

NMR Studies of Equilibrium Quotient of the Benzonitrile with Xylene Isomers and Ethylbenzene

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ABSTRACT: *The charge transfer (CT) complex formation of benzonitrile as acceptor with the aromatic donors o-, m-, p-xylene and ethylbenzene in CCl₄ solutions is investigated by chemical shift measurements relative to an external reference. The equilibrium parameters, Q and Δ_{AD} of their weak molecular complexes, as found numerically modified Cresswel- Allred (C-A) method, is compared with graphically Scatchard-Foster-Fyfe (Sc-F-F) method.*

KEY WORDS: *Charge transfer, Equilibrium parameters, Weak molecular complexes, Modified Cresswel- Allred method, Scatchard-Foster-Fyfe method*

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INTRODUCTION

Extensive experimental attention has been given to a large number of complexes formed by the weak interactions between certain classes of organic substances, as electron donor, and other substances as electron acceptor [1]. These coordination products are of particular interest to organic chemists because of their possible function as intermediates in reactions leading to stable products.^[2] These donor-acceptor complexes are in many instances so unstable that they cannot be isolated in the pure state at ordinary temperature but exist only in solutions in equilibrium with their components. However, they can usually be detected readily because of the differences in their physical properties such as absorption

spectra and NMR chemical shifts from those of the pure components [2].

A great deal of efforts have been devoted to obtain the association constants as well as other structural parameters such as absorbances, dipole moments, NMR shifts, enthalpies of formation, etc [3]-[17].

The determination of the equilibrium quotients was not the main aim of majority of investigators. For example in organic synthesis the equilibrium quotient provides a comparison of the complex forming capacities of new substances with those investigated previously, etc [16].

Different numerical or graphical methods were used to analyze and interpret the observed chemical shifts [12],[13],[18]-[20]. The problem is that there is coupling between the microscopic model which one uses to interpret the experimental data and the values of the association constant and structural parameters which one calculates [17]. Thus, it is necessary to verify the model in order to assess the reliability of the results, and often it is impossible to do this because of the nature of the system [17].

Many workers [8],[9],[21]-[24] have observed that the choice of concentration scale strongly influenced the value of the equilibrium quotients (Q) and the relative shift of the pure complexes (Δ_{AD}) derived from numerical and graphical methods. The results obtained for complexes formed between benzonitrile and aromatic donors such as *o*-, *m*-, *p*-xylene and ethylbenzene provide an example of the effects of concentration scales on the equilibrium quotient (Q) and the relative shift of the pure complex (Δ_{AD}). Our results from numerically modified Cresswell- Allred (*C-A*) method and graphically Scatchard-Foster-Fyfe (*Sc-F-F*) method on molar, mole fraction and molal scales are given in Tables 2-4.

The most reliable and most often used graphical method is based on Scatchard-Foster-Fyfe (*Sc-F-F*) equation [10], [13], [18]-[20], [25], [26].

$$\Delta_{obsd,i} / (Y_D)_i = -Q * \Delta_{obsd,i} + Q * \Delta_{AD} \quad (1)$$

Where $\Delta_{obsd,i} = \delta_{obsd,i} - \delta_A$ is the relative observed shift, weighted mean of the shifts of complexed and free acceptor; $\delta_{obsd,i}$, is that observed from the solution containing acceptor and donor, relative to that of the free acceptor; δ_A is that observed from the solution containing acceptor, and $\Delta_{AD} = \delta_{AD} - \delta_A$ is defined correspondingly as the relative shift of the pure complex. Y_D is the donor concentration in molal, molar or mole fraction scales and Q is the corresponding equilibrium quotient.

In Scatchard-Foster-Fyfe equation, (Eq.1) the linear regression between $\Delta_{obsd,i} / (Y_D)_i$ and $\Delta_{obsd,i}$ give Q (slope) and $Q * \Delta_{AD}$ (intercept).

