ON THE CALCULATION OF ASSOCIATION CONSTANTS OF POLAR MOLECULES

J. E. HOUSE, JR., R. C. REITER, AND D. W. HOPKINS
Department of Chemistry, Illinois State University,
Normal, Illinois 61761

ABSTRACT. — A previously published method of calculating dipole association constants and dipole moments from dielectric constants of dilute solutions of polar substances in a nonpolar solvent is discussed. A computer program is presented which enables simpler and more reliable treatment of the data. Some extensions of the previous method are presented and discussed.

In 1964, Treiner, Skinner, and Fuoss published a method of evaluating self-association constants and dipole moments of polar molecules in nonpolar solvents. The method involves a graphical treatment of dielectric constants and concentrations of dilute solutions of the polar substances. Further, the method assumes antiparallel dimerization of the dipoles which results in a cancellation of the contributions which the permanent dipole moments make to the dielectric constants of the solutions. The method depends upon the fact that when dipole association occurs, the total polarization increases less rapidly than when there is no such association. Thus, the rate of increase of dielectric constant with increasing concentration is indicative of the extent of solute association.

In the calculations, a rather complicated function of dielectric constant and concentration, G (ϵ, c) and derived and its reciprocal is plotted against the product of G (ϵ, c) and c. The slope and intercept of the resulting plot can be used to calculate the association constant and dipole moment of the solute (Treiner, *et al.,* 1964). The Debye-Clausius-Mosotti approximation of volume polarization was used and the volume polarization of the dimer was assumed to be twice that of the monomer.

The work described in this paper was undertaken with two main objectives. First, a computer program was developed to carry out the tedious, repeated evaluation of the function G (ϵ, c). Because the calculated values of the association constant and dipole moment are sensitive to small errors in the function G (ϵ, c), least squares evaluation of the values of the slopes and intercepts is incorporated into the program.

Second, instead of assuming that the volume polarization of the dimer is twice that of the monomer, the computer program allows a variable factor to be introduced and its effect on dipole moment and association constant to be determined. Perhaps this factor should vary as an inverse function of the strength of the forces of molecular association. The results of these extensions of the dipole association theory of Treiner, Skinner, and Fuoss are presented and discussed.

CALCULATIONS

The calculations were carried out using an IBM 360/40 computer with the program written in FORTRAN IV. The program and some general comments on its use follow.

Comments:

1. The "Fuoss G" function,

$$G = \left[\frac{1.189 \text{ x } 10^{-21}}{Es + 2}\right]\left[\frac{(E - Es)}{C\,(E + 2)} - \frac{3RHO_{solv}}{(Es - 1)\ (\beta - Mwt/1000)}\right] - \alpha 10$$

   can be reproduced from the program by substitution of the intermediate function F of S. 13 into the equation in S. 14, with Z = 2.

2. The notation X(I) represents the value of property X for the "Ith" solution. Other previously undefined key symbols and their meanings follow.

   E = ϵ = dielectric constant of the solution

   ES = E_s = dielectric constant of the solvent

   RHO_{solv} = solvent density

   BETA = β = a factor relating solvent and solution densities as RHO = RHO_{solv} + βC. (Densities varied linearly in the range used.)

   WMOL = Mwt = molecular weight of solute

   NPTS = number of data pairs to be plotted

   ALP1O = α_{10} = solute monomer electronic polarization

   Notation in the "least squares" segment of the program is standard, with "s" equivalent to "Σ".

3. The output format will result in clearly labeled results. The data read by S.05 can be any identifying material, such as solute name.

4. The program recycles until a blank card is read by S.02, the parameter read instruction.

5. As listed here, the program varies Z from 1.00 to 2.50 in increments of 0.25. Removal of S.09, S.10 and S.39, and replacement of S.11 by Z = 2. will elminate this procedure.

