Solubility of Phenylboronic Acid and its Cyclic Esters in Organic Solvents

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Abstract
The solubilities of phenylboronic acid, its pinacol ester and azaester in organic solvents (chloroform, 3-pentanone, acetone, dipropyl ether and methylcyclohexane) have been determined experimentally by a dynamic method, in which the disappearance of turbidity was determined by measuring of light intensity using a luminance probe. Phenylboronic acid has high solubility in ether and ketones, moderate in chloroform and very low in hydrocarbon. Pinacol ester and azaester show better solubility than the parent acid in all tested solvents. For pinacol ester differences between particular solvents are small, while for azaester the differences are significant. For both esters the highest solubility is observed in chloroform and the lowest in the hydrocarbon. The results have been correlated by the Wilson, NRTL and Redlich–Kister equations. For the phenylboronic acid better correlation of the data is obtained by polynomials in comparison with the above equations. It is connected with additional acid-anhydride equilibrium in the system. The influence of polarity of the solvents on the solubility is discussed.

Keywords Boronic acids · Boronic esters · Solubility · Redlich–Kister equation · Wilson equation · NRTL equation

1 Introduction
Arylboronic acids and their derivatives are an important group of compounds due to their broad applications in organic synthesis, catalysis, supramolecular chemistry, and materials engineering [1–4]. The compounds have been known for about 150 years, but increasing interest is observed after the discovery of new areas of their use. The most important fields are the synthesis of biaryl compounds in the Suzuki–Miyaura reaction (Nobel 2010) [5], the molecular receptors of sugars [6], covalent organic frameworks [7] and their use...

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as biologically active compounds [8]. Such wide applications require recognition of the physicochemical properties of these compounds. An important issue is the description of phase equilibria, including solubility in water and organic solvents. Knowledge of these data allows correct selection of the solvent for a particular reaction or for purification of the products by crystallization. They are also important for biological tests and formulation of biologically active compounds.

There is a need to find boronic acids that have good water solubility. This feature is important for the construction of molecular sugar receptors and the use of boronic acids as biologically active agents. Although it is known that substituents in phenylboronic acids significantly affect the solubility of these compounds in water, there is a surprisingly small number of solubility data in literature. Even for unsubstituted phenylboronic acid, only two values of its solubility in water are reported: “The solubility (g/100 g. of water) is approximately 1.1 at 0° and 2.5 at 25°; the solubility-temperature relationship is linear to at least 45°” [9]. One can also find some generalized and misleading statements in the literature such as “boronic acids are water soluble” [10] or “since the reactants are insoluble in water, this reaction is an > on water < reaction” [11]. Only recently, solubilities of several simple aryloboronic acid and benzoxaboroles in water were published [12]. It was found, that solubility of this class of compounds was low, with the value of 1.9 g/100 g H2O for phenylboronic acid at 20 °C and even lower for some substituted compounds. Solubility of 4-methoxyphenylboronic acid in water as a function of pH was also reported [13]. In addition, there are some examples of particular compounds well soluble in water. They are large molecules in which good solubility in water results from the presence of substituents in the fragment connected to the phenylboronic acid ring [14, 15].

The solubility of boron compounds in organic solvents is also important because of their very wide application in organic synthesis, e.g. in the Suzuki–Miyaura reaction. The choice of solvent significantly affects the efficiency and course of this reaction [16]. In many reactions boronic acid derivatives, e.g. esters or azaesters, can be used instead of the parent acids. These derivatives are easier to obtain in a pure state and have a stable composition in contrast to boronic acids, which may contain different amounts of anhydrides. Their applications in syntheses is a good alternative to boronic acids [17]. They are easy-to-use compounds, in which protecting groups can be removed from the product after completion of reaction. Knowledge of the solubility of such derivatives in typical organic solvents is therefore of great importance. However, there is a lack of such data in the literature.

