanol	Aldrich Chemical Company, Milwaukee, Wisconsin, USA	0.995
2-Methyl-2-butanol	Acros Organics, Morris Plains, New Jersey, USA	0.99
2-Methyl-1-propanol	Sigma-Aldrich Chemical Company	0.995
3-Methyl-3-pentanol	Sigma-Aldrich Chemical Company	0.995
3-Methyl-1-butanol	Sigma-Aldrich Chemical Company	>0.99
1-Pentanol	Sigma-Aldrich Chemical Company	>0.99
2-Butoxyethanol	Acros Organics	0.99
2-Ethyl-1-hexanol	Acros Organics	0.99
Benzyl alcohol	Acros Organics	0.99
2-Aminophenol	Acros Organics	0.99
2-Isopropoxyethanol	Aldrich Chemical Company	0.99
2-Propoxyethanol	Sigma-Aldrich Chemical Company	0.994
2-Ethoxyethanol	Aldrich Chemical Company	0.99
1-Heptanol	Thermo-Fischer Scientific Company, Waltham, Massachusetts, USA	0.99
1-Hexanol	Alfa Aesar	0.99+
2-Ethyl-1-butanol	Aldrich Chemical Company	0.98
Cyclohexanone	Aldrich Chemical Company	0.998
Acetophenone	Fisher Scientific, Waltham, Massachusetts, USA	0.997[a]
Butanone	Ashland Chemical Company	0.99[a], Reagent grade
Acetone	Fisher Chemical	0.995+, ACS grade
2-Hexanone	Aldrich Chemical Company	0.99+
Ethyl acetate	J.T. Baker Inc., Phillipsburg, New Jersey, USA	0.999, Spectrophotometric grade
Methyl benzoate	Matheson Coleman & Bell, East Rutherford, New Jersey, USA	0.955[a]
Ethyl benzoate	Alfa Aesar Chemical Company	0.99

[a] Analyzed in this work by gas chromatography.

Table 2: Logarithm of the water-MIBK partition coefficients of organic solutes at 293 ± 1.0 K.

Solute	log *P*

2-Methyl-2-propanol	0.021
2-Propanol	-0.271
1-Propanol	0.032
2-Butanol	0.318
2-Methyl-2-butanol	0.552
2-Methyl-1-propanol	0.721
3-Methyl-3-pentanol	1.117
3-Methyl-1-butanol	1.052
1-Pentanol	1.254
2-Butoxyethanol	0.542
2-Ethyl-1-hexanol	3.059
Benzyl alcohol	1.362
2-Aminophenol	1.025
2-Isopropoxyethanol	-0.367
2-Propoxyethanol	-0.061
2-Ethoxyethanol	-0.723
1-Heptanol	2.457
1-Hexanol	1.900
2-Ethyl-1-butanol	1.827
Cyclohexanone	1.184
Acetophenone	2.131
Butanone	0.601
Acetone	-0.089
2-Hexanone	1.102
Ethyl acetate	1.018
Methyl benzoate	2.493
Ethyl benzoate	3.024

3. Results and Discussion

The Abraham solvation parameter model is based on two linear free energy relationships that describe the logarithm of the water-to-organic solvent partition coefficient, log *P*:

$$\log P = c_p + e_p \cdot \mathbf{E} + s_p \cdot \mathbf{S} + a_p \cdot \mathbf{A} + b_p \cdot \mathbf{B} + v_p \cdot \mathbf{V} \qquad (1)$$

and the logarithm of the gas-to-organic solvent partition coefficient, log *K*:

$$\log K = c_k + e_k \cdot \mathbf{E} + s_k \cdot \mathbf{S} + a_k \cdot \mathbf{A} + b_k \cdot \mathbf{B} + l_k \cdot \mathbf{L} \qquad (2)$$

as the product of solute property times the complementary solvent property. Solute properties (referred to as solute descriptors) are defined as follows: the solute excess molar refractivity expressed in units of $(\text{cm}^3\ \text{mol}^{-1})/10$ (**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 $(\text{cm}^3\ \text{mol}^{-1})/100$ (**V**); and the logarithm of the gas-to-hexadecane partition coefficient at 298 K (**L**). The complementary solvent properties, indicated by the lowercase alphabetic characters on the right-hand side of Eqns. 1 and 2, are deduced by multi-linear regression analysis of experimental log P and log K data in accordance with the two Abraham model expressions. In the case of indirect partitioning processes involving an organic solvent that is completely miscible with water, the partition coefficient is estimated from molar solubility ratio defined as the molar solubility of the solute in the organic solvent divided by the molar solubility of the solute in water.