6. The factor 298.2 in S.30 is temperature (°K) and can be changed depending on the data used.

```
0001       DIMENSION  C(15),E
           (15),G(15)
0002   1   READ(1,2)NPTS,ES,
           BETA,WMOL,RHO,
           ALP1O
0003   2   FORMAT(I2,2X,F5.3,2X,
           F5.4,2X,F6.2,2X,
           F7.5,2X,E14.8)
0004       IF(NPTS)3,99,3
0005   3   READ(1,4)
0006   40  FORMAT(80H
        1                    )
0007       READ(1,5)(C(I),E(I),
           I=1,NPTS)
0008   5   FORMAT(F7.6,1X,F6.4)
0009       DO 9 II=1,7
0010       AI=II
0011       Z=.75+.25*AI
0012       DO 6 I=1,NPTS
0013       F=((1.1890E-21)/(ES+
           2.))*((E(I)-ES)/(E(I)
           +2.)-(ES-1.)*
        1  (BETA-WMOL/1000.)*
           C(I)/(3.*RHO))
```

```
       6 G(I)=F/C(I)-(Z*
         ALP10)/2.
      C LEAST SQUARES FIT
      FOR PLOT OF 1/G VS CG
      FOLLOWS
        SX=0.
        SXY=0.
        SY=0.
        SXX=0.
        DO 7 I=1,NPTS
        X=C(I)*G(I)
        Y=1./G(I)
        WRITE(3,50)X,Y
     50 FORMAT(1HO,2E14.7
        SX=SX+X
        SXY=SXY+X*Y
        SY=SY+Y
      7 SXX=SXX+X**2
        SLOPE=(SX*SY-NPTS
        *SXY)/(SX*SX-NPTS*
        SXX)
        CEPT=(SXY*SX-SY*
        SXX)/(SX*SX-NPTS*
        SXX)
        DEBYE=SQRT(3.*1.3805
        E-16*298.2/CEPT)*1.E+
        18
        AKEQ=SLOPE/(2.*
        CEPT*CEPT)
        WRITE(3,14)
     14 FORMAT(//////80H
       1                             )
        WRITE(3,4)
        WRITE(3,20)Z
     20 FORMAT(1HO,4HZ =
        ,F5.2)
        WRITE(3,8)CEPT,
        SLOPE,DEBYE,AKEQ
      8 FORMAT(1HO,12HIN-
        TERCEPT = ,E14.8/9H
        SLOPE  = ,E14.8/17H
        DIPOLE MOME INT =
        ,F6.2/24H ASSOCIATION
        CONSTANT = ,E14.8)
      9 CONTINUE
        GO TO 1
     99 STOP
        END
```

SAMPLE INPUT

```
.16260  3.203
.10880  2.870
.06239  2.595
.04128  2.471
.03021  2.405
.01999  2.349
.07273  2.660
.05348  2.545
.03838  2.456
.02492  2.379
PNITROANILINE
10 2.233 .0406 138.12 1.02796
  .15000000E-22
```

SAMPLE OUTPUT

```
      X                 Y
0.9264186E-23   0,2689928E 22
0.1390161E-22   0.2760829E 22
0.1906553E-22   0.2805061E 22
0.2544358E-22   0.2858479E 22
0.7411161E-23   0.2697282E 22
0.1084541E-22   0.2785510E 22
0.1478510E-22   0.2792000E 22
0.2187612E-22   0.2851968E 22
0.3629993E-22   0.2997250E 22
0.5170795E-22   0.3144584E 22
PNITROANILINE
Z = 2.00
INTERCEPT = 0.26292032E 22
SLOPE = 0.99281275E 43
DIPOLE MOMENT = 6.85
ASSOCIATION CONSTANT =
  O.71810728E 00
```

DISCUSSION

Dielectric constant, density, and concentration data of Treiner, Skinner, and Fuoss (1964) for solutions of p-nitroaniline (PNA), of m-nitrophenol (MNP), and of pyridinium dicyanomethylide (PDM) in dioxane were used in the computer calculations. A comparison of the results of these workers and the results obtained in this work is shown in Table 1. The results of the calculations for solutions of PNA, for which Treiner, *et al.*, provide the most data, show almost identical values for the association constants. The small differences are due to the use of a least squares routine for obtaining the slope and intercept of the plot of $cG(\epsilon, c)$ against $1/G(\epsilon, c)$. The values of these functions were reported by Treiner, *et al.*, for PNA solutions and the values obtained using the techniques described in this work agree closely.

