

CORRELATIONS OF PARTITION DATA OF CARBOXYLIC ACIDS IN WATER/ORGANIC SOLVENT SYSTEMS WITH SOLVATOCHROMIC PARAMETERS

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إرتباط بيانات تقسيم الأحماض الكربوكسيلية في أوساط من أنظمة الماء/والمذيبات العنصرية بعوامل التذوب (Solvatochromic)

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وجد أن معاملات التقسيم (partition) للأحماض الكربوكسيلية التي تحتوي على عدد من ٢ - ٦ ذرات كربون في صورتها أحادية الجزيئية بين الماء و عديد من المذيبات العنصرية وكذلك ثوابت الإزدواج الجزيئي لها ترتبطان معا بدلالة معاملات التذوب (Solvatochromic) ، وكثافة طاقة الإلتصاق ، الإستقطابية ، dipolarity ، وقوة قاعدية المذيب المستقبل للرباط الهيدروجيني .

وقد ثبت أن العاملين الأخيرين يؤديان إلى ثبات الصورة أحادية الجزيئي بالنسبة للصورة ثنائية الجزيء التي تتكون من خلال إزالة جزيئات المذيب عن مجموعة الكربوكسيل ولاتعتمد على المجموعة الألكيلية في الحمض الكربوكسيلي .

Key Words: Cohesive energy, Dipolarity/polarizability, Hydrogen bonding, Linear solvation energy, Partition of carboxylic acids, Solvatochromic correlations.

ABSTRACT

The partition coefficients of C₂-C₆ carboxylic acid monomeric forms between water and various organic solvents as well as the dimerization constants have been shown to be well correlated in terms of the solvatochromic parameters; cohesive energy density, dipolarity/polarizability and hydrogen bonding acceptor basicity strength of a solvent. Increasing the latter two parameters stabilizes the monomer relative to the dimer whose formation proceeds via desolvation of carboxyl group and is nearly independent of carboxylic acid alkyl chain.

INTRODUCTION

Elucidation of the various solute-solvent interactions involved in the transfer of solutes between various solvents is essential in order to understand the material transfer mechanism. Procedures proposed to assist interpretation of experimental data include the Hansch-Leo substituent constants[1], Taft et al. linear solvation energy relationships (LSER)[2] and solvent inventory techniques[3]. In the general LSER treatment[2] the multiple solute solvent interactions can be quantitatively expressed as a sum of various terms corresponding to various interactions as shown in equation 1.

$XYZ = XYZ_0 + \text{Cavity term} + \text{Polar term} + \text{Hydrogen bonding term} \dots\dots\dots (1)$

Where XYZ represents any reactivity or physiochemical parameter. The cavity term is a measure of the energy required to reorganize solvent molecules to create a cavity for a solute. The polar term accounts for the stabilization of a solute generated from dipole/dipole, and or dipole/induced dipole interactions with a solvent. the hydrogen bonding term represents the stabilization produced by hydrogen bond formation involved in hydrogen bond donor solute (HBD) hydrogen bond acceptor solvent (HBA) and or HBA solute-HBD solvent.

Equation 1 can be expressed in terms of the solvatochromic parameters of both solvent (subscript 1) and solute (subscript 2) according to equation 2.

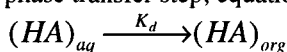
$$XYZ = XYZ_0 + h\delta_h 2_{(1)} \bar{V}_{(2)}/100 + s\pi^*_{(1)} \pi^*_{(2)} + a\alpha_{(1)}\beta_{(2)} + b\alpha_{(2)}\beta_{(1)} \dots\dots\dots (2)$$

where δ_{H2} , π^* , α and β refer to solvent cohesive energy density (square of Hildebrand solubility parameter) dipolarity/polarizability, HBD and HBA strengths, respectively; \bar{V} is the solute molar volume. The coefficients h , s , a and b describe the contribution of each type of interaction to the observed property. Equation 2 has successfully been applied to many reactivity parameters and physicochemical properties including solute-bilayer partitioning[4].

