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# ASSOCIATION OF NITROMETHANE AND NITROETHANE IN SOME AROMATIC SOLVENTS

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## ABSTRACT

A method is described for using a microcomputer to analyze dielectric constants of solutions of polar solutes as a function of concentration to evaluate dipole association constants. Details of the program and its use are presented and the results of computations for nitromethane and nitroethane in benzene, p-xylene, and mesitylene are reported. The dipole association constants are larger than expected for simple dipole association and may indicate interaction of these nitroalkanes in the aci form or the formation of multimers.

## INTRODUCTION

The thermodynamics of self association of polar molecules in relatively inert solvents is of considerable interest and has been the subject of numerous investigations (Foster, 1973; Ginell, 1979; Yadava and Mauyra, 1986). This process can be represented as

$$2M \rightleftharpoons D$$

where M is a polar monomeric species and D is a dimer of that species. Although many studies of this type involve hydrogen bonded species (Foster, 1973 and Ginell, 1979) such systems will not be considered here. Experimental techniques employed include spectrophotometric, optical, nuclear magnetic resonance, calorimetric, and electrochemical methods. Many polar species are presumed to associate although precise measurements have not been carried out to determine thermodynamic equilibrium constants for the association.

Rather infrequently, the dielectric permittivity is used as a diagnostic measure of dipole association (Yadava and Mauyra, 1986; Basu and Ghosh, 1985; and Rossotti and Rossotti, 1961). This technique is based on the fact that the dielectric permittivity ($\Sigma$) varies in a nonlinear way with increasing concentration of an associating polar solute. Thus, the analysis of these data enables calculations of association constants to be made (Kopecni, et al., 1981; House, 1984). Considering the fact that dielectric data are commonly determined, it is somewhat surprising that this technique is not used more often to determine association constants. Recently, Kopecni, Petkovic, and Laub have utilized this approach to study the association of N,N-disubstituted amides (Kopecni, et al., 1981). In the present study, we have utilized the dielectric data for solutions of nitromethane and nitroethane in aromatic solvents to investigate molecular association. Also, we present details of a computational procedure to use on a microcomputer to replace the procedure described as "tedious although straightforward" for determining association constants from dielectric data (Kopecni, et al., 1981).

## METHODS

For a solution of two components, we can write

$$\Sigma = \bar{V}_1 C_1 \Sigma_1 + \bar{V}_2 C_2 \Sigma_2 \tag{1}$$

where C is a molar concentration, $\bar{V}$ is a molar volume, $\Sigma$ is a dielectric permittivity, and the subscripts 1 and 2 refer to solvent and solute, respectively. Frequently, nonlinearity is observed which may be due to the dimerization reaction,

$$2M \rightleftharpoons D \tag{2}$$

where M is the monomeric species and D is a dimer. For this system, the dimerization constant can be written as

$$K = C_D / C^2_M \tag{3}$$

Since solute monomer and dimer are both present, Eq. (1) becomes

$$\Sigma = \bar{V}_1 C_1 \Sigma_1 + \bar{V}_M C_M \Sigma_M + \bar{V}_D C_D \Sigma_D \tag{4}$$

Now it is apparent that

$$C_2 = C_M + 2C_D \tag{5}$$

so that

$$\Sigma - \bar{V}_1 C_1 \Sigma_1 - \bar{V}_M C_M \Sigma_M = (\bar{V}_D \Sigma_D - 2\bar{V}_M \Sigma_M) C_D \tag{6}$$

Solving Eq. (3) for $C_D$ and substituting $C_M = C_2 - 2C_D$ leads to

$$C_D = g(K) = \left[\left(C_2 + \frac{1}{4K}\right) - \left(\frac{C_2}{2K} + \frac{1}{16K^2}\right)^{1/2}\right] \tag{7}$$

If we represent $\bar{V}\Sigma$ as f (an intensivity factor) we obtain

$$\Sigma - f_1 C_1 - f_M C_2 = \tfrac{1}{2}(f_D - 2f_M)\left[\left(C_2 + \frac{1}{4K}\right) - \left(\frac{C_2}{2K} + \frac{1}{16K^2}\right)^{1/2}\right] \tag{8}$$

from which K can be determined. In a previous method, this was done graphically by varying the value of K until a linear relationship was obtained for the two sides of Eq. (8). This "tedious though straightforward" method is replaced by a numerical procedure (House, 1984), but even this procedure can be very slow. In the present work, we have developed a microcomputer procedure to carry out the computations.

