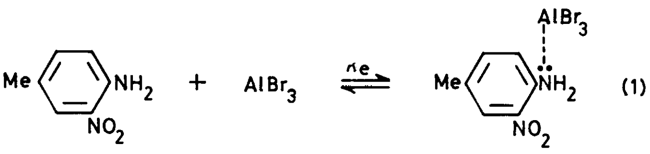
Measurements on Electron-donor–Acceptor Complex Equilibria using Fibre-optic Photometry

Thomas Dittmer, Oskar Nuyken,*† and Stephen Pask
Lehrstuhl für Makromolekulare Stoffe, TU München, Lichtenbergstraße 4, 8046 Garching, West Germany

The electron-donor–acceptor-complex equilibrium involving 4-methyl-2-nitroaniline (1) and aluminium bromide in diethyl ether has been studied over the temperature range −15°—25 °C using a fibre-optic photometer. The experimental results have been used to calculate the equilibrium constants $K_e(T)$ and the enthalpy of the complex formation ΔH_k. The major design features and advantages of the apparatus used are described and two methods of evaluating the data are compared and discussed.

Photometry is a well-established method for measuring electron-donor–acceptor (EDA)-complex equilibria. Satchell (*e.g.*, ref. 1) has published such data obtained using standard u.v.–visible photometry at room temperature for a large number of Lewis acid–base systems. Quantitative studies of such systems at lower temperatures have not been found in the literature, probably because such studies present considerable experimental difficulties.[2] Fibre-optic photometry has opened up the possibility of making relatively simple u.v.–visible photometric measurements using a mobile probe in almost any reaction vessel. For low-temperature measurements the only requirement is a suitably thermostatted reaction vessel. Furthermore, with this novel method, measurements can easily be made while maintaining the reactants either under an inert gas atmosphere or *in vacuo*.

In this paper the principles of the method and its applicability will be discussed. As an example, the EDA system 4-methyl-2-nitroaniline (1) and $AlBr_3$ in diethyl ether was chosen since this system has been reported to form a 1:1 EDA-complex at 25 °C.[3]



(1) **(2)**

Electron-donor (D) Electron-acceptor (A) EDA-complex (DA)

The electron donor (1) exhibits an intramolecular charge-transfer band at 405 nm, which is shifted to shorter wavelengths by complexation of the amino group.[4,5]

Thus, a decrease in the absorption at 405 nm with addition of $AlBr_3$ to a solution of (1) gives a measure of the degree of complexation.

Experimental

Materials.—$AlBr_3$ (99%, Aldrich) was purified by double sublimation *in vacuo* and transferred into sealed glass ampules. (The technique for determining the contents of these phials is described in ref. 6.) In order to prepare the standard solutions of $AlBr_3$ the glass phials were broken under dry N_2, in the apparatus described below, and freshly distilled diethyl ether was added. Provided the described procedure was followed and the solution was not allowed to become warm such solutions were invariably colourless. 4-Methyl-2-nitroaniline (1) (99%, Aldrich) was recrystallized twice from a 1:1 ethanol–water mixture and finally dried *in vacuo* to constant weight. Standard solutions of (1) in diethyl ether were prepared under dry N_2. Diethyl ether (98%, Uvasol–Merck) was predried over $CaCl_2$ and then transferred into the all-glass apparatus where it was kept under dry N_2 and over Na. Before use it was always freshly distilled through a 30 cm column filled with glass helices. N_2 (Linde) was dried by passing it through a column containing BTS (®) catalyst (BASF) and then through a column containing 4 Å molecular sieves (Merck).