Modified Cresswell- Allred method is a trial-and-error procedure [18], which works as follows: one selects a fictitious value for Q and calculates the corresponding

fictitious complex concentration $Y_{AD,i}$ for each experimental $Y_{A,i}$ and $Y_{D,i}$ according to equations 2 and 3.

$$U_i = Y_{A,i} + Y_{D,i} + (1/Q) \quad (2)$$

$$Y_{AD,i} = [U_i - \{(U_i^2) - (4 * Y_{A,i} * Y_{D,i})\}^{0.5}] / 2 \quad (3)$$

Then, the linear regression between the experimental $\Delta_{obsd,i}$ and $\Delta_{calc,i}$ is determined. This is done according equation 4 at this fictitious complex concentration $Y_{AD,i}$.

$$\Delta_{calc,i} = (\Delta_{AD} * Y_{AD,i}) / Y_{A,i} \quad (4)$$

The procedure is repeated with another selected value for Q , until the minimum value for the least-squares sum, $f(Q, \Delta_{AD})$ in equation 5, is found. Finally, the corresponding Q and Δ_{AD} are reported.

$$f(Q, \Delta_{AD}) = \sum (\Delta_{calc,i} - \Delta_{obsd,i})^2 \quad (5)$$

Microsoft Excel Solver program are used for evaluating the best Q and Δ_{AD} [27]. Finally, standard errors for each parameters (Q and Δ_{AD}) are found by "jackknife" procedure [28]-[30].

In this paper we have developed a modified *C-A* method that considers the initial concentration of acceptor [10],[31] using Microsoft Excel Solver program [27]. We then performed the NMR study of the complexes of benzonitrile with aromatic donors in CCl_4 solution for comparison of this modified *C-A* numerical method with *Sc-F-F* graphical methods in determining the equilibrium quotient (Q) and NMR chemical shifts of the complexes (Δ_{AD}), as well as the effects of concentration units on these parameters. Also we have compared two NMR probes for understanding the major forces responsible for complex formation in xylene isomers. This treatment has not considered the Additional Unspecific Shielding (AUS), [3]-[13] but used Solver Excel Program [27] in modified Cresswell- Allred (*C-A*) method and the least square curve fitting for graphical method.

EXPERIMENTAL

Materials

Benzonitrile as acceptor and carbon tetrachloride as solvent were obtained from Merck (Darmstadt, Germany) and their purity were checked by $^1\text{H-NMR}$.

The donor reagents i.e. *o*-xylene, *m*-xylene, *p*-xylene and ethylbenzene (more than 99% pure) were obtained from Merck and used without further purification. The external references cyclohexane and dichloromethane obtained from Merck and their purity were above 99%.

Instrumental

The external reference, either dichloromethane or cyclohexane was placed in the capillary tubes. The latter were sealed to avoid evaporation and then put in the NMR sample tube. The chemical shifts were measured using 250 MHz Bruker instrument at the instrumental temperature of 300.0 K.

General method

The equilibrium between acceptor and donor, $A + D \leftrightarrow AD$, is investigated by measuring the shift δ_i of the acceptor (A) as a function of total donor concentration $Y_{D,i}$ [9],[18], [25], [26], where “ Y ” is the corresponding concentration in molar, molal or mole fraction units. A number of solutions containing fixed concentration of the acceptor and excess varying concentration of the donor were made up gravimetrically and volumetrically into 5 ml glass stoppered volumetric flask. The reliability of the results depend upon the saturation fraction, $SF = (Y_{AD,i}) / (Y_{A,i})_0$, where subscript “0” indicates the total concentration of acceptor. This fraction could cover a broad range, and for weak complexes or low solubility of donors, it should be enough [25],[26]. The concentration of the acceptor, benzonitrile, is constant and equal to 100 μl . The range of the saturation fraction (SF) that is the most important and valuable function in studying the weak molecular complex, is obtained numerically by modified Creswell-Allred ($C-A$) method which is then used in the Scatchard-Foster-Fyfe ($Sc-F-F$) method, in Tables 1 and 5.

RESULTS AND DISCUSSION

There has been a considerable discussion and controversy about the correct performance and evaluation

of NMR shift experiments designed for the determination of molecular complex parameters, especially the equilibrium quotient for 1:1 complexes [13].

The main problems are: (1) the choice of the reference signal (internal or external) [18], (2) the choice of the concentration range or the range of saturation fraction [24], (3) the choice of concentration unit [18], and (4) the agreement (or disagreement) of the results with other methods [8],[13].