The extraction of carboxylic acids from aqueous solutions by various organic solvents has been studied by several research groups and a significant quantity of partitioning data is now available[5,6]. While several attempts have been made to correlate the partition constant in terms of regular solution theory[7] solvent dielectric constant[8], solubility parameter[5] and solvent water-interfacial tension[9] a refined picture for the various interactions involved in an extract phase between a carboxylic acid and a given solvent has not as yet emerged. Taft et al[10] have recently reported that the partition coefficient of HBD solutes including carboxylic acids between water and octanol were well correlated in terms of solvatochromic parameter. In the present paper published partitioning data related to C₂-C₆ carboxylic acids between water and various organic solvents have been correlated in terms of the solvatochromic parameters. This provides a better picture of various interacting probes responsible for the phase transfer process of these acids. Account has been taken of the fact that these carboxylic acids are capable of self association in the organic phase.

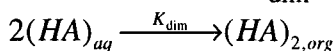
RESULTS AND DISCUSSION

In order to correlate the transfer of carboxylic acids between water and various organic solvents in terms of the solvatochromic parameter, it is important to consider that these acids dimerize significantly in the organic phase. This implies the presence of two species; the monomer and the dimer[5]. The formation of the monomer is associated with the monomer partition coefficient, K_d , representing the phase transfer step; equation 3.



$$K_d = \frac{[HA]_{org}}{[HA]_{aq}} \dots \dots \dots (3)$$

The subscripts aq. and org. denote the aqueous and organic phases, respectively. Conversely, the formation of dimer, taking place in the organic phase is governed by dimerization constant, K_{dim} of equation 4.



$$K_{dim} = \frac{[(HA)_{2,org}]}{[HA]_{org}^2} \dots \dots \dots (4)$$

Fortunately, data including K_d and K_{dim} values for C₂-C₆ carboxylic acid are available in the literature for a variety of solvents at 25 °C. Relatively few data were reported at other temperatures. Data at 30 °C were included in the present correlational analysis and no temperature correction was made since the precision error in K_d and K_{dim} determinations may be larger than the required temperature correction. The solvatochromic parameters for the various

solvents studied are listed in Table 1. The correlations produced include only those solvents for which data for a given carboxylic acid are available.

Table 1
Solvatochromic parameters*

| Solvent | δ_{H2}^2 | π | β |
|---------------------|-----------------|-------|---------|
| Benzene | 9.15 | 0.59 | 0.10 |
| Nitrobenzene | 10.0 | 1.01 | 0.39 |
| Chlorobenzene | 9.5 | 0.71 | 0.07 |
| Isopropylbenzene | 8.65 | 0.54 | 0.11 |
| Toluene | 8.9 | 0.54 | 0.11 |
| Isopropylether | 7.0 | 0.27 | 0.49 |
| Cyclohexane | 8.2 | 0.00 | 0.00 |
| n-hexane | 7.3 | -0.08 | 0.00 |
| Cyclohexanone | 9.9 | 0.76 | 0.53 |
| 1,2 dichloroethane | 9.9 | 0.81 | 0.00 |
| Carbontetrachloride | 8.6 | 0.28 | 0.00 |
| Chloroform | 9.3 | 0.58 | 0.00 |
| 2-ethylnoxyalcohol | 9.5 | 0.47 | 0.88 |

* These parameters were taken from Ref.2

The literature values of K_d and K_{dim} are compiled in Table 2. Application of (LSER) requires noncollinear relationship between various pairs of explanatory variables[4]. Such requirement, expressed in terms of squares of correlation coefficients, is shown in Table 3 for each set of data of a given carboxylic acid.

Table 2
Partition coefficient of carboxylic acids between aqueous and various organic phases and the Dimerization Constants