Principle Component Analysis based on the numerical values of the solvent properties (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) allows one to identify solvents having similar and/or dissimilar solubilizing properties, and to compare direct water-saturated organic solvent partition systems to their indirect anhydrous counterparts. Presence of large quantities of water in the organic solvent can significantly affect the polarity and hydrogen-bonding character as we have previously observed for water-saturated diethyl ether versus anhydrous diethyl ether [62], water-saturated ethyl acetate versus anhydrous ethyl acetate [63], water-saturated butanone versus anhydrous butanone [52], and other select organic solvents. Water-saturated organic solvent partition systems are denoted as “wet” in our published Abraham model correlations, while anhydrous organic solvent partition systems are indicated as “dry”. The very nature of liquid-liquid extractions requires that the equilibrium organic and aqueous phases be in physical contact with each other. The equilibrium organic phase will thus be saturated with water. For organic solvents that are completely immiscible with water (or which dissolve very small quantities of water) the solubilizing properties of the "wet" and "dry" partitioning processes are nearly identical.

The solubility of water in MIBK, about 0.85 M at 298.15 K [61, 64, 65], is likely sufficient to alter the solvent's solubilizing properties. Only direct experimental water-to-MIBK partition coefficient data will be used in developing the Abraham model correlations reported in the current study. Molar solubility ratios based on experimental solubilities in anhydrous MIBK would be needed to develop correlations for the dry water-to-MIBK partitioning process. Currently there is insufficient molar solubility data for solutes dissolved in MIBK to develop Abraham model correlations for dry MIBK.

Water-to-MIBK partition coefficients are converted to log K values by:

$$\log K = \log P + \log K_{\text{water}} \tag{3}$$

where K_{water} is the solute's gas-to-water partition coefficient, which is available for the different solutes considered in the current study [52, 62, 63, 66, 67]. We have tabulated in the eighth and ninth columns of Table S1 (Supplementary Material) the numerical values of log K and log P values for the 119 organic liquid and solid solutes that will be used to develop the Abraham model log P and log K correlations for solute transfer into MIBK. Also included in the tabulation are the references for the experimental partition coefficient data. To conserve journal space we have referenced the partition coefficient used in deriving our existing MIBK correlation equations to our earlier paper [52] that reported the correlations.

Our preliminary regression analysis of the experimental log *P* given in Table S1 in accordance with the Abraham model indicated that the experimental values for four compounds (methylamine, thenoyltrifluoroacetone, furfural, 4-hydroxyphenoxyacetic acid) appeared to be outliers as evidenced by large differences between the experimental data and values back-calculated by the preliminary Abraham model correlation. These four compounds were eliminated from the dataset. Our final regression analyses yielded the following two Abraham model correlations:

$$\log P = 0.292(0.055) + 0.832(0.059)\,\mathbf{E} - 0.771(0.064)\,\mathbf{S} - 0.122(0.050)\,\mathbf{A} - 4.534(0.091)\,\mathbf{B} + 3.901(0.062)\,\mathbf{V} \quad (4)$$

(with N = 119, SD = 0.199, R^2 = 0.984, F = 1378)

and

$$\log K = 0.134(0.053) + 0.257(0.074)\,\mathbf{E} + 1.016(0.065)\,\mathbf{S} + 3.442(0.052)\,\mathbf{A} + 0.328(0.096)\,\mathbf{B} + 0.844(0.018)\,\mathbf{L} \quad (5)$$

(with N = 118, SD = 0.207, R^2 = 0.996, F = 5082)

The correlations were obtained using the IBM SPSS Statistical 22 commercial software. The statistical information pertaining to each correlation is given below the respective correlation, where N refers to the number of experimental data points used in determining the equation coefficients, SD is the standard deviation, R^2 corresponds to the squared correlation coefficient, and F represents the Fisher F-statistic. Standard errors in the equation coefficients (at 95 % level) are given in parenthesis after the coefficient itself.

As noted in the introduction the more traditional petroleum-based organic solvents that are currently used in analytical chemistry are now slowly being replaced by more environmentally friendly organic solvents. Identification of a replacement solvent is not an easy task and involves finding a nontoxic solvent with suitable physical and solubilizing properties for a given application. Solubilizing properties are extremely important in liquid-liquid extraction as it is the solute(s) affinity for each of the two phases that comprise the partition system that determines whether or not the extraction will be successful. A major advantage that the Abraham model offers over the solution models that other research groups are using to mathematically describe experimental log *P* and log *K* data is that the derived correlations can be used to predict partition coefficients of many additional organic, organometallic and inorganic solutes dissolved in the given solvent media. An indication of the ability of Eqns. 4 and 5 to estimate partition coefficients and solubility ratios can be obtained by examining each correlation's ability to describe the 119 experimental values given in Table S1. The small standard deviations, SD = 0.199 log units and SD = 0.207 log units, and near unity squared correlation coefficients, $R^2 = 0.984$ and $R^2 = 0.996$, indicate that Eqs. 4 and 5 provide reasonably accurate mathematical descriptions of the observed experimental data used in both regression analyses. Figures 1 and 2 present a graphical comparison of the experimental data versus back-calculated values based on Eqs. 4 and 5, respectively.

