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Thermodynamic Data for the Dimethylacetamide-Iodine System

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The equilibrium constant and heat of formation for the dimethylacetamide(DMA)-iodine complex have been thoroughly investigated. The heat of formation was determined over a wide concentration range and found to be independent of concentration. Activity coefficients measured for solutions of amide in carbon tetrachloride showed significant deviation from ideality in the more concentrated solutions. This deviation has little if any effect on the equilibrium constant values measured presumably because the ratio of activity coefficients for the complex and amide is approximately constant. It is shown that the value determined for the heat of formation of the complex depends upon the wave length employed. A procedure for obtaining best data on iodine systems (ΔH values to ± 0.1 kcal.) is described. The best data for the formation of the complex are: $(\text{DMA} + \text{I}_2 \rightleftharpoons \text{DMA} \cdot \text{I}_2)$; $K^{25^\circ} = 6.9 \pm 0.2$; $\Delta H = 4.0 \pm 0.1$ kcal.

Introduction

We have in progress a program concerned with the evaluation of the donor properties of compounds commonly employed as non-aqueous solvents. One phase of this research is concerned with an evaluation of the basicity of these materials toward iodine as a reference acid in the solvent carbon tetrachloride. Reasons for the selection of this system are outlined in our original article on an infrared investigation of the interaction between dimethylacetamide (DMA) and iodine.²

In this article we report a very thorough examination of the dimethylacetamide-iodine system by ultraviolet spectroscopy. It was found that different thermodynamic data are obtained when the measurements are carried out at different wave lengths. Differences in both the enthalpy and entropy are observed. The differences are explained and a procedure for carrying out these studies is proposed.

Activity coefficients were determined for solutions of DMA in carbon tetrachloride. Deviations from ideality were observed but have little effect on the thermodynamic data obtained. The data are independent of concentration in the range studied. A suggested procedure for measuring heats of formation of iodine systems is offered which has produced results reproducible to ± 0.1 kcal.

Experimental

Purification of Reagents.—The purification procedures for all reagents are identical with those previously described.² We have found that Fisher Spectranalyzed carbon tetrachloride can be used without further purification.

Apparatus.—Spectra were recorded with a Cary model 14 M spectrophotometer. A forced air heating system employing a thermistor circuit to turn the heaters on and off was used to control the temperature. Temperature control of $\pm 0.1^\circ$ could be obtained, and no detectable temperature gradients were observed in the cell. The temperature of the solution was measured with either a calibrated thermocouple or thermistor located in a well that fit in a ground glass joint on top of a silica cell. The well extended into the solution but did not interfere with the light path. A carbon tetrachloride solution was used in a reference cell which was not thermostated but a base line was drawn. The data in Table I were obtained on the Cary instrument.

All results in Table II were obtained with a Beckman DU Spectrophotometer equipped with a similar type forced air heating system. An iodine solution of the same concentration as that employed in the equilibrium study was used as a blank³ and $A - A_0$ values were read directly.

Both the blank and sample were thermostated. Absorbance values employed represent an average of seven different readings. All values were shown to be constant for 15-30 minutes.

Sample Preparation.—Iodine and DMA master solutions were prepared by weighing the materials directly in a volumetric flask and diluting with carbon tetrachloride. The actual sample solutions were prepared from aliquots of these stock solutions. The concentration of iodine was determined accurately from the A^0 value of the sample solution at 520 μ . A molar absorptivity of 909 l. mole⁻¹ cm.⁻¹ was obtained in agreement with a reported value.⁴ The concentrations at the various temperatures studied were corrected for volume changes.⁵

Calculation of the Equilibrium Constant.—The procedure utilized to calculate the equilibrium constants has been described previously.⁵ In those experiments where the DMA/I₂ ratio is less than one it was assumed that the molar absorptivities were the same as those in excess DMA in dilute solution. This assumption appears to be valid because the isobestic point in dilute DMA solution is retained in excess iodine. The expression for the equilibrium constant reported⁶ is

$$K^{-1} = \frac{A - A^0}{\epsilon_C - \epsilon_I} - C_D - C_I + \frac{C_D C_I}{A - A^0} (\epsilon_C - \epsilon_I) \quad (1)$$

All terms are defined in the mentioned reference.

