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A Study of Ion Pairing in Acetonitrile Solutions Containing Magnesium Perchlorate Using ATR-FTIR Spectroscopy

by

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Abstract

A study of ion pairing for $Mg(ClO_4)_2$ dissolved in acetonitrile has been carried out using attenuated total reflection FTIR spectroscopy. The present results indicate that the coordination number for ligands around the Mg^{2+} ion is approximately four, and not six as previously reported. Ion pairing is relatively strong with 70 percent of the Mg^{2+} ions forming contact ion pairs with one perchlorate ion. The spectral characteristics of acetonitrile associated with Mg^{2+} have been clearly distinguished from those of the free molecule. By comparing spectra in deuterated and protonated solvents, it has been shown for the first time in solution, that the ion paired perchlorate ion has an absorption band at 933 cm^{-1}. The effect of Fermi interaction on the position of the blue shifted $C \equiv N$ band for coordinated acetonitrile is examined and discussed with respect to determination of the effect of the cation charge/radius ratio on the shifted band.

Introduction

Vibrational spectroscopy has been used extensively to study the interactions between ions and solvent molecules in electrolyte solutions.[1-2] A notable example is the interaction between the $C \equiv N$ group in nitriles such as acetonitrile and cations. In this case the $C \equiv N$ stretching frequency is shifted to higher wave numbers when it is coordinated to a strong Lewis acid such as a monoatomic cation.[3-7] The magnitude of the shift has been correlated to a parameter characterizing the polarization power of the cation, that is to the charge/radius ratio for the ion adjusted for the screening effect of non-valence electrons on the nuclear charge.[8] Although a primary correlation has been established other important features of the vibrational spectra have not been analyzed. These include the effects of ion pairing and of interaction between the band for the $C \equiv N$ stretch in coordinated acetonitrile molecules and the combination band which appears at slightly higher frequencies. The improved quality of the IR spectrum which is available through attenuated total reflectance - Fourier transform infrared spectroscopy (ATR-FTIRS) permits one to study these effects and to estimate cation solvation numbers and ion pairing constants.

The free perchlorate anion which has T_d symmetry has four vibrational modes: F_2 (1119 cm^{-1}), F_2 (625 cm^{-1}), A_1 (928 cm^{-1}) and E (459 cm^{-1}). The latter two are only Raman active. When the anion is bound through one of its oxygen atoms, its symmetry is reduced to C_{3v}, and the F_2 band at 1119 cm^{-1} is split into two bands (A_1 and E). The totally symmetrical band (A_1 mode) at 928 cm^{-1} is then IR active. Wickenden and Krause[9] reported features of the IR spectrum of $Ni(CH_3CN)_4(ClO_4)_2$ in the solid state which were assigned to perchlorate ion coordinated to Ni(II). Two bands observed at 1135 and 1012 cm^{-1} were attributed to the split F_2 mode (A_1 and E), and a third band at 945 cm^{-1} to the A_1 symmetric stretch mode. The spectral features assignable to perchlorate ion have been used to study ion pairing in non-aqueous solutions. Coetzee and Sharpe[5] observed bands at 1130 and 1070 cm^{-1} in $LiClO_4$ solutions in acetonitrile (AN). These were attributed to the split F_2 mode resulting from perchlorate ions in an ion pair. Faguy et al.[10] analyzed the spectral features in the 1200-1000 cm^{-1} region for $LiClO_4$ solutions in nitromethane, and argued that the resulting five bands could be attributed to perchlorate anion and its ion pair with lithium.

However, in the case of acetonitrile no band in the region of the symmetrical stretch (928 cm^{-1}) has been reported to date.

ATR-FTIR spectroscopy provides a much more sensitive tool for examining electrolyte solutions than the transmission techniques which have been commonly used in these studies. The aim of the present paper is to demonstrate that considerably more information about the electrolyte can be obtained by carefully examining the spectral features of the solvent molecule. In this regard, we have chosen to study ion pairing for $Mg(ClO_4)_2$ in AN. AN can be classified as a moderate Lewis base in terms of its cation solvating ability. Thus, it is considerably stronger as a Lewis base than nitromethane but also much weaker than dimethylformamide on the basis of the donor numbers for these solvents.[11] It follows that moderate ion pairing is expected in AN especially for a 2-1 electrolyte such as $Mg(ClO_4)_2$.