For the calculations on MNP and PDM solutions the agreement is not nearly as good. In the case of MNP, the association constant calculated by Treiner, *et al.*, is too high, as is the dipole moment. For PDM, the agreement between the dipole moments is good but the association constants differ greatly.

Since the value of the dipole moment is derived from the intercept of the $cG(\epsilon,c)$ *vs* $1/G(\epsilon,c)$ plot, it is obvious that the major errors in the calculations of Treiner, *et al.*, are in the intercept for MNP and the slope for PDM. These results show the extreme sensitivity of the calculations to small errors in the determinations of the slopes and intercepts of the plots of $cG(\epsilon,c)$ against $1/G(\epsilon,c)$. Because of the small variations in these functions in some cases, it would appear that reliable results are not likely to be obtained unless very accurate data are used and the calculations carried out by means other than graphical methods. However, it appears that in the case of MNP, the intercept is so much in error that the error must be caused by a systematic numerical error in carrying out the calculations. In fact, if in the equation giving $G(\epsilon,c)$ (E_s+2) is replaced by (E_s+1) the result is an error in $G(\epsilon,c)$ which would lead to the results published by Treiner, *et al.*

Intuitively, it seems quite likely that the volume polarization of the dimer should not be exactly twice that of the monomer because of mutual inductive effects. Consequently, this assumption was tested by allowing the volume polarization of the

TABLE 1.—Calculated Association Constants and Dipole Moments for PNA, PDM, and MNP.

Compound	μ		K Assoc., (l/mole.)		Slope x 10^{-43}		Intercept x 10^{-21}	
	TSF[a]	This Work[b]	TSF[a]	This Work[b]	TSF[a]	This Work[b]	TSF[a]	This Work[b]
PNA............	6.91	6.85	0.8	0.72	1.06	0.99	2.59	2.63
PDM...........	9.2	9.30	3	1.34	1.28	0.55	1.46	1.43
MNP...........	4.38	3.75	0.37	0.26	3.10	3.92	6.43	8.76

[a] Average values obtained from a graph, dipole moments, and association contants published by Treiner, *et al.*, (1964) when used in the equations $10^{18}\mu = \sqrt{3KT/\text{Intercept}}$ and $K = \text{slope}/2(\text{Intercept})^2$.

[b] Values obtained using densities and dielectric constants published by Treiner, *et al.*, when the computer method is used.

dimer to vary from 1.0 to 2.5 times that of the monomer. The results of these calculations are shown in Table 2. It is immediately obvious that the calculated values of the dipole moment and association constant are rather insensitive to the variable factor, Z. Taking the volume polarization of the dimer to be the same as that of the monomer or taking it to be 2.5 times that of the monomer results in a difference in the calculated value of the association constant of only a few per cent. Because of the introduction of relatively large errors when graphical methods are used in the calculations, the effect of varying the factor would probably be unclear or unnoticed unless the calculations were carried out by means of a computer.

Throughout the calculations it became increasingly clear that the most critical quantity in evaluating the function $G(\epsilon,c)$ is $(E_o\text{-}E_s)$. When the dielectric constant of the solution differs very little from that of the solvent, this quantity approaches

TABLE 2.—Calculated Values of Association Constants and Dipole Moments Showing the Effect of the Z Factor.