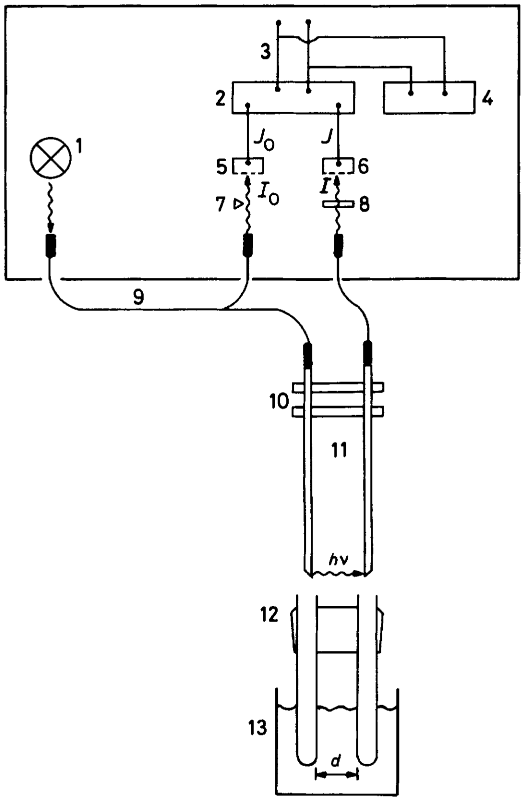


Figure 1. Fibre-optic photometer. 1 = Halogen lamp. 2 = Precision logarithmic amplifier. 3 = To printer. 4 = Digital display. 5 = Reference detector. 6 = Measuring detector. 7 = Mechanical aperture. 8 = Interference filter. 9 = Optical fibre. 10 = Adjustable holder. 11 = Quartz rods. 12 = Quick-fit joint with protecting pockets. 13 = Solution to be studied

Fibre-optics Photometry.—Figure 1 shows the essential components of the fibre-optic photometer used for this study (manufactured by Schölly, Fiberoptics Corp., 7809 Denzlingen,

---

† Lehrstuhl für Makromolekulare Chemie I, Universität Bayreuth, 8580 Bayreuth, West Germany.

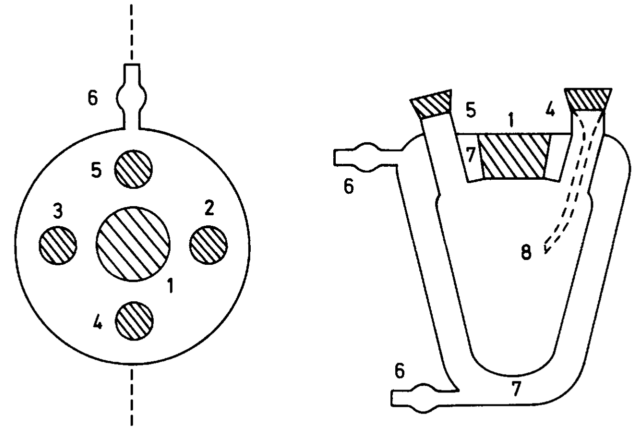


Figure 2. Reaction vessel. 1 = Connection for measuring probe. 2 = Connection for thermometer. 3 = Auxiliary connector. 4 = Main connector. 5 = Auxiliary connector. 6 = Jacket connector. 7 = Jacket. 8 = Extension of joint to ensure that all added material was in the solution rapidly

West Germany). Since this apparatus is not a common analytical standard its main principles of operation are described below. The light emitted from the halogen lamp is directed into a flexible fibre-optic cable ($\varphi = 3 \times 10^{-3}$ m; $l =$ 1.5 m). The fibre-optic cable divides into two to return a part of the light directly to the reference detector while the rest of the light is carried to the measurement probe, travels through the solution under study and then returns to the detector. An interference filter in front of the detector allows only the desired wavelengths to reach the detector. Silicon photodiode detectors were used. The currents from the detectors (J and J_0), which are proportional to the light intensities I and I_0, are treated directly in a precision logarithmic amplifier which dispenses with the need for the electronics usually contained in standard spectrophotometers for achieving a linear response. Setting the zero-point can be achieved either by the use of a mechanical aperture or electronically. Due to the spectral characteristics of the lamp, optical fibres and detectors available the photometer employed for this work could be used from 400—800 nm and had a linear absorption range from $E \leqslant 1.5 \pm 0.005$. To protect the actual measurement probe, which consists of two quartz rods in an adjustable holder, the quartz rods are inserted into quartz or Pyrex glass pockets protruding into the solution to be measured. In order to facilitate a rapid change of reaction vessel these protecting pockets were attached to a Quick-Fit joint. (For more exacting work *in vacuo* the protecting pockets can be sealed to the body of the reactor.) The 'cell length' d throughout the work reported in this paper was 0.652 cm.