There are several reasons why reliable solubility data for boronic acids are difficult to obtain in comparison with common organic compounds. One of them is an easy dehydration process of boronic acids with the formation of boroxines (Scheme 1).

![Scheme 1](image-url) Dehydration of phenylboronic acid with the formation of boroxine
As a result of this reaction, commercial boronic acids are mixtures of acid and anhydride containing variable amounts of both components. The equilibrium of the dehydration reaction depends on the substituents in the aryl ring and on the solvent. Due to the significant differences in the solubility of the acid and anhydride, it is difficult to obtain repeatable solubility data. Another factor that causes difficulties in solubility determination of boronic acids is their ability to form micellar systems [18]. Moreover, experimental determination of basic thermodynamic parameters, such as melting temperature or enthalpy of fusion, needed to describe the solid-liquid equilibrium by some models, is difficult for boronic acids. These compounds, when heated up in an open vessel, first undergo a dehydration process, often a multistage one, so the melting parameters are actually measured for the anhydride [19]. As mentioned above, compared to acids, esters and azaesters are stable compounds with a specific composition. In the present work we investigated cyclic ester 2 and azaester 3 shown in Fig. 1.

The aim of the present work is the solubility determination of phenylboronic acid 1 as well as its pinacol- (2) and azaester (3) in common organic solvents and to show possibility of using typical correlation equations to describe the experimental data.

2 Experimental Section

2.1 Chemicals Used

Phenylboronic acid (Alfa Aesar, ≥ 98%) (1) was crystallized from water and dried on air. Pinacol ester (2) (Fluorochem, 98%) was used without further purification. Azaester (3) was synthesized and purified according to [20] (see Supplementary material). Purity of the compounds was checked by 1H and 11B NMR (see Supplementary material). Solvents (chloroform, Chempur, 98.5%; acetone, Chempur, 99.5%; 3-pentanone, Alfa Aesar, 99%; dipropyl ether, Alfa Aesar, 99%; methylcyclohexane, Sigma-Aldrich, ≥ 99%) were dried before use using conventional methods.

2.2 Experimental Procedure

Solubility was determined using a synthetic method described in [21]. A biphasic sample of known composition (accuracy of 0.00016 of mole fraction) was slowly heated while stirred rigorously and disappearance of turbidity was taken as the solid-liquid equilibrium

Fig. 1 The compounds investigated in the present work
point. The extent of turbidity was measured by the intensity of a light beam crossing the measuring cell. An ordinary LED (white light, 20°, 10000 mcd) was used as a source of light. Light intensity was measured by the LP 471 LUM 2 luminance probe supplemented by Photo-Radiometer HD2102.1 (DeltaOHM, Italy). The temperature was measured using a Pt100 resistance probe P 650 (DOSTMANN electronic, Germany) with an accuracy of ± 0.03 K and stability of ± 0.01 K. Heating rate was 1 K·h⁻¹. It was checked that reduction of heating rate down to 0.3 K·h⁻¹ did not influence significantly the determined solubility temperature. Measured temperatures and light intensities were acquired independently and transformed into the light intensity versus temperature dependence. This dependence was correlated by two straight lines and filtered. A typical observed dependence is shown in Supplementary material (Fig. S4). Standard uncertainty of the solubility temperature was estimated to be 0.5 or 1 K. The latter value concerns solubilities of azaester in chloroform or 3-pentanone as for these systems relatively high scattering of the data was observed, and for the azaester + methylcyclohexane mixture with very low solubility and, as a result, a very steep solubility curve. The results were correlated using Redlich–Kister, Wilson, and NRTL models [22–24]. For the compound 2 better correlation was achieved with polynomials.

The phase transitions and thermal stability of the samples were studied using differential scanning calorimetry (DSC). The DSC data were obtained using Q200 scanning calorimeter (TA Instruments). Heat flow calibration was performed using standard sapphire samples. The temperature and cell constant were calibrated with high purity by mass fraction (0.99999) indium. Samples were placed in aluminum Tzero unhermetic pans. An empty pans was used as the reference. Data analysis was carried out using the TA Universal Analysis application. Three cycles of heating, cooling and heating at 10 K·min⁻¹ for each scan were carried out in the flow of nitrogen.

