# Study on Association of Substituted Benzoic Acids And Other Acids By Physical Methods

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## الخلاصة

يشتمل البحث على تحضير اثنا عشر حامض عضوي اليفاتي مع حامض البــــنزويك المعوض . لقد اثبتت الهيئات التركيبية لهذه الحوامض بالطرق الفيزيائية .

الهدف الرئيسي للبحث يشتمل على دراسة امكانية التكتل هذه في الحوامض وبالطرق الفيزيائية مثل اطياف الاشعة فوق البنفسجية وتحت الحمراء ، درجــــة الانصــــهار وطريقـــة التوزيع .

لقد اثبتت الدراسة ان ميكانيكيات التكتل للاحماض الواردة انفا وفي مذيب البنزين امــا عن طريق الاصرة الهدروجينية او بطريقتي الاصــــرة الهدروجينيـــة والايــــون المولـــد للدايوبول. اعتماداً على درجة حرارة التجربة والهيئة التركيبية للحامض . الحقيقة ان طريقـــة الايون المولد للدايوبول قد وجدت هنا لاول مرة و قد اقترحت من قبل النتائج العملية التي تـــم الحصول عليها اخيراً ، فقد قدم البحث تفسيرات مناسبة وملائمة لكل فقرة والتي دعمت امـــا بالمصدر اللازم او الشكل والجدول المناسبين او المخطط اللازم لذلك .

## ABSTRACT

This paper deals with the preparation of twelve aliphatic and substituted benzoic acids. The structures of these acids are confirmed by some physical methods.

The main object of the paper is studying the possibility of association in these acids by physical methods, namely the UV, IR spectra, melting point and distribution method.

The mechanisms of association in these acids in benzene are happen by either hydrogen bonding alone or hydrogen bonding in addition to the ion induce dipole association methods. This depends on the structure of the acid and the temperature of the solution . The idea of ion induce dipole is founded here for the first time as suggested from the collected experimental results.

Finally, a suitable interpretation is given for any point as supported by either reference, graph, table or scheme.

# INTRODUCTION

Several methods (1-3) had been used to study the association in solution. The equilibrium constant of the dimerization reaction of benzoic acid had been determined by either indirect(1) measurement of vapour pressure lowering or by distribution(4) method. Wall and Rouse[1] had applied the former method for the association study of benzoic acid and its ortho and meta methyl derivatives. They found that the values of association constants of benzoic and ortho toluic acids are approximately equal. In the meantimes, the value of enthalpy of dissociation of polymeric ortho toluic acid to the corresponding monomer is lower than the value of meta toluic acid. A clear answer to the last is given by the existence of steric effect in o-toluic acid.

Earlier report in our laboratory, Azzouz(5) and Saleh had applied the distribution method in studying the dimerization reaction of 2,3-dihydroxybenzylidene-4-hydroxyaniline in benzene. The mechanism of association reaction is given by intermolecular hydrogen bonding of two phenolic groups. The influence of polarity and the temperature on the association process are also included. The process of association had been also confirmed from the calculated thermodynamic functions, namely $\Delta G$, $\Delta H$ and $\Delta S$. Schiff bases as 2,3-dihydroxybenzylidene-2-hydroxyaniline and 2,3-dihydroxy-benzylidene aniline can exist as monomers in the nitrobenzene.

The present investigation is an extension of the previous study. It deals with the application of four physical methods such as UV, IR spectra, melting point and distribution method in studying the association reactions of acids. The study also deals with the effect of chemical structure of acid and the temperature on the value of association constant. Really, it is an important study, which opens a way to other subsequent future works on naturally occurring polymeric systems of special importance in vitro such as DNA or other polymeric materials.

# EXPERIMENTAL

**Materials and Methods :**

The following chemicals are used throughout this work as supplied from Fluka. They are o,m,p-flurobenzaldehyde, m,p-anisaldehyde, o,p-nitrobenzaldehyde, p-carboxybenzaldehyde, maleic acid, fumaric acid, salicylic acid, sodium carbonate, benzene, nitrobenzene and sodium meta bisulfite.