We used an NMR study of the benzonitrile with aromatic donors in carbon tetrachloride solution as an example of the kinds of difficulties that one runs into in studying the weak molecular complexes. It seems pertinent to reexamine some of these problems in greater detail. In the present article, we concern ourselves mainly with a simple model, reserving a discussion of the more detailed system for a future article.

We used the external reference for removing the problems of non-specific van der Waals contributions to nuclear shielding [6]. In this studies a storage emphasize was placed on efforts on the comparison of numerical modified $C-A$ method with graphically Scatchard-Foster-Fyfe ($Sc-F-F$) method, choice of concentration unit and the consistent of the results from two probes.

We have studied five systems for comparing the numerically modified Creswell- Allred ($C-A$) method and the graphical Scatchard-Foster-Fyfe ($Sc-F-F$) method on molar, mole fraction and molal scales. For three of the systems cyclohexane was the external reference and for two systems it was dichloromethane. For two systems with *p*-xylene as donor, the results with cyclohexane and dichloromethane, as external references are compared, Tables 1-4.

In order to see which forces could provide a significant effect in the xylenes-benzonitrile complexes, we have made NMR shift measurements on two probes (ortho and meta hydrogens) of benzonitrile.

Three forces are expected to be responsible for the interaction of weak molecular complexes: charge transfer, dipole - induced dipole and dispersion forces. In the xylenes- benzonitrile complexes, because of the small size of donors and the acceptor, the dispersion forces do not seem significant.

On the basis of the NMR results in Tables 5-7,

especially for *p*-xylene system, almost identical parameter values for the two probes are obtained. This indicated that good superposition of the π -orbitals of the

interacting molecules exists. It is clear that the planes of benzonitrile

Table 1: Range of saturation fraction for benzonitrile-aromatic donor complexes

| | Donor | External references | Range of saturation fraction | | |
|---|---------------------|---------------------|------------------------------|-------------|---------------------|
| | | | Molal scale | Molar scale | Mole fraction scale |
| 1 | <i>o</i> -Xylene | Cyclohexane | 0.296-0.730 | 0.133-0.321 | 0.164-0.398 |
| 2 | <i>m</i> -Xylene | Cyclohexane | 0.316-0.704 | 0.174-0.292 | 0.241-0.404 |
| 3 | <i>p</i> -Xylene I | Cyclohexane | 0.256-0.695 | 0.073-0.196 | 0.116-0.310 |
| 4 | <i>p</i> -Xylene II | Dichloromethane | 0.271-0.698 | 0.095-0.154 | 0.139-0.352 |
| 5 | Ethylbenzene | Dichloromethane | 0.323-0.604 | 0.189-0.346 | 0.211-0.391 |

Table 2: Equilibrium parameters for complexes of benzonitrile with aromatic donor in carbon tetrachloride at 300.0 K for molar scale

| | Donor | Scatchard-Foster-Fyfe (Sc-F-F) method | | Creswell-Allred (C-A) method | | Data points |
|---|---------------------|---------------------------------------|---|------------------------------|---|-------------|
| | | $Q \pm \Delta Q$ | $\Delta_{AD} \pm \Delta \Delta_{AD}(\text{Hz})$ | $Q \pm \Delta Q$ | $\Delta_{AD} \pm \Delta \Delta_{AD}(\text{Hz})$ | n |
| 1 | <i>o</i> -Xylene | 0.09±0.01 | 536.1±28.2 | 0.10±0.01 | 519.0±21.3 | 6 |
| 2 | <i>m</i> -Xylene | 0.09±0.01 | 508.3±48.4 | 0.10±0.01 | 507.1±45.4 | 7 |
| 3 | <i>p</i> -Xylene I | 0.06±0.02 | 781.1±108.2 | 0.05±0.01 | 838.9±120.1 | 6 |
| 4 | <i>p</i> -Xylene II | 0.04±0.01 | 917.5±147.4 | 0.04±0.01 | 870.6±98.9 | 6 |
| 5 | Ethylbenzene | 0.17±0.02 | 319.7±41.6 | 0.17±0.02 | 325.7±27.7 | 7 |

