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Descriptors for the α,ω-dicarboxylic acids from oxalic acid to sebacic acid

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ABSTRACT

We use literature data on solubilities in water and solvents, water-solvent partition coefficients and vapor pressures at 298 K to obtain Abraham (Absolv) descriptors for the neutral, unionized, forms of oxalic acid, malonic acid, glutaric acid, succinic acid, pimelic acid, suberic acid, azaleic acid and sebacic acid. With a knowledge of equations for partition coefficients for numerous water-wet solvents, water to dry solvents and water to ionic liquid systems, we can then predict partition coefficients of the various acids in a huge number of systems. We set out the solubility of the acids in water and these, together with estimated partition coefficients yield solubilities of the acids into the corresponding solvents. The descriptors themselves show that the acids are dipolar, are strong hydrogen bond acids and reasonably strong hydrogen bond bases, although their hydrogen bond acidity is less than expected for compounds containing two (independent) carboxylic acid groups.

1. Introduction

The α,ω-dicarboxylic acids, see Table 1, are a very important class of chemicals that are used in organic synthesis and in the production of polymers. Adipic acid itself is a major industrial chemical with some 2.5 billion kilos produced annually All the α,ω-dicarboxylic acids are of environmental significance and several properties of environmental importance, such as the vapor pressure of the acids, have been determined [1–3]. The solubility of the carboxylic acids is a very important property, and various solvents can be used in the separation and crystallization processes of the acids. Solubilities of the carboxylic acids have been determined in various solvents and solvent mixtures, but the number of possible solvents that can be used is very large, and there is no systematic method for the prediction of solubilities, especially in recently available 'green' solvents such as ionic liquids. Interestingly, the melting point of the series of acids shows a well-known [4] "odd-even" pattern, Table 1. This, in turn, will lead to an "odd-even" pattern of solubilities in water, and in any other given solvent. In Table 1, MF is the molecular formula, MW is the molecular weight, CAS-No is the chemical abstracts assigned number and mp/°C is the melting point in degrees Centigrade.

Our aim is to use literature data on a variety of properties including solubilities, water-solvent partition coefficients and vapor pressure to calculate Abraham, or Absolv, descriptors for these acids. These descriptors can then be incorporated into a series of linear free energy relationships, LFERs, that can be used to predict further water-solvent partition coefficients and further solubilities in a very large number of solvents. These solvents include typical organic solvents, water-methanol and water-ethanol mixtures and a variety of ionic liquids.

2. Methodology

We use two well-known general linear free energy relationships, Eqs. (1) and (2), that can be used to correlate and to predict the transfer of neutral solutes from water to solvents and from the gas phase to solvents. The dependent variable in Eq. (1) is log P, where P is the molar water to solvent partition coefficient for a series of solutes, and in Eq. (2) is log K where K is the dimensionless gas phase to solvent partition

$$\mathrm{Log}\ P = c + e\,\mathbf{E} + s\,\mathbf{S} + a\,\mathbf{A} + b\,\mathbf{B} + v\,\mathbf{V} \quad (1)$$

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Table 1
Some properties of the α,ω-dicarboxylic acids.

Acid	MF	MW	CAS-No	mp/°C
Oxalic	C2H2O4	90.04	144-62-7	188
Malonic	C3H4O4	104.06	141-82-2	136
Succinic	C4H6O4	118.09	110-15-6	185
Glutaric	C5H8O4	132.12	110-94-2	97
Adipic	C6H10O4	146.14	124-04-9	152
Pimelic	C7H12O4	160.17	111-16-0	106
Suberic	C8H14O4	174.19	505-48-6	143
Azeleic	C9H16O4	188.22	123-99-9	106
Sebacic	C10H18O4	202.25	111-20-5	133

$$\text{Log } K = c + e\,\mathbf{E} + s\,\mathbf{S} + a\,\mathbf{A} + b\,\mathbf{B} + l\,\mathbf{L} \tag{2}$$

Use of Eq. (1) and Eq. (2) for the determination of descriptors has been reviewed several times [5–9]. In Eqs. (1) and (2) the independent variables, or descriptors, are properties of the neutral solutes as follows [5–9]: **E** is the solute excess molar refraction in $\text{cm}^3\ \text{mol}^{-1}/10$, **S** is the solute dipolarity/polarizability, **A** is the overall solute hydrogen bond acidity, **B** is the overall solute hydrogen bond basicity, **V** is McGowan's characteristic molecular volume in $\text{cm}^3\ \text{mol}^{-1}/100$ [10] and **L** is the logarithm of the gas to hexadecane partition coefficient at 298 K. The coefficients in Eq. (1) and Eq. (2) are shown in Table 2 for partition from water and the gas phase to the various solvents that we shall encounter [11–23]. Many solvents used in partitioning with water dissolve significant quantities of water at equilibrium, and their properties are then not the same as their properties when they act as dry solvents. We indicate these solvents in Table 2 as ‘wet’ solvents.