| Solvent | Log K_d | Log K_{dim} | Ref. |
|----------------------|-----------|---------------|-----------|
| | | | |
| Isopropyl ether | -0.76 | -0.23 | 5 |
| n-hexane | -3.06 | 3.59 | 12 (30°C) |
| Carbontetrachloride | -2.49 | 2.72 | 5 |
| 1,2-dichloroethane | -1.60 | 1.47 | 5 |
| Benzene | -2.07 | 2.16 | 5 |
| Nitrobenzene | -1.44 | 0.85 | 5 |
| Toluene | -2.06 | 2.01 | 13 |
| 2-ethylhexylalcohol | -0.30 | 0.00 | 5 |
| Propionic Acid | | | |
| Isopropyl ether | -0.09 | -0.30 | 5 |
| n-hexane | -2.56 | 3.94 | 5 |
| Cyclohexanone | 0.52 | 0.00 | 5 |
| Carbon tetrachloride | -1.90 | 3.14 | 5 |
| 1,2-dichloroethane | -0.99 | 1.53 | 5 |
| Benzene | -1.36 | 2.21 | 5 |
| Nitrobenzene | -0.86 | 0.97 | 5 |
| Isopropyl benzene | -1.64 | 2.48 | 5 |
| Chlorobenzene | -1.53 | 2.49 | 5 |
| Toluene | -1.47 | 2.39 | 5 |
| Cyclohexane | -2.54 | 3.71 | 5 |
| 2-ethylhexyl alcohol | 0.30 | 0.00 | 5 |
| Chloroform | -0.96 | 1.94 | 5 |
| Butyric Acid | | | |
| Isopropyl ether | 0.48 | -0.37 | 5 |
| n-hexane | -1.64 | 3.48 | 12 |
| Cyclohexane | -1.61 | 3.36 | 3(30°C) |
| Carbontetrachloride | 1.42 | 3.46 | 14 |
| 1,2-dichloroethane | -0.39 | 1.45 | 5 |
| Benzene | 0.79 | 2.28 | 5 |

Table 2, Contd.

| Solvent | Log K _d | Log K _{dim} | Ref. |
|----------------------|--------------------|----------------------|---------|
| Nitrobenzene | -0.34 | 0.97 | 5 |
| Toluene | -0.75 | 2.13 | 3(30°C) |
| Chlorobenzene | -0.75 | 2.13 | 15 |
| 2-ethylhexyl alcohol | 0.86 | 0.00 | 5 |
| Chloroform | -0.30 | 1.74 | 16 |
| Valeric Acid | | | |
| Isopropylether | 1.05 | -0.20 | 5 |
| 1,2-dichloroethane | 0.23 | 1.35 | 5 |
| Benzene | -0.16 | 2.36 | 5 |
| Nitrobenzene | 0.23 | 1.01 | 5 |
| Toluene | -0.28 | 2.45 | 16 |
| 2-ethylhexyl alcohol | 1.36 | 0.00 | 5 |
| Chloroform | 0.23 | 1.91 | 16 |
| Hexanoic acid | | | |
| Isopropylether | 1.48 | -0.19 | 5 |
| 1,2-dichloroethane | 0.82 | 1.19 | 5 |
| Benzene | 0.28 | 2.40 | 17 |
| Nitrobenzene | 0.77 | 0.96 | 5 |
| Toluene | 0.45 | 2.16 | 16 |
| Chloroform | 0.96 | 1.61 | 16 |

Temperatures others than 25°C are indicated in parentheses.

Previously similar correlations[4,11] have shown that the intercept in equation 2 is not significantly different from zero. Equation 5 was therefore employed in all correlational analysis of a given carboxylic acid in a set of HBA and non HBA solvents.

$$\text{Log K} = \delta h^2_{(1)}/100 + s\pi^*_{(1)} + b\beta \dots\dots\dots(5)$$

The coefficients are listed in Table 3. Two analyses were carried out for each individual acid; one included all solvents listed in Table 2 and the other excluded chloroform and 2-ethylhexyl alcohol, both are HBD solvents. Inclusion of data for these two solvents does not generally alter the results obtained from correlations excluding them. The solvent dipolarity/polarizability, π^* in equation 5, was modified by the term $\pi^* + d\delta$ to account for differences in dipolarity/polarizability characteristics among various classes of solvents. The parameter δ is a "polarizability correction term" equal to 0.0 for nonchlorinated aliphatic 0.5 for polychlorinated aliphatic and 1.0 for aromatic solvents. The coefficient, d, calculated according to the method of Taft[12] was taken to be -0.25.