3 Results and Discussion

For the solubility measurements of boronic compounds 1–3, four types of organic solvents were chosen, namely: chloroalkane (chloroform), cyclic alkane (methylcyclohexane), ether (dipropyl ether) and ketone (acetone or 3-pentanone). The results are shown in Figs. 2, 3 and 4 and raw experimental data are given in Table S1 of Supplementary material.

The best solubility of phenylboronic acid is observed in dipropyl ether. These data confirm that linear or cyclic ethers are the best solvents for the synthesis or reactions of boronic acids. Lower solubility is observed for the ketone. The solubility in chloroform is relatively good, and the slope of this curve suggests the possibility of using this solvent for the crystallization of boronic acids. Very low solubility in methylcyclohexane confirms the usefulness of hydrocarbons to remove organic impurities in the synthesis of boronic acids. Attempts to determine the solubility of the acid in 3-pentanone were unsuccessful due to the discrepancy between data. However, it was possible to obtain reproducible results in the case of acetone.

The curves shown in Fig. 2 show an unusual course: they intersect with each other. Moreover, the dispersion of results is much larger than for other compounds. There are several reasons of such behavior. Phenylboronic acid undergoes an equilibrium dehydration reaction (Scheme 1). This means that not only two components (solute–boronic acid, and solvent) are present in the system, but also boroxine and water. The completely different nature of the acid and anhydride causes significant differences in their solubility,
depending on the type of solvent. Moreover, the miscibility of water being formed with some solvents, e.g. acetone, in contrast to its very low solubility in others, e.g. cyclohexane, causes a considerable complexity of the system studied.

Solubilities of pinacol ester of phenylboronic acid are shown in Fig. 3.

The esterification of the boron group with pinacol significantly increases solubility compared to the parent acids: very high solubility was observed for all solvents used even at low temperatures. This indicates the possibility of using pinacol esters of boronic acids
to carry out reactions in any type of organic solvents. The differences between particular solvents are small. The highest solubility was observed in chloroform and the lowest in methylcyclohexane.

Solubility of azaester of phenylboronic acid is shown in Fig. 4. Compared to pinacol ester, for azaester there are significant differences between individual solvents: the compound shows very good solubility in chloroform slightly weaker in 3-pentanone, but much lower in methylcyclohexane and dipropyl ether. The tendency is similar to that of pinacol esters: better solubility appears in polar solvents.

The above solubility data were described by typical $G^E$-models, namely: the Wilson, NRTL and Redlich–Kister equations. To perform these correlations, it was necessary to know basic thermodynamic parameters, i.e. melting temperatures and enthalpies of fusion. These data for the investigated compounds were determined by the DSC method (see Figs. S5–S7 in supplementary material) and are collected in Table 1.

Contrary to the esters 2 and 3, which melt congruently without decomposition, boronic acid dehydrates into boroxine during heating according to Scheme 1. The temperature of about 220 °C reported in the literature as the melting point of phenylboronic acid, actually is temperature of melting of triphenylboroxine. The data given in Table 1 for 1 were estimated from the DSC diagram assuming that the first peak at ca. 90 °C corresponds to the melting of this compound, while that at ca. 108 °C corresponds to the dehydration. Due to the complexity of acid-containing systems, the correlation of data using a polynomial is most justified.

### Table 1  Melting temperatures and enthalpies of fusion of investigated compounds

|                     | Phenylboronic acid (1) | Pinacol ester (2) | Azaester (3) |
|---------------------|------------------------|-------------------|--------------|
| $\Delta H_m$/kJ mol$^{-1}$ | 14.90$^a$              | 13.26 ± 0.1       | 44.83 ± 0.4  |
| $T_m$/°C            | 90.04$^a$              | 26.17 ± 0.5       | 131.03 ± 0.5 |

$^a$Estimated value
Correlation curves for the compounds 1–3 are shown in Figs. 2, 3 and 4. Additionally, ideal solubility given by Eq. 1 with $\gamma_1 = 1$ was determined for the compounds 2 and 3.