Activity Coefficient Measurements.—Solutions of DMA in carbon tetrachloride were placed in an ebulliometer constructed from a Cottrell-Choppin molecular weight apparatus which was modified to contain the essential features of the apparatus used by Othmer.⁶ The apparatus was wrapped with glass wool and asbestos tape. After equilibrium was attained in the system, samples of the liquid and vapor were obtained. The samples were analyzed with a Perkin-Elmer spectrometer in accordance with the procedure already described³ and the amide concentration calculated. The partial vapor pressure of the amide, P_D , in the vapor was calculated from Dalton's law, $P_D = N_D P_T$, where P_T is the total vapor pressure and N_D is the mole fraction. Deviations from ideality as defined by Henry's law were used to estimate activity coefficients, *i.e.*, $P_D^* = K_H C_D$, where C_D is the concentration of amide in the solution, K_H is the Henry's law constant, and P_D^* is the partial vapor pressure in dilute solution. The activity coefficient of the amide, γ_D , equals $P_D/K_H C_D$.

Statistical Treatment of The Data.—Two different methods were employed to estimate the error in equilibrium constants. When fewer than seven values were considered, the range was determined and multiplied by the appropriate constant⁷ to produce an error representing a 95% confidence level. For more than six values, the sample variance was calculated and the error for 95% confidence determined from the equation $M = \bar{X} \pm ts/\sqrt{n}$. All terms are defined in the reported reference.⁷ The ΔH and ΔS values were determined and the error calculated by the method of least squares.⁷ Systematic errors have been eliminated in so far as was possible by utilizing different personnel and different equipment. Heats of formation are reproduced to

(1) Taken in part from Ph.D. theses, University of Illinois.

(2) C. D. Schmulbach and R. S. Drago, *J. Am. Chem. Soc.*, **82**, 4484 (1960).

(3) Sister M. Brandon, O.P., M. Tamres and S. Searles, *ibid.*, **82**, 2129 (1960).

(4) P. A. D. DeMaine, *J. Chem. Phys.*, **26**, 1192 (1957).

(5) N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81**, 6138 (1959).

(6) D. F. Othmer, *Ind. Eng. Chem.*, **35**, 614 (1943).

(7) H. A. Laitinen, "Chemical Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 547.

TABLE I
THERMODYNAMIC DATA FOR DMA-I₂ IN CCl₄^a

Temp., °C.	Wave length (mμ)	K	(ε _C - ε _I)
46.7	445	3.7 ± 0.3	1090
46.7	520	3.7 ± .2	-722
46.3	445	3.8 ± .1	1060
46.3	520	3.8 ± .6	-680
37.2	445	4.8 ± .4	1000
37.2	520	4.1 ± 1.0	-767
36.5	445	4.8 ± 0.2	1080
36.5	520	4.5 ± .2	-719
36.5	545	4.6 ± .4	-656
36.2	520	4.4 ± .2	-733
31.5	445	5.4 ± .5	1060
31.5	520	5.3 ± .2	-715
29.4	515	5.0 ± 1.5	-720

TABLE II
EFFECT OF CONCENTRATION ON THE THERMODYNAMIC DATA FOR THE DMA-IODINE SYSTEM^a

C _D	C	C _D /C _A	-ΔH	K ₂₁	-ΔS
0.0023	0.00700	0.33	3.8 ± 0.2	7.3 ± 0.3	9.9 ± 0.9
.0043	.00510	1	4.0 ± .1	6.7 ± .2	10.6 ± .5
.0097	.0101	1	3.8 ± .2	6.7 ± .2	8.9 ± .7
.0111	.00071	16	4.1 ± .3	7.1 ± .4	9.8 ± 1.1
.0117	.00190	6	3.9 ± .3	6.7 ± .3	9.2 ± 1.0
.0482	.00270	18	4.1 ± .2	6.9 ± .2	9.8 ± 0.8
.0585	.00130	46	4.3 ± .2	5.9 ± .3	10.9 ± .7
.0749 ^b	.00190	39	4.6 ± .1	6.1 ± .2	12.6 ± .6
.0829 ^b	.00191	44	4.6 ± .1	6.1 ± .2	12.6 ± .6
.0939 ^b	.00160	58	4.7 ± .2	6.1 ± .2	12.2 ± .8
.1560	.00139	112	4.9 ± .2	6.1 ± .3	12.7 ± .8
.1560	.00139	112	4.1 ± .2	6.7 ± .3	10.0 ± .8
.1560 (550 mμ)	.00139	112	3.7 ± .3

^a The concentrations of amide C_D and iodine C_I are in moles/l., -ΔH in kcal./mole; K in l./mole; -ΔS in e.u.; ε_C - ε_I = 1050 ± 20. ^b Indicates experiments at 520 mμ, all others were carried out at 450 mμ.