Table 3
Correlations of Monomer Partition coefficients (M) and Dimerization constants (D) in terms of the solvatochromic parameters of solvents.

| | Acetic acid | | Propionic acid | | Butyric acid | | Valeric acid | | Hexanoic acid | |
|--|-------------|-------|----------------|-------|--------------|-------|--------------|-------|---------------|-------|
| | M | D | M | D | M | D | M | D | M | D |
| h | -4.4 | 5.5 | -3.6 | 4.4 | -2.3 | 5.2 | -0.50 | 4.8 | 0.51 | 4.3 |
| s | 3.6 | -4.9 | 3.7 | -3.2 | 2.5 | -5.1 | 0.63 | -4.3 | 0.14 | -4.1 |
| b | 1.7 | -2.5 | 1.8 | -3.1 | 1.7 | -2.5 | 1.6 | -2.4 | 1.5 | -1.7 |
| r ² | 0.967 | 0.968 | 0.956 | 0.908 | 0.919 | 0.977 | 0.829 | 0.956 | 0.828 | 0.996 |
| r ² ($\delta^2 h$ Vs β) | 0.414 | | 0.395 | | 0.321 | | 0.420 | | 0.363 | |
| r ² ($\delta^2 h$ Vs π^*) | 0.818 | | 0.819 | | 0.803 | | 0.944 | | 0.937 | |
| r ² (π^* Vs β) | 0.443 | | 0.480 | | 0.373 | | 0.398 | | 0.387 | |

The coefficients, h, for log K_d correlations increase linearly as expected with the molar volumes of the acids according to equation 6 (r = 0.992)

$$h = -8.97 (\pm 0.53) + 0.76 (\pm 0.005) \bar{V} \dots\dots\dots(6)$$

The similarity of the corresponding coefficients in log K_{dim} correlations for all acids suggests an identical solvent reorganization step associated with the dimerization. Such solvent reorganization is more likely to reflect changes in the solvation sites of carboxyl group. Consistent with this interpretation is the fact that the coefficients s and b in log K_{dim} correlations presumably weighting the polar and hydrogen bonding interactions of carboxyl group, are nearly independent of the carboxylic acid used. The observed similarity of the coefficients of cavity terms implies that the effect of alkyl chain is insignificant in the dimerization process. A general expression equation 7 can thus be derived for the dimerization of these acids.

$$\text{log K}_{\text{dim}} = 5.21 (\pm 0.16) \delta h^2_{(1)} - 5.12 (\pm 0.29) \pi^*_{(1)} - 2.43 (\pm 0.19) \beta_{(1)} \dots\dots\dots(7)$$

The result of such correlation is displayed in Fig. 1.

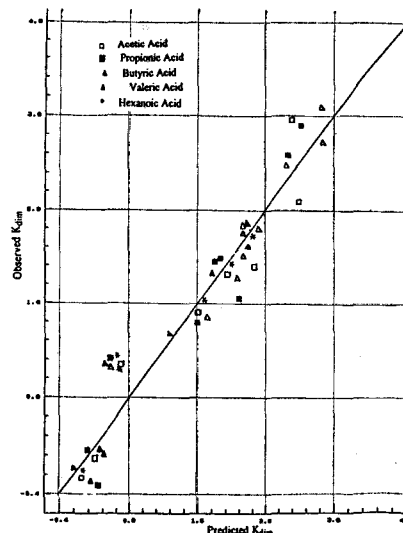


Figure 1. Correlation of logarithmic of dimerization constants of carboxylic acids at 25°C.

This equation implies that the magnitudes of the dimerization constants for these aliphatic acids are dominated by the cohesive energy density dipolarity/polarizability and HBA strength of the solvent.

Finally it may be noted from Table 3 that the coefficients s and b for monomer partition are positive while those associated with the dimerization are negative. Such change in sign is not unreasonable since increasing π^* and β for the solvent would be expected to stabilize greatly the monomer relative to the dimer thereby decreasing the dimerization constant.

LIST OF SYMBOLS

| | |
|--------------|---------------------------------------|
| LSER | Linear solvation energy relationships |
| δ_h^2 | Solvent cohesive energy density. |
| π^* | Dipolarity/polarizability |
| α | Hydrogen bonding doner acidity |
| β | Hydrogen bonding acceptor basicity |
| K_d | Monomer partition coefficient |
| K_{dim} | Dimerization constant |
| \bar{V} | Molar volume of an acid |
| $d\delta$ | Polarizability correction term |
| h | Coefficient of cavity term |
| s | Coefficient of polar term |
| b | Coefficient of hydrogen bonding term |

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