For a dilute solution where the concentration of dimer approaches zero, it can be shown that

$$\frac{\Sigma}{C_1} = f_1 + f_M \frac{C_2}{C_1} \tag{9}$$

Therefore, a plot of $\Sigma/C_1$ vs. $C_2/C_1$ yields the intensivity factor for the solvent as the intercept and that for the monomer, $f_M$, as the slope of the plot.

## CALCULATIONS

Having determined the necessary input data from the published dielectric constants at various concentrations, the computation is initiated by performing linear regression using the two sides of Eq. (8) as variables. The initial trial value for K is 0.1 and the initial value for $\Delta K$ is 0.1. The value of the correlation coefficient is retained so that the next value of K, 0.2, can be used to see if a more nearly linear fit results. In the iterative process, $K_{i+1} = K_i + 0.1$. If incrementing K leads to an improved linear relationship, the process is repeated with the new correlation coefficient being retained as the test value. Linear regression is performed iteratively until $K_i$ reaches a value where the linear regression results in a lower correlation coefficient. When this condition results, $K_i$ is decremented by two incremental units, which is necessary to assure that $K_i$ is reduced to a value lower than the optimal value. The value of the increment in K is reduced to 0.01 and the iterative linear regression is performed again until the test shows that a lower correlation coefficient is reached. If desired, the step refinement in the increment $\Delta K$ can be repeated to establish the value of K to greater accuracy. The refinement of $\Delta K$ can be carried out as many times as desired so that the desired number of step refinements (RS) must be specified at the beginning of the computation. If the initial increment in K is 0.1 ($\Delta K = 0.1$, given as DK in the program), the value of K is thus obtained to within $\pm (0.1)^{RS}$. For all practical purposes, there is no need to determine K to greater than three decimal places. A program listing in BASIC is given in the Appendix.

We have found that the calculated values for K are highly dependent on the values of $f_1$ and $f_M$. Accordingly, we have carried out numerical experimentation to evaluate this dependence.

## DATA

The association of nitromethane and nitroethane in benzene, p-xylene, and mesitylene was studied using the recently published data of Yadava and Singh (1982). The dielectric constants were reported at 30°C for solutions in which the concentrations were given as weight fractions. However, if the densities of the solutions are known, the molarities can be calculated. The weight fraction of solute, $W_2$, is related to the molarity by

$$C = 1000\, \rho\, W_2/M_2 \tag{10}$$

where C is the molarity, $W_2$ is the weight fraction of solute, $M_2$ is the molecular weight of the solute, and $\rho$ is the density of the solution. For the dilute solutions used, it is assumed that the density can be represented by

$$\rho = X_1\rho_1 + X_2\rho_2 \tag{11}$$

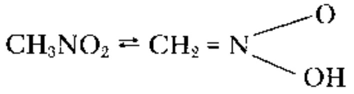
where $\rho_1$ and $\rho_2$ are the densities of the pure components and $X_1$ and $X_2$ are the mole fractions of the solvent and solute, respectively. Since the weight fraction of solute is the number of grams of solute divided by the number of grams of solution, we can write

$$X_2 = (W_2/M_2)/[(W_1/M_1) + (W_2/M_2)] \tag{12}$$

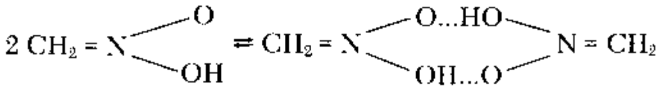
where $M_1$ and $M_2$ are the molecular weights of solvent and solute, respectively, and $W_1$ and $W_2$ are their weight fractions. Thus, using these procedures, it is possible to calculate the molar concentrations $C_1$ and $C_2$ of Eq. (8) from the weight fractions given by Yadava and Singh (1982). This procedure has been used with the data published for systems of $CH_3NO_2$ and $C_2H_5NO_2$ in benzene, p-xylene, and mesitylene.