## Preparation of Carboxylic Acids :

A similar procedure(6) is followed for the preparation of all substituted benoic acids as, 4-nitrobenzoic acid (4-NBA), 2-nitrobenzoic acid (2-NBA), 2-flurobenzoic acid (2-FBA), 3-flurobenzoic acid (3-FBA), 4-flurobenzoic acid (4-FBA), 3-methoxybenzoic acid (3-FBA), 4-methoxybenzoic acid (4-MBA), 2-hydroxybenzoic acid (2-HBA), trans-cinnamic acid (TCA), 4-carboxybenzoic acid (4-CBA), maleic acid (MA) and fumaric acid (FA).

The summary of the method is :- A 0.5g of sodium carbonate and 75-80 ml of distilled water are transferred to 250ml round bottom flask equipped with a reflux condenser. After warming the mixture, 1.5g of any aldehyde is added to the mixture followed by a careful addition of about 4.0g of $KMnO_4$. The mixture is refluxed for about three hours, followed by cooling and acidification with dilute $H_2SO_4$. The final mixture is refluxed again for about 30 minutes, cooling followed by addition of sodium meta bisulfite to destroy any excess permanganate and a recovery of the solid acid precipitate. Recrystalization for the crude acid is performed by using ethanol solvent and after addition of small quantity of charcoal.

The identification of each acid is carried out by comparing some of its physical properties as melting point, UV and IR spectra as shown in Table (1), in addition to the use of simple iodide-iodate test(6).

## Distribution Method :

This method had been applied in studying the extent of association of all acids in benzene, by using a similar procedure adopted elsewhere(5).

## Instrumentation :

1. All IR spectra of substituted benzoic acids and other acids are measured in solid or conceration of $10^{-3}$ M in benzene by using PYE Unicam SP1100.

2. All UV spectra are measured in matched 1x1x3 $cm^3$ silica cells by using Shimadzu UV-160, UV-visible computerized spectrophoto-meter.

3. The pH or potential of any solution had been measured by using Philips PW 9421 pH meter.

# RESULTS AND DISCUSSION

The extent of association of substituted benzoic acids and other acids are obtained by using the following methods :

## 1. Spectroscopic Methods :
### 1.1. UV Spectra Method :

The UV spectra have been used in the investigation of hydrogen bonding (5,7) , in acids under study. These spectra are measured in ethanol and benzene solvents as in Table (1). This shows that $E_{max}$ values of the acids in these solvents are greater than one thousand, which support the $\pi \longrightarrow \pi^*$ transitions. The negative sign of wave number of transition, i.e. $\Delta V$ is an indication of unspecified hydrogen bonding (5,7). Therefore, an evidence supporting the association(8) in these acids is obtained here by the aid of hydrogen bonding.

### 1.2. IR Spectra Method :

This method is widely used in studying the hydrogen bonding(9) or association property in different compounds. It has been applied previously in the investigation of hydrogen bonding in oximes(10), imines(7) and others (5,9,10).

A preliminary study on hydrogen bonding in acids is measured in solid state. This shows a broad and intense spectra in the region 2500-3300 cm$^{-1}$. This indicates a strong hydrogen bonding of unspecified inter or intra type. This encourage us to measure the IR spectra of all acid compounds as listed in Table (1) and in benzene solution. Actually benzene solvent as known as inert solvent and has moderate solubilities of organic acids. It has applied previously in some studies (11,12), irrespective of its tendency to form solute-solvent interaction of $\pi$-type (13,14), and of a weak energy if compared with the real hydrogen bond energy. Therefore, the formal interaction can be ignored from the study.

Now for each acid under study, two solutions of concentrations $1 \times 10^{-3}$M and $0.5 \times 10^{-3}$M are prepared, followed by measuring their IR spectra against a blank solvent. The following informations are collected as :

1. For acids 2-FBA, 2-HBA, 2-NBA and MA, an intense hydrogen bonding bands in the range 3000-3300cm$^{-1}$ are obtained. These hydrogen bonding bands are unaffected by dilution process. Hence these acids contain an intramolecular(10) hydrogen bonding. In other words, that these acids are difficult to associate by intramolecular hydrogen bonding alone.

2.  Conversely, for acids 4-NBA, 4-FBA, 3-FBA, 4-FBA, 3-MBA, 4-MBA, 4-CBA and TCA, a similar hydrogen bonding bands are observed. Their intensities are varied by dilution(10) process. Hence these acids have an intermolecular hydrogen bonding. A possible association in these acids are expected by intermolecular (5,10) hydrogen bonding. Also Table (1) shows the following results (15,16).