0.1 kcal. The benzene-iodine heat reported in the literature was reproduced exactly in our Laboratory.

Results and Discussion

A. Loss of the Isobestic Point in Concentrated DMA Solution (Fig. 1).—Spectra typical of those obtained in this study are illustrated in Figs. 1 and 2. Equilibrium constants were calculated from the absorbance changes at 545, 520 and 445 mμ. Typical K⁻¹ vs. (ε_C - ε_I) plots are presented in Fig. 3 to illustrate the precision of the data. The equilibrium constant values are summarized in Table I.

Our treatment of the data⁵ reveals several interesting pieces of information regarding iodine systems that are not revealed by other treatments that smooth out all the data. In Fig. 1, as in most of the spectra obtained in this concentration range (0.1 to 0.4 M DMA), the curve in the most concentrated solution falls below the isobestic point⁹

(8) The K values are in terms of l. mole⁻¹. The ε_C-ε_I values are in terms of l. mole⁻¹ cm.⁻¹. The studies at 37.2 and 29.4° were performed using five centimeter cells; all other results were obtained from 1 cm. cells. The K values reported above are the average values obtained, often from several experiments at a given temperature. These results lead to the following thermodynamic data; with an error for the 95% confidence level:

-ΔH = 4.1 ± 0.8 kcal. mole⁻¹; -ΔS = 10.3 ± 2.5 e.u.

The concentration range employed was from 0.02 to 0.38 M in DMA and from 3 × 10⁻⁴ to 8 × 10⁻⁴ M in I₂.

(9) An isobestic point indicates an equilibrium between two absorbing species which have overlapping absorption bands and which each obeys Beer's Law.

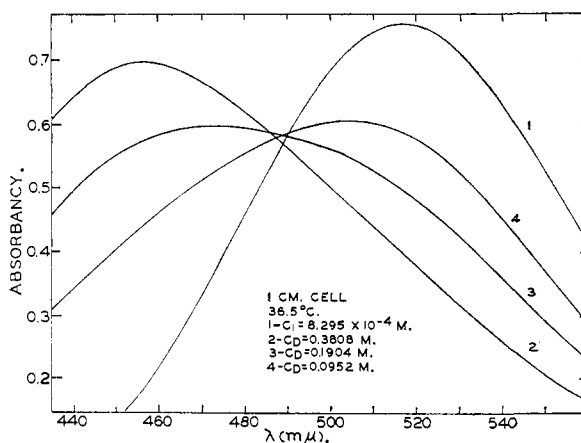


Fig. 1.—Visible spectra of DMA-I₂ in CCl₄.

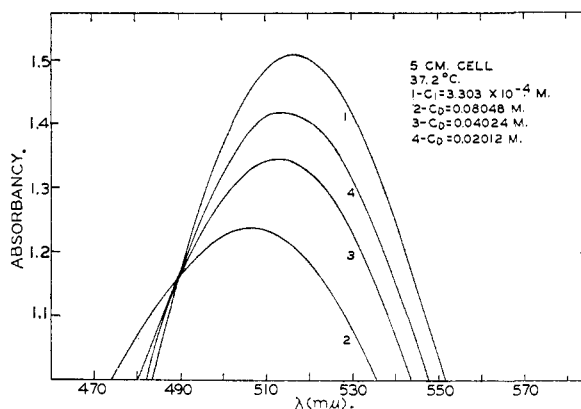


Fig. 2.—Visible spectra of DMA-I₂ in CCl₄.