Table 3: Equilibrium parameters for complexes of benzonitrile with aromatic donors in carbon tetrachloride at 300.0 K for mole fraction scale

| | Donor | Scatchard-Foster-Fyfe (Sc-F-F) method | | Creswell-Allred (C-A) method | | Data points |
|---|---------------------|---------------------------------------|---|------------------------------|---|-------------|
| | | $Q \pm \Delta Q$ | $\Delta_{AD} \pm \Delta \Delta_{AD}(\text{Hz})$ | $Q \pm \Delta Q$ | $\Delta_{AD} \pm \Delta \Delta_{AD}(\text{Hz})$ | n |
| 1 | <i>o</i> -Xylene | 1.21±0.11 | 414.6±41.0 | 1.22±0.14 | 416.0±32.0 | 8 |
| 2 | <i>m</i> -Xylene | 1.37±0.04 | 365.6±11.1 | 1.41±0.04 | 364.0±6.9 | 7 |
| 3 | <i>p</i> -Xylene I | 0.86±0.06 | 509.5±35.6 | 0.82±0.08 | 530.4±38.2 | 6 |
| 4 | <i>p</i> -Xylene II | 0.98±0.10 | 388.2±42.2 | 1.04±0.11 | 377.7±27.6 | 6 |
| 5 | Ethylbenzene | 1.83±0.21 | 289.4±34.1 | 1.88±0.21 | 288.7±20.7 | 8 |

Table 4: Equilibrium parameters for complexes of benzonitrile with aromatic donors in carbon tetrachloride at 300.0 K for molal scale

| | Donor | Scatchard-Foster-Fyfe (Sc-F-F) method | | Creswell-Allred (C-A) method | | Data points |
|---|---------------------|---------------------------------------|---|------------------------------|---|-------------|
| | | $Q \pm \Delta Q$ | $\Delta_{AD} \pm \Delta \Delta_{AD}(\text{Hz})$ | $Q \pm \Delta Q$ | $\Delta_{AD} \pm \Delta \Delta_{AD}(\text{Hz})$ | n |
| 1 | <i>o</i> -Xylene | 0.31±0.03 | 232.4±28.4 | 0.34±0.04 | 227.5±9.6 | 10 |
| 2 | <i>m</i> -Xylene | 0.36±0.03 | 207.8±19.6 | 0.36±0.04 | 210.8±7.5 | 10 |
| 3 | <i>p</i> -Xylene I | 0.28±0.04 | 227.3±35.2 | 0.28±0.06 | 229.7±21.5 | 10 |
| 4 | <i>p</i> -Xylene II | 0.29±0.03 | 194.8±19.6 | 0.31±0.03 | 192.6±7.7 | 10 |
| 5 | Ethylbenzene | 0.42±0.03 | 189.4±15.5 | 0.44±0.03 | 188.1±7.1 | 9 |

Table 5: Range of saturation fraction for benzonitrile-aromatic donor complexes for first and second NMR probes

| | Donor | External references | Range of saturation fraction | | Data points |
|---|---------------------|---------------------|------------------------------|-------------|-------------|
| | | | Probe 1 | Probe 2 | n |
| 1 | <i>o</i> -Xylene | Cyclohexane | 0.278-0.558 | 0.257-0.531 | 6 |
| 2 | <i>m</i> -Xylene | Cyclohexane | 0.375-0.514 | 0.364-0.502 | 5 |
| 3 | <i>p</i> -Xylene I | Cyclohexane | 0.290-0.669 | 0.299-0.678 | 9 |
| 4 | <i>p</i> -Xylene II | Dichloromethane | 0.269-0.696 | 0.271-0.698 | 10 |

Table 6: Results of molal scale for ortho hydrogen of benzonitrile

| | Donor | Scatchard-Foster-Fyfe (Sc-F-F) method | | Creswell-Allred (C-A) method | | Data points |
|---|---------------------|---------------------------------------|---|------------------------------|---|-------------|
| | | $Q \pm \Delta Q$ | $\Delta_{AD} \pm \Delta \Delta_{AD}(\text{Hz})$ | $Q \pm \Delta Q$ | $\Delta_{AD} \pm \Delta \Delta_{AD}(\text{Hz})$ | n |
| 1 | <i>o</i> -Xylene | 0.28±0.07 | 249.6±68.0 | 0.31±0.08 | 239.6±30.1 | 6 |
| 2 | <i>m</i> -Xylene | 0.28±0.08 | 238.8±80.4 | 0.30±0.09 | 229.4±42.8 | 5 |
| 3 | <i>p</i> -Xylene I | 0.30±0.05 | 217.5±38.6 | 0.33±0.051 | 211.3±14.1 | 9 |
| 4 | <i>p</i> -Xylene II | 0.29±0.03 | 194.8±19.6 | 0.31±0.028 | 192.6±7.7 | 10 |