## RESULTS AND DISCUSSION

The procedure described previously has been utilized with the data for N,N-dimethylacetamide (DMA) in hexane (Kopecni, et al.) and the nitro compounds in aromatic solvents (Yadava and Singh, 1982) to calculate the association constants. The results of these calculations are shown in Table 1. In the case of DMA in hexane, the results are identical to those obtained using the calculator program (House, 1984). For the nitro compounds, the K values are substantially greater than those expected for molecules which interact by dipole-dipole forces only (Treiner, et al., 1964). The reason for these large K values is not known. It may well be due to the formation of higher aggregates than dimers or the formation of dimers that are bound by forces other than dipole-dipole forces. For example, it is known that nitromethane can undergo transformation to an aci form (Millar and Springall, 1966), which can be shown as


$$CH_3NO_2 \rightleftharpoons CH_2 = N\begin{matrix} \diagup O \\ \diagdown OH \end{matrix} \qquad (13)$$

Consequently, association of the aci form could proceed in much the same fashion as in the case of the carboxylic acids.


$$2\,CH_2 = N\begin{matrix} \diagup O \\ \diagdown OH \end{matrix} \rightleftharpoons CH_2 = N\begin{matrix} \diagup O...HO \diagdown \\ \diagdown OH...O \diagup \end{matrix} N = CH_2 \qquad (14)$$

It is possible that interaction in this way will lead to dielectric behavior that does not lend itself to the analysis by the method of Kopecni, Petkovic and Laub (1981).

In this work, $f_1$ and $f_M$ were evaluated from the dielectric constants and molar volumes directly. This procedure does not lead to much difference for the $f_1$ value, but $f_M$, the intensivity of the monomer, is considerably different when evaluated this way compared to its evaluation by linear regression. We have found that the K values are dependent on the $f_M$ value used in the calculations. This problem was not previously addressed (Kopecni, et al., 1981). Accordingly, the evaluation of K has been carried out using the data of Kopecni, et al., for MDA in hexane while varying $f_M$ and $f_1$ from their reported values of 1.7921 and 0.2464, respectively. The results obtained are shown in Table 2, and they clearly indicate that the calculations are much more dependent on $f_M$ than on $f_1$. This situation is so severe, in fact, that unless one is reasonably sure of the $f_M$ value, little confidence can be placed in the calculated value of K.

We have also carried out calculations to determine the magnitude of the effects caused by variations in the $f_M$ values used for the nitromethane and nitroethane. Table 3 shows the results of these calculations. It should be noted here that the variations in $f_M$ are larger than those tested for the case of DMA in hexane. The intent here was to determine what would be the resulting error in K if $f_M$ is substantially in error. It is unlikely that the $f_M$ values are actually in error by amounts anything like this large. Smaller errors than those tested are reasonable so the magnitudes of the dimerization constants are probably correct.

The explanation for the trends in K values is not straightforward. There are at least three separate factors to consider. These are the energy of the interaction of the nitroalkane molecules with each other, the solvation enthalpy of the monomers, and the solvation enthalpy of the dimers. Except for the K for $CH_3NO_2$ association in benzene, the association constants appear to increase in a general way with the addition of methyl groups to the aromatic ring. It is not clear which of the enthalpies described above is responsible for this effect.

While questions and uncertainties still remain, this work has shown that the dimerization of nitroalkanes can be studied by means of dielectric constants of dilute solutions. It has also demonstrated the nature of the errors that can result in the calculated K when the intensitivity factors for the monomer and solvent are in error. While hydrogen bonding or the formation of multimers may be responsible for the unexpectedly large values for the association constants, the results should be correct as far as trends are concerned. We are also performing molecular orbital calculations to determine configurational energies for the nitro and aci forms of nitromethane to try to determine some estimation of the relative amounts of these forms in the gas phase of nitroalkanes.