I.  All acids in Table (1) shows a relatively weak intensity in the range (3450-3500) $cm^{-1}$ for stretching of free hydroxyl group.

II.  A strong band is observed in the range (1750-1785) $cm^{-1}$ for stretching carbonyl group. Also a sharp and strong absorption in the range (1950-1625) $cm^{-1}$ for asymmetric stretching of the same group.

III.  All acids in table (1) with exception of FA and MA shows a medium absorption for aromatic systems.

IV.  2-NBA and 4-NBA show a sharp and medium intesnsities for asymmetric and symmetric stretching frequencies for $NO_2$ group in the range (1450-1550) $cm^{-1}$ and (1345-1365) $cm^{-1}$ respectively.

V.  For acids 2-FBA, 3-FBA and 4-FBA, there are a sharp and strong bands for stretching of C-F bond.

VI.  4-MBA and 3-MBA show a medium intensities bands referring for stretching ether linkage $-C-OCH_3$.

VII.  A strong bands are observed in the range (1670-1680) $cm^{-1}$ for stretching frequency of $C = C$ bands in the trans form for acids FA and TCA.

VIII.  A doublet of bands at frequencies 1610 $cm^{-1}$ and 1670 $cm^{-1}$ for stretching $C = C$ in the cis form and for acid MA.

## 2. Melting Point Method :

This is an approximate method used for the occurrence of hydrogen bonding in any system(9). Recently, it had been applied in the investigation of hydrogen bonding of Schiff bases(7) derived from the reaction of 2-hydroxy-1-napthylaldehyde with a varieties of aliphatic and aromatic primary amines.

The results of such method when applied to carboxylic acids under investigation are shown also in Table (1). This clearly shows that acids 4-NBA, 3-FBA, 3-MBA, 4-MBA, 4-CBA, TCA and FA which have a homolytic association by means of intermolecular hydrogen bonding have generally higher melting point than their corresponding acids as 2-NBA, 2-FBA, 2-MBA and MA of possesing, an intramolecular hydrogen bonding, taking into consideration a comparison between similar structures. This result comes in agreement(9) with compounds o-acetamidocetophenone, p-acetamidoacetophenon, N-(o-nitrophenyl)

benzamide and N-(p-nitrophenyl) benzamide which having a melting points of 78, 167, 193 and 196°C respectively.

### 3. Distribution Method :

Recently this method[5] had been applied in the determination of equilibrium constant for the dissociation reaction of polymer to its corresponding monomers, according to the reaction $B_n \rightleftharpoons nB$, using the following equation : $\log C_w = 1/n \log C_o + constant$ , where $C_w$ and $C_o$ are concentrations of solute in water and organic phases respectively, n represents the degree of association of solute.

At the beginning of this investigation it was thought of great importance to calibrate this method by using a standard benzoic acid (2-4). Then after an intensive efforts have been made to develop the classical titrimetric method of detection of end points for acids in organic and aqueous layers, by any electrical methods of analysis such as pH metrically or potentiometrically. The last methods as founded to be tedious and time consuming, hence they are discarded from our programme.

The distribution method was applied to investigate the degree of association (n) for carboxylic acids from above equation, the results are shown in Figures (1-4) and summarized in Tables (2-3).

In order to understand the subject and make it easy to the reader, hence the following division of results are thought to be necessary:

1. All 2-NBA, 2-FBA, 2-HBA, and MA acids that are included in Table (2) have a degrees of association range values between 0.695-1.155. These numbers confirm that all these acids are exist as monomers in benzene. Also these findings are in agreement with the UV and IR spectra mentioned previously for these acids : Actually the existence of these acids in an intramolecular hydrogen bonding or chelate like structure as stated before, prevent the possibility of theirs association. In other words, the last bonding will increase the stability of these acids, because the functional groups of such acids are included or busy in the intramolecular hydrogen bonding.

2. Acids as 4-NBA, 3-FBA, 4-FBA, 4-MBA and FA which are shown in Table (3) have a degrees of association range values between 1.463-2.243. These finding asist that these acids are exist in a dimeric forms in benzene, due to theirs existence in an intermolecular hydrogen bonding. This comes in agreement with the UV and IR spectra mentioned before.