Apparatus.—For all the photometric measurements discussed in this paper and for preparing the standard solutions a closed glass vessel was employed. The individual parts of the apparatus were connected *via* Quick-Fit joints with PTFE gaskets. Only grease-free PTFE taps were used. Thus, all operations could be carried out either *in vacuo* or under dry N_2 so that the influence of water was minimized. The burettes used were thermostatted (± 0.1 °C) at their calibration temperature of 20 °C. The actual volume at each reaction temperature was calculated using the cubic expansion coefficient for diethyl ether.[7] The reaction vessel (shown in Figure 2) was also thermostatted using a two-stage thermostat/kryostat system to maintain temperatures between -15 and 25 °C to within ± 0.1 °C. The reaction vessel was stirred magnetically.

U.v.–Visible Equilibrium Experiments.—Before starting each experiment the apparatus was repeatedly evacuated and filled with dry N_2. After distilling the required volume of diethyl ether into the reaction vessel a given volume of standard solution of (**1**) was added to give a starting concentration of the donor component $[D]_a \approx 2 \times 10^{-4}$ mol l^{-1}. The initial absorption of the solution E_a was then measured and the ε_D calculated using the Lambert–Beer law. Thereafter, stepwise addition of a standard $AlBr_3$ solution ($[A]_o = 10^{-3}$—10^{-1} mol l^{-1}) allowed the measurement of several values of the equilibrium absorption E_e in a single experiment. The temperature for any one experiment was always held constant. The stepwise dilution of the solution with respect to (**1**) and the resulting reduction in E_a were mathematically compensated. The initial volume in the reaction vessel was generally about 60 ml and the total volume of $AlBr_3$ solution added was never more than 12 ml.

U.v.–Visible E_* Experiments.—For these experiments an $[A]_0 = 1.25$ mol l^{-1} was prepared at 25 °C by adding a more concentrated standard $AlBr_3$ solution. The equilibrium absorption E_e ($E_e \ll E_0$) was then measured as a function of temperature between -15—25 °C.

U.v.–Visible Control Experiments.—By varying the temperature at any particular set of concentrations it was possible to ensure that the reaction between (**1**) and $AlBr_3$ was indeed reversible. It was also checked that the change in E_e correlated with the values calculated from experiments carried out at any temperature. Furthermore, after varying the temperature identical values of E_e were obtained on returning to the starting temperature. Such experiments demonstrated that the system studied is stable for at least 3 h and does not involve any irreversible side reactions. Additional control experiments in which a solution of (**1**) was added stepwise to a solution of $AlBr_3$ also yielded conformable results ($[D]_0 = 2 \times 10^{-5}$—2×10^{-4} mol l^{-1}).

Results and Discussion

Basic Algebra.—In order to calculate the equilibrium constants from the experimental results there are two basic procedures available. Both procedures are based on the same elementary equations: *

$$K_e = [DA]_e/([D]_e \times [A]_e) \tag{2}$$

$$E_0 = \varepsilon_D \times d \times [D]_0 \quad \text{(No complexation)} \tag{3}$$

$$E_e = \varepsilon_D \times d \times [D]_e + \varepsilon_{DA} \times d \times [DA]_e \quad \text{(Equilibrium)} \tag{4}$$

$$E_* = \varepsilon_{DA} \times d \times [DA]_e = \varepsilon_{DA} \times d \times [D]_0 \quad \text{(Negligible residual D)} \tag{5}$$

$$[D]_0 = [D]_e + [DA]_e \tag{6}$$

$$[A]_0 = [A]_e + [DA]_e \tag{7}$$

Manipulation of equations (2)—(7) yields either equation (8) or (9a) and (9b) which express the equilibrium constants as a function of experimentally obtainable parameters.[8–10]

---

* For a summary of abbreviations used in the equations see the Appendix.