Equations 6 and 7 represent our earlier Abraham model expressions for solute transfer into MIBK:

$$\log P = 0.383 + 0.801\,\mathbf{E} - 0.831\,\mathbf{S} - 0.121\,\mathbf{A} - 4.441\,\mathbf{B} + 3.876\,\mathbf{V} \qquad (6)$$

(with N = 86, SD = 0.272, $R^2 = 0.977$, F = 676)

and

$$\log K = 0.244 + 0.183\,\mathbf{E} + 0.987\,\mathbf{S} + 3.418\,\mathbf{A} + 0.323\,\mathbf{B} + 0.854\,\mathbf{L} \qquad (7)$$

(with N = 86, SD = 0.257, $R^2 = 0.994$, F = 2523)

that were published ten years ago based on 32 fewer data points. Careful comparison of our revised and earlier correlations reveals that the additional log *P* and log *K* values did not significantly alter the calculated equation coefficients. This is to be expected whenever the correlation is constructed using a large database of chemically diverse solutes whose solute descriptors span a large range of numerical values as was the case in our earlier study and current study. From a predictive standpoint we prefer the updated correlations with the improved statistical information as evidenced by the lower standard and higher squared correlation coefficient.

In determining the revised Abraham model correlations we used only water-to-MIBK partition coefficient data based on direct liquid-liquid partitioning. We did not use any molar solubility ratios in the regression analysis. Molar solubility ratios are used in those instances where the organic solvent is completely miscible with water, or when the solubility of water in the organic solvent is extremely small and will not affect the organic solvent's solubilizing properties. Our unpublished mole fraction solubility data for benzoic acid ($x_{\text{solute}} = 0.1949$), 2-methylbenzoic acid ($x_{\text{solute}} = 0.1661$), 3-methylbenozic acid ($x_{\text{solute}} = 0.1670$), 3-nitrobenzoic acid ($x_{\text{solute}} = 0.1413$), 3,5-dinitrobenzoic acid (($x_{\text{solute}} = 0.05834$), 2-hydroxybenzoic acid ($x_{\text{solute}} = 0.1724$), and 2-chloro-5-nitrobenzoic acid ($x_{\text{solute}} = 0.1011$) were converted to molar solubilities and to molar solubility ratios, $C_{\text{solute,org solv}}/C_{\text{solute,water}}$, as described in several of our earlier publications [68-71]. The molar solubility ratios are defined as the molar solubility of the solute in the organic solvent, $C_{\text{solute,org solv}}$, divided by the molar solubility of the solute in water, $C_{\text{solute,water}}$. In Table 3 we have tabulated the experimental log $C_{\text{solute,MIBK}}/C_{\text{solute,water}}$ and the calculated log $C_{\text{solute,MIBK}}/C_{\text{solute,water}}$ based on Eqn. 4 assuming that log P = log $C_{\text{solute,org solv}}/C_{\text{solute,water}}$. This would be the assumption used for "dry" partitioning processes. For all seven carboxylic acid solutes the molar solubility ratio calculated based on Eqn. 4 is significantly larger than the experimental value, with the average difference between calculated and experimental value being 0.287 log units. Solute descriptors used in the calculations are given in several of our earlier publications [35-41]. The large difference between calculated and experimental values, combined with the observation that Eqn. 4 over-estimated the molar solubility ratios of seven carboxylic acids, further suggests that the solubilizing properties of "wet" MIBK are different than those of anhydrous ("dry") MIBK.

Table 3. Comparison of experimental logarithms of molar solubility ratios, log $C_{solute,MIBK}/C_{solute,water}$, and calculated values based on Eqn. 4.