## LITERATURE CITED

Basu, R., and M. Ghosh, Indian J. Chem., *24A*, 227 (1985).
Foster, R., Molecular Complexes, Vol. I and II, Crane, Russak, & Co., New York, 1973.
Ginell, R., Association Theory, Elsevier, Amsterdam, 1979.
House, J.E. Jr., Comput. Chem., *8*, 123 (1984).
Kopecni, M.M., R. Laub, and Dj. M. Petkovic, J. Phys. Chem., *85*, 1595 (1981).
Millar, I.T., and H.D. Springall, Sidgwick's Organic Chemistry of Nitrogen, 3rd ed., Oxford, 363 (1966).
Rossotti, F. and H. Rossotti, Determination of Stability Constants, McGraw-Hill, New York, 318 (1961).
Treiner, C., J.F. Skinner, and R.M. Fuoss, J. Phys. Chem., *68*, 3406 (1964).
Yadava, R.R., and S.R. Mauyra, Indian J. Chem., *25A*, 460 (1986).
Yadava, R.R., and V.N. Singh, Indian J. Chem., *21A*, 17 (1982).

# APPENDIX

A program is given here to perform the calculation of dipole association constants by the method described by Kopecni, et al. [6]. The program listed is the simplest version in which the concentrations and dielectric constants are input manually. In the program listing, CS is the concentration of the solvent, CA is the concentration of the solute, E is the dielectric constant, and KD is the association constant. These concentration symbols follow the original terminology of Kopecni, et al. [6] and allow for numerical subscripting without confusion. The initial value of KD is taken to be 0.1 as is the increment DK. The number of specified step refinements (RS) to be carried out on DK is given as three in step 90 of the program, but this and the starting values for KD and DK can be changed as desired. As presented, the computation can handle as many as 30 data points, and the number used must be specified at the beginning of the run. Linear regression is performed iteratively until a trial value of KD gives a lower correlation coefficient and then the KD value is decremented and step refinement occurs. Thus, KD is eventually found to within ± $(0.1)^{RS}$ where RS is the number of step refinements that occur.

```
10 PRINT "DIPOLE ASSOCIATION — HOUSE AND KEMPER"
20 DIM E(30)
21 DIM CS(30)
22 DIM CA(30)
25 DIM X(30)
26 DIM Y(30)
30 PRINT "# OF DATA PAIRS?"
35 INPUT P
40 PRINT "FM="
45 INPUT FM
50 PRINT "FS="
55 INPUT FS
80 KD=0.1
85 DK=0.1
90 RS=3
95 Q=0
100 FOR U=1 TO P
110 PRINT "CS";U;"="
115 INPUT CS(U)
120 PRINT "CA";U;"="
125 INPUT CA(U)
130 PRINT "E";U;"="
135 INPUT E(U)
140 NEXT U
150 J=0
151 K=0
152 L=0
153 M=0
154 R2=0
155 B=0
156 A=0
```

```
157 FOR Z=1 TO P
160 Y(Z)=E(Z)-FS*CS(Z)-FM*CA(Z)
170 X(Z) =(CA(Z)+1/(4*KD))-SQR((CA(Z)/(2*KD))+(1/(16*(KD^2))))
180 J=J+X(Z)
190 K=K+Y(Z)
200 L=L+X(Z)^2
210 M=M+Y(Z)^2
220 R2=R2+X(Z)*Y(Z)
230 NEXT Z
240 B=(P*R2-K*J)/(P*L-J^2)
250 A=(K-B*J)/P
260 J=B*(R2-J*K/P)
270 M=M-K^2/P
280 K=M-J
290 R2=J/M
300 R=SQR(R2)
310 PRINT "KD=";KD
320 PRINT "R=";R
330 PRINT
335 R1=ABS(R)
340 IF R1>Q THEN 400
350 KD=KD-2*DK
355 Q=0
360 DK=DK*0.1
365 KD=KD+2*DK
370 RS=RS-1
380 IF RS=O THEN 999
390 GOTO 150
400 KD=KD+DK
410 Q=R1
415 GOTO 150
999 END
```