Table. Equilibrium constants and absorption coefficients according to the methods of Drago and Satchell

	According to Drago				According to Satchell			
T/°C	ε_{DA}/l mol^{-1} cm^{-1}	$\pm \Delta\varepsilon_{DA}$/%	$\bar{K}_e$/l mol^{-1}	$\pm \Delta\bar{K}_e$/%	ε_{DA}/l mol^{-1} cm^{-1}	$\pm \Delta\varepsilon_{DA}$/%	$\bar{K}_e$/l mol^{-1}	$\pm \Delta\bar{K}_e$/%
25.0	340	27	21.7	5	250	40	20.9	3
15.4	320	29	39.3	6	250	40	36.2	6
5.0	230	47	74.2	7	250	40	75.8	8
−5.0	340	40	155	9	250	40	150	13
−15.0	270	28	370	5	250	40	313	13

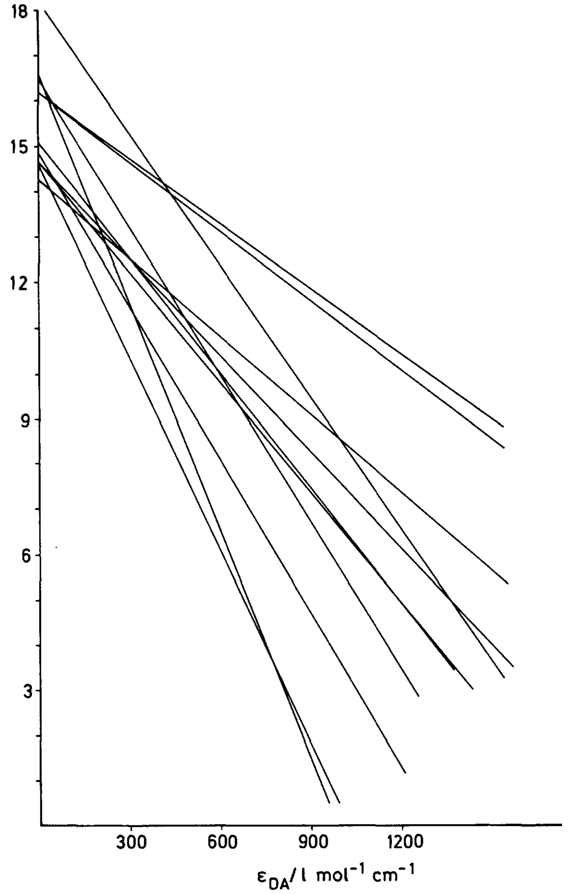


Figure 3. Simultaneous graphical determination of K_e and ε_{DA}

The Method according to Drago.[8]—The values for E_0, ε_D, and E_e are directly obtainable from the photometric measurements, and $[A]_0$ and $[D]_0$ are experimental parameters (see Experimental section) but using Drago's method the values for ε_{DA} and K_e^{-1} are calculated simultaneously. Thus, using (8), and several

$$K_e^{-1} = \left\{\frac{d \times (\varepsilon_{DA} - \varepsilon_D)}{E_e - E_0} \times [D]_0 \times [A]_0\right\} - [D]_0 - [A]_0 + \frac{E_e - E_0}{d \times (\varepsilon_{DA} - \varepsilon_D)} \qquad (8)$$

sets of data ($[A]_0$, $[D]_0$, E_0, E_e, and ε_D), the dependence of K_e^{-1} on the value of ε_{DA} is calculated and the corresponding curves plotted. Optimally, all the curves pass through a single point corresponding to a particular K_e^{-1}, ε_{DA} data-pair. In practice several intersection points are obtained and the average values calculated. This procedure is equivalent to solving simultaneous equations for all possible pairs of data. As an example Figure 3 shows a graph of the data for T = 5.0 °C using equation (8). The small area in which most of the intersections lie corroborates the assumption that the system involves a simple 1:1 EDA-complex. Outliers were identified using Nalimov's test[11] and eliminated. A summary of the results obtained is given in the Table.