Solute	log $C_{solute,MIBK}/C_{solute,water}$ (exp)	log $C_{solute,MIBK}/C_{solute,water}$ (Eqn. 4)
Benzoic acid	1.756	1.954
2-Methylbenzoic acid	2.183	2.390
3-Methylbenzoic acid	2.266	2.510
3-Nitrobenzoic acid	1.735	2.073
3,5-Dinitrobenzoic acid	2.083	2.309
2-Hydroxybenzoic acid	2.068	2.482
2-Chloro-5-nitrobenzoic acid	2.492	2.877

4. Summary

Updated Abraham solvation parameter model correlations have been determined for describing solute partitioning into wet MIBK from both water and from the gas phase. The derived log *P* and log *K* correlations are based on 119 and 118 experimental data points, respectively. The updated correlations provide a reasonably accurate mathematical description of the observed partitioning behavior of solutes into MIBK as documented by an overall standard deviation of 0.21 log units. Based on our past experience in using the Abraham model we expect that Eqns. 4 and 5 will provide reasonable predictions of the partition coefficients of additional organic compounds into MIBK, provided that the solute descriptor values of the additional compounds fall within the area of predictive chemical space range defined by the data sets used in deriving Eqns. 4 and 5.

Unpublished solubility data for seven carboxylic acid solutes dissolved in MIBK further suggest that the solubilizing properties of water-saturated MIBK and anhydrous MIBK are different.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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Figure 1

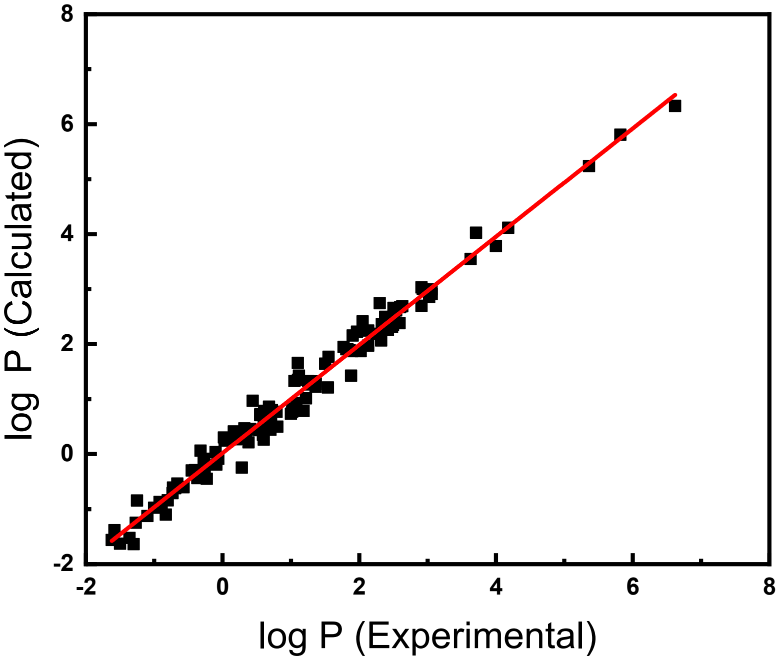

Figure 1. Comparison of the experimental log *P* data versus back-calculated values based on Eqn. 4.

Figure 2

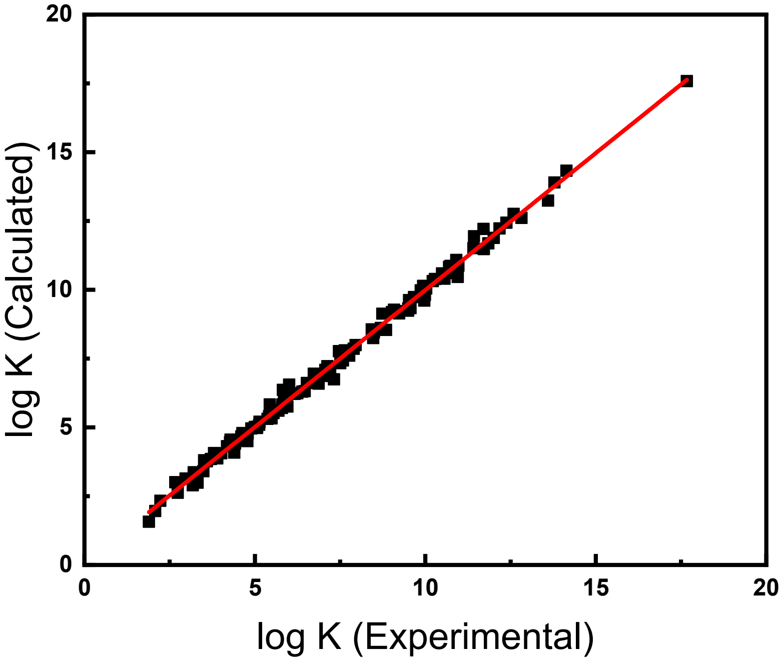

Figure 2. Comparison of the experimental log *K* data versus back-calculated values based on Eqn. 5.