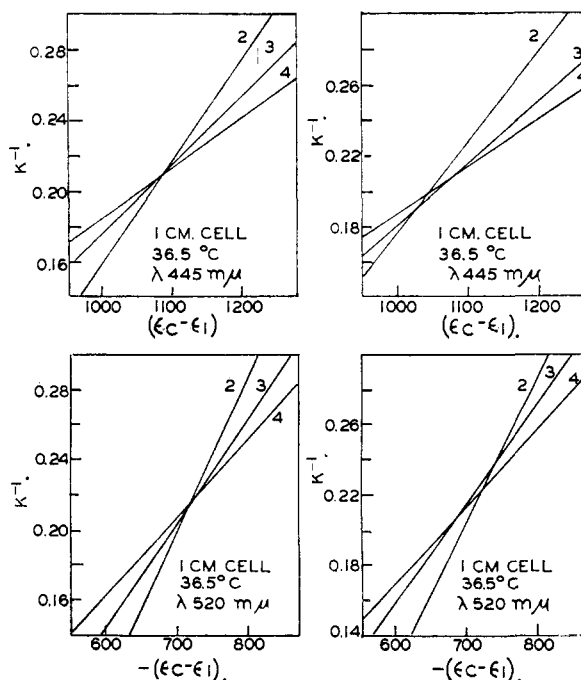


Fig. 3.—(ε_C - ε_I) vs. K⁻¹ plots.

around 490 mμ. This cannot be due to chemical reaction for curve 2 of Fig. 1 is obtained immediately after mixing and does not change in the 440

to 550 $m\mu$ region over a period of 1.5 hr. It is proposed that the loss of the isosbestic point is from a shift in the wave length of the polar, complex absorption peak by the addition of excess DMA. Solvent shifts of this sort are quite common.¹⁰ A regular displacement of the complex peak upon the addition of DMA would result in spectra similar to those in Fig. 1. This proposal satisfies other aspects of our data. In spite of the loss of the isosbestic point the equilibrium constants calculated from the absorbance at the maximum of either the blue shift (445 $m\mu$) or free iodine peak (520 $m\mu$) are in agreement. Good crossings are obtained for the K^{-1} vs. $(\epsilon_C - \epsilon_I)$ plots at all concentrations (0.04 to 0.4 M DMA) indicating that the data in concentrated solutions obey the same equilibrium constant expression as those in more dilute solution. The same K is obtained from curves that have an isosbestic point (Fig. 1) as from curves that do not (Fig. 2). Shifting of the complex peak has a negligible effect on the absorption value at 445 $m\mu$ because the absorption bands are broad.¹¹ A shifting of the complex peak has a negligible effect at 515 $m\mu$ because the contribution of the complex absorption to the total absorption is small in this region for the DMA system. The spectra obtained by Ketelaar¹² on the dioxane-iodine system are similar to those obtained above and can also be explained by a shifting of the complex peak.

Deviations in K should occur if the calculations are carried out on the side of a shifting peak. This concept was used to determine whether or not the iodine peak was shifting. A constant K and good crossings for the K^{-1} vs. $(\epsilon_C - \epsilon_I)$ plots at 520 and 545 $m\mu$ indicate that any change in the iodine peak is negligible. Only a shifting of the complex iodine peak is consistent with all of the above observations.

B. Effect of Base Concentration on Thermodynamic Data.—The thermodynamic data reported in Table I represent values obtained over a wide concentration range. If one applies the $\epsilon_C - \epsilon_I$ values obtained in this study to individual solutions of different amide concentration, the results reported in Table II are obtained. A pronounced difference in ΔH and ΔS is observed at the different wave lengths employed, but the data obtained are independent of concentration in the range studied.

In order to assess the effects of non-ideal behavior of the amide on this system, activity coefficients were evaluated for DMA-carbon tetrachloride solutions. The results of this study are summarized in Table III.

Allowing for the error in selecting the Henry's law line, it may be concluded that even at elevated temperatures, the data show definite deviations from ideality at DMA molar concentrations of 0.10 and greater. In view of the appreciable dipole moment of DMA (3.79 Debye) association from dipole-dipole interactions is ex-

TABLE III
ACTIVITY COEFFICIENT FOR DMA IN CCl_4 : $\gamma = \gamma_1/\gamma_2\gamma_3$