The Method according to Satchell.[9,10]—In the same way as for Drago's method the directly obtainable experimental

$$K_e = \frac{E_0 - E_e}{E_e - E_*} \times \frac{1}{[A]_e} \qquad (9a)$$

$$[A]_e = [A]_0 - \frac{E_0 - E_e}{E_0 - E_*} \times [D]_0 \qquad (9b)$$

parameters are $[A]_0$, $[D]_0$, E_0, and E_e. However, using Satchell's method values for E_* ($= \varepsilon_{DA} \times d \times [D]_0$) and ε_{DA} are experimentally determined and not, as is the case for Drago's method, simultaneously calculated with K_e. With the system studied and the experimental set-up used for this work it was not possible to determine E_* directly since this would have necessitated the addition of solid $AlBr_3$ to a solution of (**1**) until $E_e = E_*$ = constant. Thus, ε_{DA} was determined by adding a very high concentration of $AlBr_3$ to shift the equilibrium towards the complex side and E_e measured at 25 °C. (See Experimental section.) The very small value of E_e ($E_e \ll E_0$) suggested two extreme possibilities for the values of ε_{DA}:

(a) A simple equilibrium pertains but: if $E_e = \varepsilon_D \times d \times [D]_e$ and $E_* = 0$

$$\varepsilon_{DA} = 0 \qquad (10)$$

or (b) The complexation is essentially complete and thus:

$$[D]_e \longrightarrow 0;\ [DA]_e \longrightarrow [D]_0$$

and $$E_e = \varepsilon_{DA} \times d \times [D]_0 = E_*$$

so that $$\varepsilon_{DA} = \frac{E_e}{d \times [D]_0} \qquad (11)$$

With the two values of ε_{DA} from equation (10) and (11) first approximations of E_e and K_e could be calculated for an equilibrium experiment at 25 °C from equations (5), (9a), and (9b). With the values of K_e so obtained and those for $[A]_0$ and $[D]_0$, the values for $[A]_e$, $[D]_e$ and $[DA]_e$ could be calculated for an E_* experiment. Using a modification of equation (4):

$$\varepsilon_{DA} = \frac{E_e - \varepsilon_D \times d \times [D]_e}{d \times [DA]_e} \qquad (4')$$

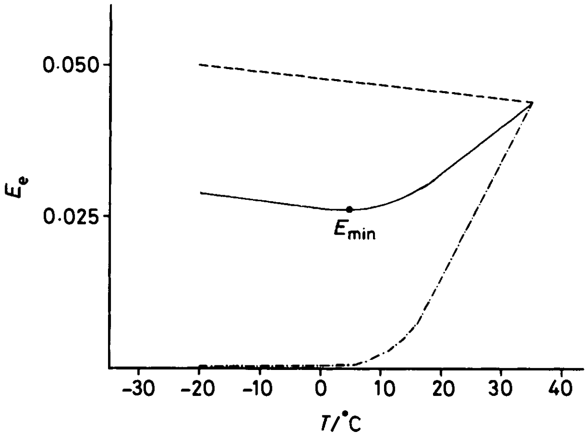


Figure 4. Temperature variation during an E_*-type experiment. —— Observed; –'–·– extreme case a; ––– extreme case b

it is then possible to calculate new values for ε_{DA}. With these values the iteration can be continued until the values obtained for two successive iterations are essentially identical. In this study it was found that no more than two iterations were necessary to arrive at values of ε_{DA} and K_e which were identical from the two extreme cases (see Table).

Varying the temperature during an E_*-type experiment allowed a check on the values obtained at 25 °C and at other temperatures (see Figure 4). For the remaining equilibrium experiments E_* could be calculated from equation (5) with the established value for ε_{DA}.

To determine the minimum of a plot of E_e *vs.* T/°C (see Figure 4) according to equation (5):

$$E_{min.} = E_* = \varepsilon_{DA} \times d \times [D]_0$$

As can be seen in Figure 4 the calculated and observed value for $E_{min.}$ are in good agreement. {For comparison the curves for the extreme cases [equations (10) and (11)] are also given in Figure 4.}

Rearrangement of equation (9a) yields:

$$\log \frac{E_0 - E_e}{E_e - E_*} = \log [A]_e + \log K_e \qquad (9a')$$

Thus, according to equation (9a) plots of the data for different temperatures should give a series of parallel straight lines with slopes $m = 1$ if the assumption of a 1:1 stoicheiometry of the EDA-complex is correct. Figure 5 shows the data from this study and is confirmation of the 1:1 stoicheiometry over the temperature range -15 to 25 °C. By harmonic averaging all the values for K_e obtained at each temperature the values of $\bar{K}_e$ listed in the Table were obtained.