Table 1. Calculated dimerization constants.

| Solute | Solvent | $f_M$ | $f_1$ | K | Corr. Coef. |
|---|---|---|---|---|---|
| DMA[+] | Hexane | 1.7291 | 0.2464 | 0.184 | 0.97847 |
| $CH_3NO_2$ | Benzene | 1.9487 | 0.2038 | 10.40 | 0.96561 |
| $CH_3NO_2$ | *p*-Xylene | 1.9487 | 0.2806 | 9.18 | 0.97739 |
| $CH_3NO_2$ | Mesitylene | 1.9487 | 0.3185 | 26.80 | 0.99632 |
| $C_2H_5NO_2$ | Benzene | 2.0159 | 0.2038 | 4.88 | 0.99492 |
| $C_2H_5NO_2$ | *p*-Xylene | 2.0159 | 0.2806 | 7.87 | 0.99499 |
| $C_2H_5NO_2$ | Mesitylene | 2.0159 | 0.3185 | 274.50 | 0.99122 |

[+] N,N-Dimethylacetamide; data from Ref. [6].

Table 2. Effects of the $f_M$ and $f_1$ values on the calculated association constants for DMA.$^+$

| $f_1$ | $f_M$ | K | Corr. Coef. |
|---|---|---|---|
| 0.2464 | 1.60 | 0.547 | 0.98817 |
| 0.2464 | 1.65 | 0.389 | 0.98539 |
| 0.2464 | 1.68 | 0.305 | 0.98322 |
| 0.2464 | 1.70 | 0.253 | 0.98150 |
| 0.2464 | 1.7291 | 0.184 | 0.97847 |
| 0.2464 | 1.74 | 0.160 | 0.97714 |
| 0.2464 | 1.76 | 0.118 | 0.97437 |
| 0.2464 | 1.80 | 0.046 | 0.96710 |
| 0.2464 | 1.84 | 0.013 | 0.95618 |
| 0.20 | 1.7291 | 0.113 | 0.97401 |
| 0.21 | 1.7291 | 0.127 | 0.97501 |
| 0.23 | 1.7291 | 0.158 | 0.97703 |
| 0.24 | 1.7291 | 0.174 | 0.97793 |
| 0.2464 | 1.7291 | 0.184 | 0.97847 |
| 0.25 | 1.7291 | 0.190 | 0.97877 |
| 0.26 | 1.7291 | 0.207 | 0.97956 |
| 0.28 | 1.7291 | 0.242 | 0.98102 |
| 0.30 | 1.7291 | 0.279 | 0.98233 |

$^+$The correct values are $f_M = 1.7291$ and $f_1 = 0.2464$

Table 3. Effects of $f_M$ values on calculated association constants.

| System | $f_M$ | K | Corr. Coef. |
|---|---|---|---|
| $C_2H_5NO_2$ in *p*-xylene$^+$ | 1.75 | 1.138 | 0.95200 |
| | 2.00 | 7.277 | 0.99453 |
| | 2.25 | 19.573 | 0.99904 |
| $CH_3NO_2$ in *p*-xylene$^+$ | 1.50 | 0.013 | 0.57420 |
| | 1.75 | 3.542 | 0.94321 |
| | 2.00 | 10.959 | 0.98119 |
| | 2.25 | 21.899 | 0.99087 |
| $C_2H_5NO_2$ in benzene$^{++}$ | 1.75 | 0.290 | 0.91337 |
| | 2.00 | 4.459 | 0.99432 |
| | 2.25 | 12.815 | 0.99842 |
| $C_2H_5NO_2$ in mesitylene$^{+++}$ | 1.75 | 56.946 | 0.93044 |
| | 2.00 | 256.470 | 0.99048 |

$^+$Using $f_1 = 0.28060$

$^{++}$Using $f_1 = 0.20490$

$^{+++}$Using $f_1 = 0.31906$