C_D of liquid, moles/l.	P_0 , mm.	K_{HCD}	γ_D
0.010	0.08	0.086	1
.018	.16	.15	1
.027	.23	.23	1
.036	.28	.31	0.90
.041	.34	.37	.92
.064	.49	.55	.89
.081	.61	.69	.88
.099	.76	.85	.89
.153	1.17	1.31	.89
.195	1.48	1.67	.89
.254	1.78	2.18	.82
.298	2.00	2.56	.78
.346	2.36	2.98	.79
.391	2.58	3.36	.77

pected. Cryoscopic data for solutions of DMA in benzene also indicate association in this concentration range.¹³ It appears that the true equilibrium constant (K_a) is best expressed by

$$K_a = \gamma K = \frac{\gamma_1[\text{DMA-I}_2]}{\gamma_2[\text{DMA}]\gamma_3[\text{I}_2]}$$

Since iodine is a non-polar substance, γ_3 is assumed to be a constant close to unity in the concentration range employed. Corrections were made for the DMA concentrations and the K vs. $\epsilon_C - \epsilon_I$ plots were recalculated using the activity of DMA instead of concentration. Spurious crossings were obtained for there is no K that now describes this system. Any¹⁴ activity coefficient correction employed resulted in poorer crossings. The correction was not a legitimate one. Since good crossings are obtained without the correction over a concentration range in which γ_2 is changing, the ratio of γ_1/γ_2 must be a constant in this concentration range. The change in γ_1 must be proportional to the change in γ_2 at this temperature. The constancy of the ratio of activity coefficient has been proposed previously by other investigators¹⁵ for iodine systems.

The deviation of the complex from ideality occurs in spite of the very low concentration of the complex. This behavior is similar to an effect observed with ionic solutions. It has been shown¹⁶ that the activity coefficient of an electrolyte in an indifferent electrolyte is a function of the ionic strength of the media. The excess of polar DMA molecules appears to have a similar effect upon the activity coefficient of the complex in carbon tetrachloride.

The most accurate data reported in Table II are the ΔH values. These results are affected very little by the range of error in ϵ_c as long as ϵ_c is constant at different temperatures. They are obtained by measuring the equilibrium constant on a single solution as a function of temperature so weighing and dilution errors are minimized. These arguments do not apply to the K values. The ΔH values indicate that the proposal by DeMaine

(13) H. O. Chaplin and L. Hunter, *J. Am. Chem. Soc.*, **1114** (1937).

(14) Any refers to various values obtained from different Henry's law lines.

(15) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949); R. M. Keefer and L. J. Andrews, *ibid.*, **75**, 3561 (1953).

(16) G. N. Lewis and M. Randall, *ibid.*, **43**, 1112 (1921).

(10) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253, 3267 (1958).

(11) Actually a slight change in ϵ_0 inside experimental error could occur and escape detection.

(12) J. A. A. Ketelaar, *et al.*, *Rec. trav. chim.*, **70**, 499 (1951); **71**, 1104 (1952).

referred to as the Liquid Lattice Penetration Theory¹⁷ does not apply to this system. According to this theory K and ΔH are independent of the donor concentration only if the number of unfilled donor aggregates available for complexing exceeds the iodine concentration. A series of experiments was carried out at various mole ratios of DMA to iodine (1:1 through 16:1) but at a constant, dilute, DMA concentration (Table II, lines 3, 4 and 5). No detectable change in ΔH was observed.

C. The Effect of Wave Length on the Thermodynamic Values Measured.—The general procedure of studying absorbance changes on a single solution as a function of temperature is a new approach to the determination of ΔH values on these iodine systems. It enables more accurate data to be obtained. When the experiment is carried out by the standard procedure the results reported in Table I are obtained. If there are any small effects in the ΔH value due to concentration changes or changing extinction coefficients these are all averaged out. The resulting ΔH has a wide error limit to include all these changes. The two extremes in ΔH reported in Table II are covered by the error limits in Table I.

Our new procedure enables a ΔH value determination on a single solution so errors in making up the various solutions required for the standard procedure are eliminated. The concentration variable and the wave length variable can be studied in detail and measured precisely.

The thermodynamic values reported in Table II are independent of the reported experimental error that exists in the $\epsilon_c - \epsilon_f$ value reported in Table I. Even an experimental error of 10% in this number has an effect on ΔH of only 0.1 kcal. This is true as long as the term $(C_D - C_I)/(A - A_0)(\epsilon_c - \epsilon_f)$ of equation 1 is sufficiently greater than $-(C_D + C_I)$ (e.g., a low value for K is obtained or dilute solutions are employed). However, the value of $\epsilon_c - \epsilon_f$ must be constant at all temperatures studied. Calculations show that a change in the magnitude of the $\epsilon_c - \epsilon_f$ value from 730 at 22.8° to 699 at 42° in the 520 $m\mu$ region causes a change in ΔH from 4.7 to 4.1 kcal.