Equilibrium Constants.—The Table lists the $\bar{K}_e(T)$ and $\varepsilon_{DA}(T)$ values obtained from the two methods described above. The standard errors refer to a 99% confidence level. The small absolute value of ε_{DA} leads to large relative errors for this parameter. This has little relevance with respect to the equilibrium constants using Drago's method ($\varepsilon_D \ll \varepsilon_{DA}$) but using Satchell's method [equation (9a)] the errors are carried directly into those for $\bar{K}_e$, especially when E_e is small. Since, as the temperature decreases, the value of E_e decreases, the error in $\bar{K}_e$ is particularly large at lower temperatures. This is the reason for the greater discrepancy between the two methods of evaluation at -15 °C.

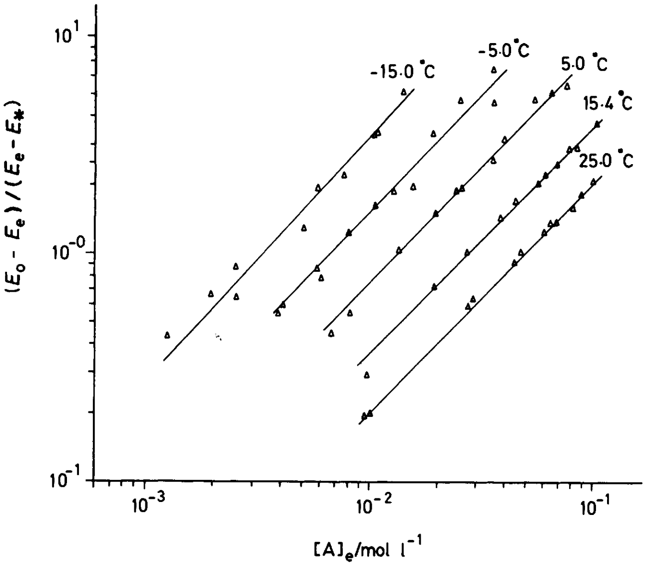


Figure 5. Plot of equation (9a′) for different temperatures

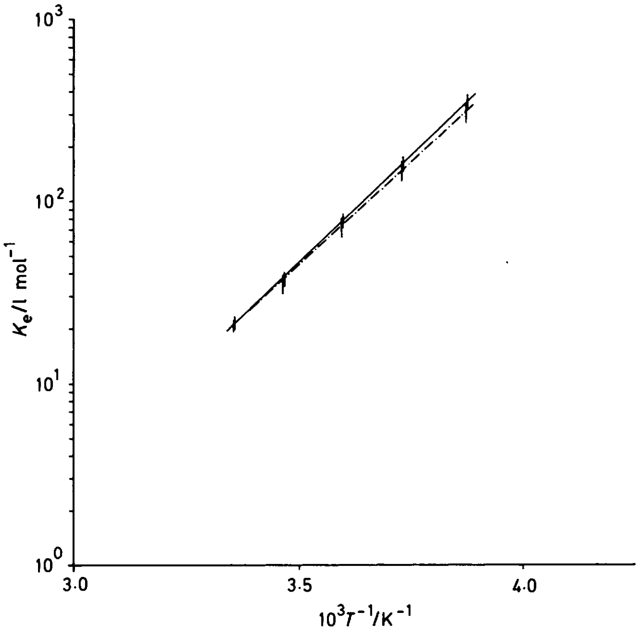


Figure 6. Plot of the van't Hoff equation (12)

Calculation of ΔH_K *using the van't Hoff Equation.*—For equilibrium systems in solution, according to van't Hoff:[12] A plot according to equation (12) for the data obtained from

$$\ln \bar{K}_e = \frac{\Delta H_K}{RT} + \text{const.} \qquad (12)$$

this work is shown in Figure 6. The values for ΔH_K and the standard errors obtained from the two evaluation methods are:

Method according to Drago: $\Delta H_K = -45$ kJ mol^{-1} ± 3%
Method according to Satchell: $\Delta H_K = -43$ kJ mol^{-1} ± 12%.