## Table (3) shows also the followings :

i. The degree of association n for acids 4-NBA, 3-FBA and 4-FBA are slightly changed by the variation of temperatures. Elevation of temperature of any acid is accompanied by decreasing the n value. This is in agreement with the Davis *et.al.*(13) findings on the interaction of acids with triethylamine and 1,3-diphenylguanidine. It is in accordance with the hydrogen bonding studies (18-22) adopted in the last two decades.

ii. Acid FA is exist in a dimeric form between temperatures range (283-303)K with exception of 303K. This means that at such relatively higher temperature an actual weakening(10) of hydrogen bonding is taken place. It adds an additional support to the last paragraph.

iii. Acids 4-CBA and TCA show a direct relationship between n and the temperature . It is believed that such abnormality is due to the following two folds reasons :

1. Acid 4-CBA contains two carboxylic groups. So presumable expectation, that these acids may associate by more than one association method, possibly by hydrogen bonding as shown above, and the ion induce dipole methods(23).

2. The idea of ion induce dipole is suggested here from the results shown in Table (3). So by elevation of temperature, the acid will certainly absorb heat. This may accompained by an increase of ionization process or in the numbers of positive ($H^+$) and negative ($A^-$) ions produced from acid HA. The ion induce dipole formed may be shown in the following scheme.

$$H^+ + HA \longrightarrow \boxed{+} \quad \boxed{- \; +}$$

$$A^- + HA \longrightarrow \boxed{-} \quad \boxed{+ \; -}$$
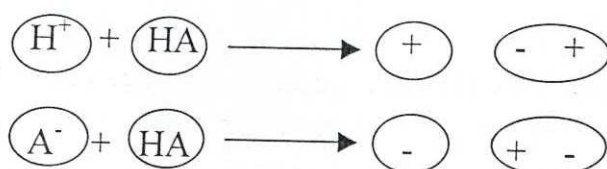
Now it is believed that 4-CBA and TCA are associate by two association methods (8,23), the intermolecular hydrogen bonding and the ion induce dipole. Honestly, when the outhors comeback to the literature, unfortunately no relationship is observed between the ion induce dipole and the temperature. Finally, it is thought that the last topic may open to us an interesting future work for some new studies.

## CONCLUSIONS

1. This study indicates the occurrence of intra or inter molecular hydrogen bonding in acids under study by UV, IR, melting points and distribution method.

2.     Acids are associate in nonpolar benzene solvent by intermolecular hydrogen bonding and to different extent, depending on the structure of acid and the temperature as follows :

a. Acids 2-NBA, 2-FBA, 2-HBA and MA are exist as monomers at $10^{o}C$ and FA at $30^{o}C$.

b. A dimeric existence for acids 4-NBA, 3-FBA, 4-FBA, 3-MBA, 4-MBA and FA at different temperatures as in Table (3), also acids 4- CBA and TCA at $10^{o}C$.

c. Trimeric existence for acids 4-CBA (15, 20, 25, $30^{o}C$) and TCA (15,20,25$^{o}C$).

d. Tetrameric existence of TCA at $30^{o}C$.

   3. The degree of association (n) for acid is affected by the temperature and in the following manner :

a. An inverse relationship between n and the temperature, if the association is happen by hydrogen bonding for acids 4-NBA, 3-FBA, 4-FBA, 3-MBA, 4-MBA and FA. This is in accordance with previous studies (1-4,22).

b. A direct relationship between n and the temperature in acids 4-CBA and TCA. Here the association is suggested by hydrogen bonding and the ion (8) induce dipole methods.