Table 7: Results in molal scale for meta hydrogen of benzonitrile

| | Donor | Scatchard-Foster-Fyfe (Sc-F-F) method | | Creswell-Allred (C-A) method | | Data points |
|---|---------------------|---------------------------------------|---|------------------------------|---|-------------|
| | | $Q \pm \Delta Q$ | $\Delta_{AD} \pm \Delta \Delta_{AD}(\text{Hz})$ | $Q \pm \Delta Q$ | $\Delta_{AD} \pm \Delta \Delta_{AD}(\text{Hz})$ | n |
| 1 | <i>o</i> -Xylene | 0.24±0.06 | 269.0±76.4 | 0.28±0.08 | 254.0±40.8 | 6 |
| 2 | <i>m</i> -Xylene | 0.26±0.08 | 244.7±81.7 | 0.29±0.09 | 235.6±44.5 | 5 |
| 3 | <i>p</i> -Xylene I | 0.33±0.04 | 207.2±31.3 | 0.34±0.06 | 205.0±15.7 | 9 |
| 4 | <i>p</i> -Xylene II | 0.28±0.02 | 202.4±16.7 | 0.30±0.03 | 198.9±9.8 | 10 |

and xylenes can easily align parallel to each other and so charge transfer forces can arise to a significant extent. The agreement between the value of equilibrium parameters for the two probes leads us to conclude that the charge transfer is the predominant force [15].

Of course, one cannot rule out the role of dipole-induced dipole forces because these forces appear in all donor-acceptor interactions [15].

Also the agreement in the equilibrium quotient (Q) and the relative shift of the pure complex (Δ_{AD}) obtained from different acceptor signals (different probes in benzonitrile) is an important criteria for the reliability of the results and for the correctness of the 1:1 model [3].

Generally there is a good agreement between the corresponding values obtained by different methods, not only for equilibrium quotient (Q) but also for the relative shift of the pure complex (Δ_{AD}).

From studies on benzonitrile and aromatic donors in carbon tetrachloride solution several significant points emerge:

a) Considering the initial acceptor concentration, small standard error for Δ_{AD} and less sensitivity to the number of data points the numerical modified *C-A* method, is preferred. (See Tables 2-4)

b) The magnitudes of the results on the three concentration scales are considerably different and the differences are much larger than would be expected from an error analysis of the data. So suitable concentration scale must be used for comparison of the equilibrium parameters. [24]. (See Tables 2-4)

c) If suitable concentration unit and range of saturation fraction were chosen, the type of external

references would not impose any significant effect. (See Tables 4, 6, 7)

d) It is apparent that the molal scale is the best because the random order of the values of Δ_{AD} and Q on the mole fraction and molar scales are removed. (See Tables 4, 6, 7)

e) A new method for obtaining the best concentration unit for comparison of the equilibrium parameters, is the reliability of the results in a series of isomers. In other words if the equilibrium parameters in a concentration unit for a series of isomers show less discrepancy, that concentration unit is more suitable, provided that other experimental conditions especially the range of saturation fraction are considered. (compare Tables 4 with 2 and 3)

f) The equilibrium quotient for ethylbenzene is greater than for *o*-, *m*-, *p*-xylene. This may be related to the number of substituents on the xylene donors and therefore steric hindrance to the approach of the acceptor molecule. (See Table 4)

g) Both modified numerical and graphical methods are sensitive to the range of saturation fraction and number of data points. In other words, for both methods; the larger the range of the saturation fraction and the more the number of data points; the more accurate are the equilibrium parameters.

h) The numerically modified *C-A* method is cumbersome and require a suitable iterative program but the graphical method is strongly dependent on the number of data points.

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