<table>
<tr><th colspan="5">Data for PNA</th></tr>
<tr><th>Z</th><th>10^{−22} x Intercept</th><th>10^{−43} x Slope</th><th>Dipole Moment</th><th>K</th></tr>
<tr><td>1.00</td><td>0.2579</td><td>0.9285</td><td>6.92</td><td>0.6979</td></tr>
<tr><td>1.25</td><td>0.2592</td><td>0.9441</td><td>6.90</td><td>0.7029</td></tr>
<tr><td>1.50</td><td>0.2604</td><td>0.9600</td><td>6.89</td><td>0.7079</td></tr>
<tr><td>1.75</td><td>0.2617</td><td>0.9762</td><td>6.87</td><td>0.7130</td></tr>
<tr><td>2.00</td><td>0.2629</td><td>0.9928</td><td>6.85</td><td>0.7181</td></tr>
<tr><td>2.25</td><td>0.2642</td><td>1.010</td><td>6.84</td><td>0.7234</td></tr>
<tr><td>2.50</td><td>0.2655</td><td>1.027</td><td>6.82</td><td>0.7287</td></tr>
<tr><th colspan="5">Data for MNP</th></tr>
<tr><td>1.00</td><td>0.8259</td><td>0.03252</td><td>3.87</td><td>0.2384</td></tr>
<tr><td>1.25</td><td>0.8379</td><td>0.03405</td><td>3.84</td><td>0.2424</td></tr>
<tr><td>1.50</td><td>0.8504</td><td>0.03567</td><td>3.81</td><td>0.2466</td></tr>
<tr><td>1.75</td><td>0.8632</td><td>0.03740</td><td>3.78</td><td>0.2509</td></tr>
<tr><td>2.00</td><td>0.8764</td><td>0.03924</td><td>3.75</td><td>0.2554</td></tr>
<tr><td>2.25</td><td>0.8901</td><td>0.04121</td><td>3.72</td><td>0.2601</td></tr>
<tr><td>2.50</td><td>0.9041</td><td>0.04330</td><td>3.70</td><td>0.2649</td></tr>
<tr><th colspan="5">Data for PDM</th></tr>
<tr><td>1.00</td><td>0.1412</td><td>0.5287</td><td>9.35</td><td>1.325</td></tr>
<tr><td>1.25</td><td>0.1417</td><td>0.5334</td><td>9.34</td><td>1.329</td></tr>
<tr><td>1.50</td><td>0.1421</td><td>0.5382</td><td>9.32</td><td>1.334</td></tr>
<tr><td>1.75</td><td>0.1425</td><td>0.5428</td><td>9.31</td><td>1.337</td></tr>
<tr><td>2.00</td><td>0.1429</td><td>0.5473</td><td>9.30</td><td>1.341</td></tr>
<tr><td>2.25</td><td>0.1433</td><td>0.5520</td><td>9.28</td><td>1.345</td></tr>
<tr><td>2.50</td><td>0.1437</td><td>0.5567</td><td>9.27</td><td>1.349</td></tr>
</table>

zero. Thus, subtraction of α_{10} can result in a $G(\epsilon,c)$ which is about zero or even a negative quantity. This can result in a negative value for the association constant, which has no physical significance.

Treiner, *et al.*, have stated that the energy of interaction of a pair of dipoles varies as the square of the dipole moment,

$$K \approx 10^{-3} Na^3 e^{-u/kT}$$

where N is Avogadro's number, a^3 is the volume occupied by a pair of dipoles, and u is the energy of interaction. Therefore, a linear relationship should exist between log K and μ^2. Their report presents such a relationship. In view of the errors in the values they reported for the association constants, it appears somewhat fortuitous that the linear relationship was obtained. The present results do not enable one to say with certainty that the relationship is linear.

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LITERATURE CITED

TREINER, C., J. F. SKINNER, and R. M. FUOSS. 1964. Dipole Association. J. Phys. Chem., *68,* 3406-3409.

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