Table (1) some physical & chemical properties of carboxylic acids

| No. | Symbol | m.p °C | Iodide-iodate test | IR spectrum in benzene (cm⁻¹) | U.V spectra in | | | | Wave number U (cm⁻¹) | | ΔU (cm⁻¹) |
| | | | | | Ethanol | | Benzene | | | | |
| | | | | | $\lambda_{max}$ (nm) | $E_{max}$ (L.mole⁻¹.cm⁻¹) | $\lambda_{max}$ (nm) | $E_{max}$ (L.mole⁻¹.cm⁻¹) | Ethanol | Benzene | |
| 1 | 4NBA | 237–239 | +ve | 3475(w), 3180(b), 1750(s), 1600(s), 1540(s), 1450(m), 1400(m), 1345(m), | 277 | 364 | 255 | 2584 | 36101.1 | 39215.7 | -3114.6 |
| 2 | 2NBA | 143–145 | +ve | 3460(w) 3200(b), 1750(s), 1600(s),1550(m), 1475(m), 1445(s),1410(m), 1365(m), | 277 | 1448 | 229 | 6100 | 36101.1 | 43668.1 | -7567.0 |
| 3 | 2FBA | 121–125 | +ve | 3480(w), 3210(b), 1780(s), 1600(s),1545(m), 1440(m), 1410(m), 1065(s) | 279 | 2608 | 274 | 1744 | 35842.3 | 36496.4 | -654.1 |
| 4 | 3FBA | 122–124 | +ve | 3455(w), 3200(b), 1780(s), 1600(s),1540(m), 1435(m), 1410(m), 1070(s) | 279 | 2940 | 276 | 1860 | 35842.3 | 36231.9 | -389.6 |
| 5 | 4FBA | 182–183 | +ve | 3480(w), 3205(b), 1780(s), 1590(s),1520(m), 1440(m), 1400(m), 1080(s) | 277 | 856 | 231 | 6784 | 36101.1 | 43290.0 | -7188.9 |
| 6 | 3MBA | 104–107 | +ve | 3460 (w), 3140–2980 (vb), 1750(s), 1600(s), 1550(m), 1455(m),1410(m), 1300(m) | 278 | 292 | 253 | 6976 | 35971.2 | 39525.7 | -3554.5 |

| No. | Symbol | m.p °C | Iodide-iodate test | IR spectrum in benzene (cm⁻¹) | U.V spectra in | | | | Wave number U (cm⁻¹) | | ΔU (cm⁻¹) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Ethanol | | Benzene | | | | |
| | | | | | $\lambda_{max}$ (nm) | $E_{max}$ (L.mole⁻¹.cm⁻¹) | $\lambda_{max}$ (nm) | $E_{max}$ (L.mole⁻¹.cm⁻¹) | Ethanol | Benzene | |
| 7 | 4MBA | 181–184 | +ve | 3480(w), 3220(b), 1780(s), 1750(s), 1600(s), 1550(m), 1440(m),1410(m), 1245(m) | 277 | 5452 | 244 | 7820 | 36101.1 | 40983.6 | −4882.5 |
| 8 | 2MBA | 157–160 | +ve | 3450(w), 3200(b), 1775(s), 1750(s), 1600(s), 1550(m), 1450(m), 1405(m) | 308 | 3472 | 304 | 4252 | 32467.5 | 32894.7 | −427.2 |
| 9 | 4CBA | > 400 | +ve | 3500(w), 3250(b), 1785(s), 1600(s),1500(m), 1440(m), 1405(m), 1250(m) | 277 | 2676 | 275 | 2388 | 36101.1 | 36363.6 | −262.5 |
| 10 | TCA | 132–134 | +ve | 3500(w),3180 – 2900 (vb), 1755(s), 1680(s), 1625(s), 1545(m),1510(m), 1460(m), 1410(m) | 291 | 7656 | 281 | 7512 | 34364.3 | 35587.2 | −1222.9 |
| 11 | FA | 301–302 | +ve | 3460(w), 3220(b), 1750(s), 1670(s), 1620(s), 1550(m), 1410(m) | 226 | 2088 | 233 | 5036 | 44247.8 | 44843.1 | −595.3 |
| 12 | MA | 137–139 | +ve | 3480(w), 3250(b), 1760(s), 1670(s), 1610(s), 1550(m), 1400(m) | 225 | 2060 | 213 | 1180 | 44444.4 | 46948.4 | −2504.0 |

b = broad,     s = sharp,     m = medium,     w = weak,     vb = very broad,     * : $\Delta\bar{U} = \bar{U}_{ethanol} - \bar{U}_{benzene}$

## Table (2) Results of non associated carboxylic acids in benzene at 10 $^{\circ}$C

| No. | Symbol | Intercept | Slope | Degree of association (n) | Correlation coefficient | Standard error |
|-----|--------|-----------|-------|---------------------------|-------------------------|----------------|
| 2 | 2-NBA | 1.42818 | 1.43958 | 0.695 | 0.979118 | 0.017598 |
| 3 | 2-FBA | 0.688716 | 1.21247 | 0.825 | 0.999188 | 0.010515 |
| 8 | 2-HBA | 0.8359 | 1.24674 | 0.802 | 0.999795 | 0.003225 |
| 12 | MA | - 0.813514 | 0.866024 | 1.155 | 0.953551 | 0.014598 |