Conclusions.—Even considering the errors involved the two methods of evaluation agree exceptionally well. Each method has both advantages and disadvantages; using the method of Satchell the ε_{DA} values are confirmed experimentally, using Drago's method these values are simply calculated. Nevertheless, the values of K_e from Drago's method contain smaller errors. The increased experimental time involved using Satchell's method must be compared with the time-consuming graphical approach of Drago's method. For the system studied here the two methods are comparable in terms of the time required. The value of $K_e(T = 25\ °C)$ published by Satchell[3] for the same system as described in this work is 37.2 l mol^{-1}.

The present authors consider the inconsistency between the value from this work and that of Satchell to be possibly due to the influence of moisture and/or to the differences in experimental approach. Considering the large value of ΔH_K it is clear that an exact temperature control is of paramount importance for the measuring of such equilibrium constants; this is considerably easier using the fibre-optic set up described in this paper.

No values of ΔH_K which can be directly compared with the values determined in this work could be found in the literature. However, a value of -11.5 kJ mol^{-1} has been reported by Brown[13] for the enthalpy of formation of the π-complex between 1,3,5-trimethylbenzene and $AlBr_3$ in cyclopentane so that the value reported above for a σ-complex is probably of the correct magnitude.

Appendix

Summary of the abbreviations used in this work and their dimensions:

K_e = Equilibrium constant (l mol^{-1}).
$[A]_o$ = Total concentration of $AlBr_3$ (mol l^{-1}).
$[D]_0$ = Total concentration of 4-methyl-2-nitroaniline (**1**) (mol l^{-1}).
$[A]_e$ = Equilibrium concentration of free $AlBr_3$ (mol l^{-1}).
$[D]_e$ = Equilibrium concentration of free 4-methyl-2-nitroaniline (**1**) (mol l^{-1}).
$[DA]_e$ = Equilibrium concentration of the EDA-complex (**2**) (mol l^{-1}).
ε_D = Molar absorption coefficient of 4-methyl-2-nitroaniline (**1**) at 405 nm (l mol^{-1} cm^{-1}).
ε_{DA} = Molar absorption coefficient of the EDA-complex (**2**) at 405 nm (l mol^{-1} cm^{-1}).
E_0 = Absorption of 4-methyl-2-nitroaniline (**1**) ($[A]_0 = 0$, $[D]_e = [D]_0$).
E_e = Equilibrium absorption.
E_* = Absorption of the EDA-complex (**2**) ($[D]_e = 0$, $[DA]_e = [D]_0$).
d = 'cell length' of the measuring probe (0.652 cm).

References

1 D. P. N. Satchell and R. S. Satchell, *Chem. Rev.*, 1969, **69**, 251.
2 M. Pestemer, 'Anleitung zum Messen von Absorptionsspektren im Ultraviolett und Sichtbaren,' Thieme Verlag, Stuttgart, 1964, p. 22.
3 A. Mohammad and D. P. N. Satchell, *J. Chem. Soc. B*, 1967, 726.
4 J. N. Murell, *Quart. Rev.*, 1961, **15**, 191.
5 J. N. Murell, 'Elektronenspektren organischer Moleküle,' Bibliographisches Institut, Mannheim, 1967, p. 240.
6 S. D. Pask, *Chem. Ind. (London)*, 1981, 329.
7 D'Ans Lax, 'Taschenbuch für Chemiker und Physiker,' Springer Verlag, 1964, Vol. 1, p. 803.
8 N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, 1959, **81**, 6138.
9 D. P. N. Satchell and J. N. Wardell, *J. Chem. Soc.*, 1964, 4134.
10 K. Bukka and R. S. Satchell, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1110.
11 S. Noack, 'Auswertung von Mess- und Versuchsdaten mit Taschenrechner und Tischcomputer,' Walter de Gruyter Verlag, Berlin, 1980, p. 373.
12 W. J. Moore, 'Physikalische Chemie,' Walter de Gruyter Verlag, Berlin, 1976, p. 334/355.
13 H. C. Brown and W. J. Wallace, *J. Am. Chem. Soc.*, 1953, **75**, 6265.

Received 26*th January* 1987; *Paper* 7/126