The data we shall use is mostly in the form of directly obtained water to solvent partition coefficients as log *P*, or as solubilities, *Cs*, in various solvents. These solubilities can be transformed into water to solvent partition coefficients through Eq. (3) where *Cw* is the solubility in water. Eq. (3) is valid only if no hydrate in water or solvate in the solvent is formed – that is the same species must be in equilibrium with water and the solvent.

$$P = Cs/Cw \text{ or } \log P = \log Cs - \log Cw \tag{3}$$

Values of *P* obtained from solubilities can then be transformed into corresponding gas to solvent partition coefficients, *Ks*, through Eq. (4), where *Kw* is the gas to water partition coefficient.

$$Ks = P^{*}Kw \text{ or } \log Ks = \log P + \log Kw \tag{4}$$

Once values of log *P* and log *Ks* are available for a given solute, a set of simultaneous equations can be set up and solved for the unknown descriptors. For most of the carboxylic acids, log *Kw* can be obtained from known values of the acid vapor pressure [3] at 298 K, equivalent to the gaseous concentration, *Cg*, in mol dm^{-3}, and the solubility in water, *Cw*, expressed as mol dm^{-3}, Eq. (5).

$$\text{Log } Kw = \log Cw - \log Cg \tag{5}$$

Then the unknown descriptors, **E**, **S**, **A**, **B**, **V** and **L**, can be obtained through solution of a set of simultaneous equations where log *P* is the dependent variable. The ‘Solver’ add-on to the Microsoft Excel program provides a particularly convenient method for the solution of these simultaneous equations. Since the number of equations is always larger than the number of unknowns, a trial-and-error procedure is adopted to obtain the unknowns that give the best-fit to the equations. Reviews of our methods [5–9], especially that of Clarke and Mallon [9] give examples of the ‘Solver’ procedure. All the data we use were determined at 298.15 K or were interpolated (and sometimes shortly extrapolated) to 298.15 K using the Apelblat equation, Eq. (6), where *x* is the solute mol fraction solubility, *T* is the absolute temperature and *A*, *B* and *C* are fitting constants.

$$\text{Ln } x = A + B/T + C \ln T \tag{6}$$

3. Results

Malonic acid. Experimental partition coefficients into a number of alcohols, diethyl ether, ethyl acetate and methylisobutyl ether are available [24], and solubilities of malonic acid in several solvents have been determined by Daneshfar et al. [25] and by Zhang et al. [26]. These can be converted into log *P* values through Eq. (3) using log $Cw = 0.596$ [25]. In addition, we used the data of Daneshfar et al. [26] to obtain enthalpies of solution of malonic acid into the solvents water, ethanol, propan-2-ol and acetonitrile, and combined the enthalpy of solution with a known [27] enthalpy of sublimation ($111.4\ \text{kJ mol}^{-1}$) to obtain the corresponding enthalpies of solvation from the gas phase to solution, for which we had already derived equations, Table 3 [28–32]. These are given in terms of $\Delta Hsolv/100$ in order that the dependent variable should be of a similar magnitude to those of log *P*. We took log $Kw = 10.76$ from log $Cg = -10.163$ [3] and log $Cw = 0.596$ [25] and $\mathbf{V} = 0.6801$ [10] and so we were left with the unknown descriptors **E, S, A, B** and **L**. It is useful to be able to calculate **E** and hence have one less descriptor to obtain. From a calculated refractive index [33] we find that $\mathbf{E} = 0.528$, whereas directly calculated values of **E** are 0.34 [34] and 0.31 [35]. The **E**-value for a typical monocarboxylic acid such as propanoic acid is 0.233 [35] from which we expect **E** for a dicarboxylic acid to be around 0.466. Cai et al. [2] determined the refractive index of glutaric acid experimentally, from which we derive a value of 0.485 for **E**. This is in the middle of the various estimates for malonic acid, and so we take $\mathbf{E} = 0.485$ for malonic acid, and for all the other dicarboxylic acids that we consider, leaving only **S, A, B** and **L** to be determined for malonic acid.

Including equations for directly measured water-solvent partitions, equations for indirectly obtained values through Eq. (3), equations for derived gas-solvent partitions through Eq. (4), equations for enthalpies of solvation, and two further equations for log *Kw*, we have a total of 28 simultaneous equations for the four unknowns. These can be solved, to yield a standard deviation, SD, in the dependent variable of 0.139 log unit, with the descriptors in Table 4. For the directly determined values of log P into ‘wet’ solvents, and the indirectly determined values into ‘dry’ solvents, the average error between the nine observed and calculated values, Table 5, AE = 0.012 and the SD = 0.132 log units.

Succinic acid. There is considerably more data for succinic acid than for malonic acid. We have eight direct partition coefficients [24], and solubilities in nine solvents [26,36–38]. The solubility in water is available, log $Cw = -0.162$ [39] and so the nine solubilities can be converted into nine indirect partition coefficients, leading to a total of 17 partition coefficients. The value of log *Cg* is –10.52 [3], and together with log *Cw* leads to 10.36 for log *Kw*. The latter can be used to convert all the 17 or to be log *P* values into log *Ks* through Eq. (4). The enthalpy of sublimation of succinic acid is $121.7\ \text{kJ mol}^{-1}$ [27] and combined with enthalpies of solution yielded enthalpies of solvation into five solvents. Altogether we have a total of 46 simultaneous equations from which to derive **E**, **S**, **A**, **B** and **L**. The equations were solved with SD = 0.115 log units and yield the descriptors given in Table 4. Details of the observed and calculated values for log P are in Table 6. The AE between observed and calculated values is 0.014, and the SD = 0.142 log units. In