### Table (3) Results of associated carboxylic acids in benzene

| No. | Sample | Temperature (K) | Intercept | Slope | Degree of association (n) | Correlation Coefficient | Stand. Error of Est. |
|-----|--------|-----------------|-----------|-------|---------------------------|-------------------------|----------------------|
| 1 | 4NBA | 283 | −1.85647 | 0.501003 | 1.996 | 0.999765 | 0.00234632 |
|   |      | 288 | −1.50784 | 0.535962 | 1.866 | 0.999126 | 0.00246346 |
|   |      | 293 | −1.33351 | 0.623646 | 1.604 | 0.988544 | 0.0175854 |
|   |      | 298 | −1.31051 | 0.612201 | 1.634 | 0.999797 | 0.00205913 |
|   |      | 303 | −1.56624 | 0.632798 | 1.580 | 0.996414 | 0.0205698 |
| 4 | 3FBA | 283 | −1.96158 | 0.492268 | 2.031 | 0.998232 | 0.00763207 |
|   |      | 288 | −1.8997 | 0.530173 | 1.886 | 0.997809 | 00683275. |
|   |      | 293 | −1.59142 | 0.569437 | 1.756 | 0.996559 | 0.0124212 |
|   |      | 298 | 1.51569 | 0.602016 | 1.661 | 0.998251 | 0.00708468 |
|   |      | 303 | −1.43883 | 0.632464 | 1.581 | 0.998426 | 0.00632264 |
| 5 | 4FBA | 283 | −1.98461 | 0.47709 | 2.096 | 0.998003 | 0.00510897 |
|   |      | 288 | −1.72942 | 0.508969 | 1.965 | 0.995907 | 0.014144 |
|   |      | 293 | −1.51276 | 0.574563 | 1.741 | 0.996893 | 0.0114882 |
|   |      | 298 | −1.24793 | 0.604546 | 1.654 | 0.989418 | 0.0261979 |
|   |      | 303 | −1.35337 | 0.615826 | 1.624 | 0.997671 | 0.00665791 |
| 6 | 3MBA | 283 | −2.08879 | 0.493307 | 2.027 | 0.997298 | 0.00558134 |
|   |      | 288 | −1.30878 | 0.543944 | 1.838 | 0.997951 | 0.00699932 |
|   |      | 293 | −2.01654 | 0.432287 | 2.313 | 0.995812 | 0.00410268 |
|   |      | 298 | −1.80254 | 0.621987 | 1.608 | 0.998508 | 0.0159219 |
|   |      | 303 | −1.46765 | 0.587043 | 1.704 | 0.996732 | 0.0109073 |
| 7 | 4MBA | 283 | −1.8082 | 0.512 | 1.953 | 0.993133 | 0.0124479 |
|   |      | 288 | −1.89157 | 0.552879 | 1.809 | 0.999107 | 0.00382304 |
|   |      | 293 | −2.08185 | 0.445774 | 2.243 | 0.996098 | 0.0078749 |
|   |      | 298 | −1.45622 | 0.603819 | 1.656 | 0.999368 | 0.0045106 |
|   |      | 303 | −1.26435 | 0.621112 | 1.610 | 0.997026 | 0.0071589 |