The model description of the solubility data is based on the solubility equation which directly results from the condition of phase equilibrium, i.e. equality of chemical potentials of a compound existing in solid and liquid phase. For a system in which pure solid (1) is in equilibrium with liquid mixture and additionally if (i) no transition points in the solid phase appear, (ii) a solute is stable up to the melting temperature, and (iii) the enthalpy of melting is independent of temperature, the solubility is expressed by the following general equation.

\[
R \ln \left[ x_1 \gamma_1 (x_1, T) \right] = -\Delta H_{m1} \left( \frac{1}{T} - \frac{1}{T_{m1}} \right)
\]  

(1)

where $x_1$, $\gamma_1$, $\Delta H_{m1}$, and $T_{m1}$ are the mole fraction, activity coefficient, enthalpy and temperature of melting of the component (1), respectively. It should be noted that this equation cannot be used for the solubility of phenylboronic acid since condition (ii) is not fulfilled for this case. If the activity coefficient is equal to one, the ideal solubility is obtained which is drawn in Figs. 3 and 4 as a dotted line. For the pinacol ester + {3-pentanone or chloroform} systems, rather low negative deviations from ideality are observed what manifests itself by solubilities slightly higher than ideal ones. Usually, such behavior is explained by attractive interactions between unlike molecules higher than those occurring in pure components. The character of deviations from ideality for other solvents is not obvious as they are less significant but probably they are slightly positive. For the systems with azaesters as solute this trend is repeated with the deviations from ideality being more significant and differences between various solvents considerably greater. The positive deviations from ideality increase from dipropyl ether to methylcyclohexane and negative ones increase from 3-pentanone to chloroform. In the first two systems relatively weak interactions between the solute and the solvent are expected because of the non-polar or only slightly polar character of the solvents. For the last one, a strong interaction in the form of hydrogen bond between chloroform and azaester is probably responsible for the observed high solubility. In these hydrogen bonds chloroform’s molecule acts as a hydrogen bond donor.

In the approach expressed by Eq. 1, a model used to describe solubility data concerns in fact the dependence of the solute activity coefficients as a function of concentration and temperature. Since this dependence results directly from the excess Gibbs energy ($G^E$), it is the function which defines the model and, as a consequence, the solubility equation. As the model parameters are being adjusted to the experimental data, they have mainly correlational character and their physical significance is restricted rather to qualitative considerations. The following $G^E$ models were used to represent solubility data:

The Redlich–Kister equation [22]:

\[
G^E = x_1 x_2 \sum_{i=0}^{n} a_i (x_1 - x_2)^i
\]

where $n$ is the order of the $G^E/x_1 x_2$ polynomial, that is $n + 1$ determines the number of model parameters.

The Wilson equation [23]:

\[
\frac{G^E}{RT} = -x_1 \ln \left( x_1 + x_2 A_{12} \right) - x_2 \ln \left( x_2 + x_1 A_{21} \right)
\]
where
\[ A_{12} = \left( \frac{V_2^0}{V_1^0} \right) \exp \left( \frac{\Delta g_{12}}{RT} \right) \]
\[ A_{21} = \left( \frac{V_1^0}{V_2^0} \right) \exp \left( \frac{\Delta g_{21}}{RT} \right) \]

and the NRTL equation [24]:
\[ G = x_1 x_2 \left[ \frac{G_{21,1} \Delta g_{21}}{x_1 + x_2 G_{21}} + \frac{G_{12,1} \Delta g_{12}}{x_2 + x_1 G_{12,1}} \right] \]

where
\[ \Delta g_{12} = g_{12} - g_{22}, \quad \Delta g_{21} = g_{12} - g_{11}, \quad G_{12} = \exp \left( -a \frac{\Delta g_{12}}{RT} \right), \quad G_{21} = \exp \left( -a \frac{\Delta g_{21}}{RT} \right) \]