In an attempt to gain additional information on this subject, the iodine curve was studied at 25 and 46° in the wave length region from 580 to 400 $m\mu$. The value for ϵ_f at the maxima decreased from 910 to 890. This change has an effect on ΔH . Broadening of the curve was noted in the wing areas but there was essentially no change at 550 $m\mu$. ($\epsilon_f = 642$ at 25° and 648 at 44°.) At 450 $m\mu$ the change in ϵ_f was negligible. A value of 156 was obtained at 44° while a value of 151 was obtained at 25°. This has a negligible effect on the $\epsilon_c - \epsilon_f$ value and the ΔH measured at 450 $m\mu$.

Unfortunately, the complex peak cannot be examined in such detail. Errors in K affect the accuracy of the resolution of this curve. However, the large ΔH value obtained at 520 $m\mu$ indicates a change in the ϵ_c value as a function of tempera-

ture in this region. Crude resolution of the complex curve supports this proposal. At 550 $m\mu$ the value of ϵ_f does not change and the complex absorption is very slight so any change in $\epsilon_c - \epsilon_f$ would be minor and have a negligible effect on the ΔH value. The agreement in ΔH obtained at 550 and 450 $m\mu$ suggests that any changes in the complex maxima (450 $m\mu$) are slight compared to the larger $\epsilon_c - \epsilon_f$ value.

Further evidence for a change in the ϵ_c value in the 520 $m\mu$ region can be obtained from the isosbestic point which appears at higher wave lengths at elevated temperatures. The shift of the complex curve with concentration is also not as pronounced at the elevated temperatures. Both these changes would result in a larger average ϵ_c value at 520 $m\mu$ at the elevated temperatures. A ΔH value would be obtained which is too large if $\epsilon_c - \epsilon_f$ is assumed to be constant.

D. A Comparison of the Infrared and Ultraviolet Methods.—The data obtained from infrared spectroscopy² are less reliable than the ultraviolet data. Conditions were employed in the infrared study which produced an equilibrium constant that was very greatly dependent upon the value of $\epsilon_c - \epsilon_A$. Physical limitations (solubility, etc.) also resulted in a set of data which could not be solved uniquely for K and $\epsilon_c - \epsilon_A$, for overlap could not be handled by an equation.⁵ An attempt was made to resolve the curves using the Ramsay equation. An absorbance due to the complex under the free amide peak of about 0.01 absorbance unit was calculated for solutions containing the highest concentrations of complex. This resulted in an ϵ_c value of 7.5 at 1662 cm^{-1} and an $\epsilon_c - \epsilon_A$ value of -61. An equilibrium constant of 9.5 at 25° resulted. The accuracy of the Ramsay equation is such that an error of 0.01 absorption unit is to be expected. If there is no overlap of the peaks at 1662 cm^{-1} , e.g., $\epsilon_c = 0$, and a value of $\epsilon_c - \epsilon_A = 68$ is employed in the calculations, an equilibrium constant at 25° of 8.0 ± 0.7 and a $-\Delta H$ of 4.4 ± 0.8 is obtained from a least squares treatment of the data. The error is reported at the 95% confidence level. The infrared data are found to be consistent with the more accurate ultraviolet data.

E. Suggested Procedure for the Ultraviolet Determination of Thermodynamic Data on Iodine Systems.—In order to get reliable data for the heat of formation of molecular complexes of iodine, it is necessary to measure the equilibrium constant and extinction coefficients under experimental conditions that give widely different slopes to the K vs. $\epsilon_c - \epsilon_f$ lines. This should be done at the two temperature extremes to eliminate the possibility of large changes outside of experimental error in $\epsilon_c - \epsilon_f$ with temperature. Small changes in $\epsilon_c - \epsilon_f$ with temperature (about 10%) can produce appreciable differences in ΔH . These effects can be detected by our method of performing the ΔH experiment on a single solution at several different frequencies. The data obtained on the complex curve should produce the best results. If a large blue shift is obtained these results should be reproduced at or above 550 $m\mu$.

(17) P. A. D. LeMaine, *J. Chem. Phys.*, **26**, 1192, 1199 (1957).