| No. | Sample | Temperature (K) | Intercept | Slope | Degree of association (n) | Correlation Coefficient | Stand. Error of Est |
|-----|--------|-----------------|-----------|-------|---------------------------|-------------------------|---------------------|
| 9 | 4CBA | 283 | −1.89531 | 0.557391 | 1.794 | 0.996124 | 0.00629055 |
|   |      | 288 | −2.32992 | 0.38013 | 2.631 | 0.993397 | 00644377 |
|   |      | 293 | −2.56435 | 0.360061 | 2.777 | 0.971855 | 0.909222 |
|   |      | 298 | −2.51124 | 0.321223 | 3.113 | 0.982984 | 0.00946095 |
|   |      | 303 | −2.52542 | 0.304973 | 3.279 | 0.996922 | 0.00313641 |
| 10 | TCA | 283 | ··2.16114 | 0.447874 | 2.233 | 0.992411 | 0.0118972 |
|   |      | 288 | −2.14677 | 0.384379 | 2.602 | 0.997985 | 0.00696337 |
|   |      | 293 | −2.37287 | 0.341282 | 2.930 | 0.998710 | 0.00498163 |
|   |      | 298 | −2.58208 | 0.310348 | 3.222 | 0.995233 | 0.00887362 |
|   |      | 303 | −2.44037 | 0.277537 | 3.603 | 0.997767 | 0.00269656 |
| 11 | FA | 283 | −2.05442 | 0.495854 | 2.017 | 0.997626 | 0.00338025 |
|   |      | 288 | −2.01674 | 0.512376 | 1.952 | 0.995518 | 0.00568909 |
|   |      | 293 | −2.04246 | 0.516232 | 1.937 | 0.992933 | 0.00613553 |
|   |      | 298 | ··1.43832 | 0.683637 | 1.463 | 0.996091 | 0.00576637 |
|   |      | 303 | −1.02875 | 0.81371 | 1.229 | 0.999146 | 0.00549 |
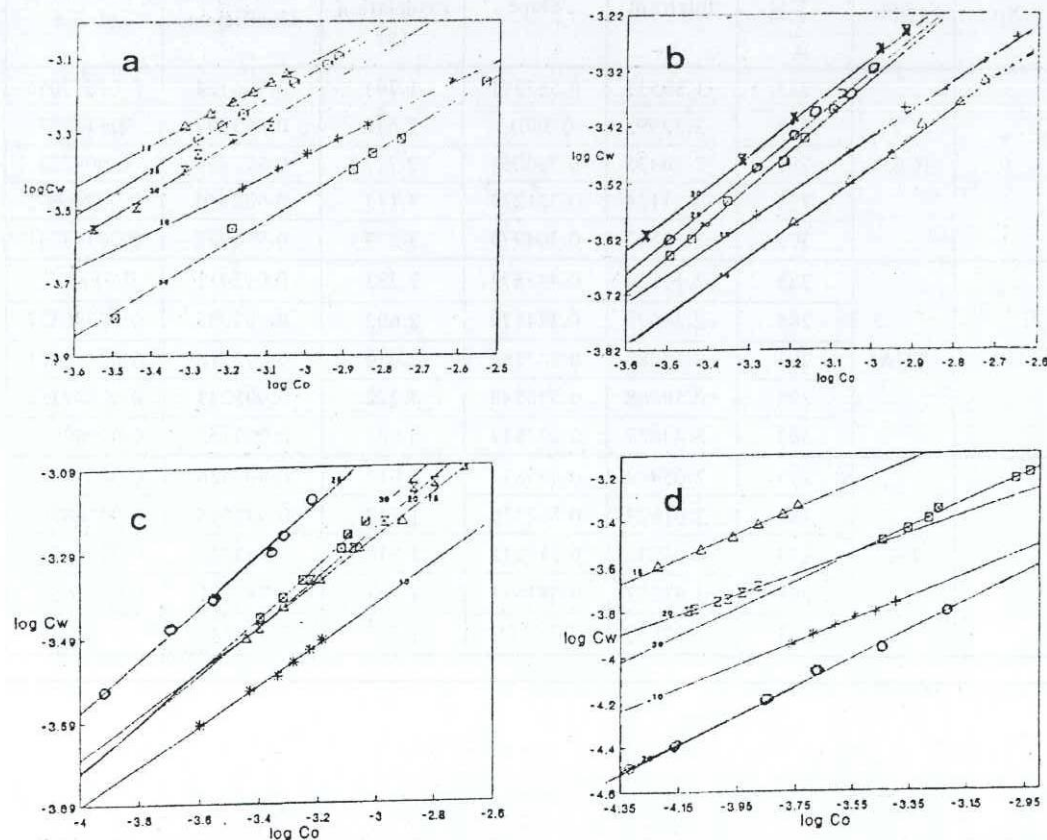
Fig.1  Plot of $\log C_w$ versus $\log C_o$ for:

a-  4-Nitrobenzoic acid
b-  3-Flurobnzoic acid
c-  4-Flurobenzoic acid
d-  3-Methoxybenzoic acid

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