The \( a_i \), \( \alpha \), \( \Delta g_{12} \) and \( \Delta g_{21} \) parameters are independent of \( x_1 \) and \( T \). The latter two parameters are interpreted as residuals between energy of interaction between like and unlike molecules. The nonrandomness parameter \( \alpha \) has been fixed to 0.2. The ratio of molar volumes of pure components \( V_2^0/V_1^0 \) which appears in the Wilson equation was assumed to be equal to one, because of difficulties in the estimation of the molar volume of a pure solute in the hypothetical liquid state. Nevertheless we do not recognize contributions as significant, since the \( \Delta g_{12} \) and \( \Delta g_{21} \) parameters can incorporate the volume ratios while being adjusted to the experimental data. The Wilson and the NRTL equations possess a certain theoretical background in spite of some crude simplifications included. The Redlich–Kister equation does not have any theoretical support as it is a simple power series. However, it has one practical advantage over other models—a variable number of adjustable parameters which makes the model flexible and being able to describe even complicated dependencies. The adjusted parameters with the standard deviations are given in Table S2 of the Supplementary Material. The number of the Redlich–Kister parameters was established in such a way to guarantee the data reproduction with standard deviations close to the experimental uncertainty, i.e. 1 K for the azaester + {chloroform, or 3-pentanone, or methylcyclohexane} systems and 0.5 K for other mixtures. Two adjustable parameters turned out to be sufficient except for the azaester + chloroform system, for which three parameters were necessary. All the models give fairly similar results, although some differences are noticeable. Surprisingly, the Redlich–Kister equation, in spite of its mainly empirical character, gives standard deviations that are most consistent with experimental uncertainties. The superiority of the Redlich–Kister equation in the description of the azaester + chloroform system results from three adjustable parameters against two for other models. If the two-parameter Redlich–Kister equation is used, all models give almost the same standard deviations.

The solubilities in systems with phenylboronic acid (1) as a solute cannot be described by Eq. 1., since this compound decomposes into anhydride before reaching its temperature of melting. As the thermodynamic characterization of its decomposition is unknown, only purely empirical equation can be applied. These solubilities were described by polynomial in the form:
\[ T = \sum_{i=0}^{n} a_i x_1^i \]

The polynomial order was established in a similar way as the number of the Redlich–Kister parameters although a strict procedure could not be applied because of
a limited number of experimental data. The values of adjusted parameters together with standard deviations are shown in Table S2 of the Supplementary Material.

In order to compare the solubility of investigated compounds in particular solvents, solubility values for the same reduced temperature ($T_r = T/T_m$). The equilibrium temperatures vs. relative permittivity of the solvent [25], calculated for $T_r = 0.89$ using the correlation equations, are shown in Fig. 5.

For the phenylboronic acid 1 solubility increases with the increasing value of relative permittivity with the exception of dipropyl ether. The same tendency is for both esters (2 and 3) with the exception of chloroform.

4 Conclusions

Phenylboronic acid reveals high solubility in ether and ketone and very low in hydrocarbon. Pinacol ester and azaester show better solubility than parent acid in all tested solvents. For pinacol ester differences between particular solvents are small, while for azaester the differences are significant. For both esters the highest solubility is observed in chloroform and the lowest in hydrocarbon. Generally, the solubility positively correlates with the polarity of solvents although some exceptions can be noted.

For the phenylboronic acid better correlation of the data is obtained by polynomials in comparison with the Wilson, NRTL or Redlich–Kister equations, what can be explained by an additional equilibrium reaction with the formation of anhydride. For the esters, the Redlich–Kister equation gives standard deviations which are the most consistent with experimental uncertainties.

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