Experimental

Acetonitrile (Fisher, HPLC grade), deuterated acetonitrile (Alderich, 99.5 atomic %), and carbon tetrachloride (Fisher, spectranalyzed) were used without further purification. High purity $Mg(ClO_4)_2$ from Strem (99.9%) was dried over benzene vapor under vacuum for two days.

A custom-built flow-through ATR cell[10], composed of a germanium crystal and a Teflon holder was mounted in a SpectraTech variable angle ATR accessary. A Bruker, IFS 113v FTIR spectrometer equipped with a HgCdTe detector cooled with liquid nitrogen was used to collect the spectra.

In order to avoid solvent evaporation, the sample chamber of the bench was not under vacuum but purged with nitrogen gas. Thus, the bench was not completely free of carbon dioxide or water vapor. Their concentration was maintained at a minimum and constant value by the purging gas. The ATR cell was filled with solution under a constant pressure of nitrogen gas, and the dripping rate of the solution was kept approximately constant while taking a spectrum. The cell was thoroughly rinsed with a new solution until a constant intensity of the coordinated C≡N stretch band was obtained.

All single beam spectra were collected from 3300 to 800 cm^{-1} with a resolution of 2 cm^{-1} and an incidence angle of 45°. Absorbance spectra were referenced to that of an empty cell and averaged over 5 parallel runs. Because of the software used to generate the plots shown in this paper, the spectra are made up of linear segments with a length of 2 cm^{-1}.

Results

ATR spectra in the C ≡ N stretch region are shown in Fig. 1 for pure AN and for AN solutions containing $Mg(ClO_4)_2$ at various concentrations. There are two bands for pure AN, the C ≡ N stretch at 2253 cm^{-1} (ν_2) and the combination band at 2293 cm^{-1} ($\nu_3 + \nu_4$), which results from a combination of the C-C stretch (ν_4) and CH_3 deformation (ν_3) modes.[12] These bands are involved in Fermi resonance as is shown from the analysis which follows. In the case of the $Mg(ClO_4)_2$ solutions, there is obviously one new band at 2316 cm^{-1} (band I) which was not reported in previous studies of this system.[2,3] The band at 2293 cm^{-1} in the pure solvent (band II) seems to shift to lower frequencies with increasing $Mg(ClO_4)_2$ concentration such that its peak occurs at 2289 cm^{-1} in the most concentrated solution studied. The effect of the $Mg(ClO_4)_2$ on the IR spectrum is seen more clearly when the spectrum of the pure solvent is subtracted from those for the solutions (see Fig. 2). A negative band whose magnitude increases with increase in electrolyte concentration is seen at 2253 cm^{-1} (band III). This feature is clearly due to the corresponding decrease in concentration of free AN. Band I shows no change in intensity or position as one would expect, but band II at 2289 cm^{-1} now is reduced in intensity and remains fixed in position with change in electrolyte concentration. Thus, the band observed in the original spectra at this position is actually composed of two bands, one of which is due to the combination band for the free solvent (2293 cm^{-1}) and the other, to a new band at 2289 cm^{-1} which appears in the presence of the electrolyte. The latter is attributed to the C ≡ N stretch mode for solvent coordinated to Mg^{2+} and corresponds to a blue shift of 36 cm^{-1}. Band I is associated with the combination band of the associated solvent molecule ($\nu_3 + \nu_4$) as can be confirmed from the positions of the ν_3 (1375 cm^{-1}) and ν_4 bands (939 cm^{-1}) for this species. It is interesting to note the intensity and band width changes which accompany formation of the ion-dipole complex. In the pure solvent, the C ≡ N stretch band is 5.6 times as intense as the combination band, whereas for the coordinated solvent, the intensity ratio is close to 1.0. At the same time, the full width at half peak height for $\nu_3 + \nu_4$ with respect to ν_2 is 0.5 for the unassociated molecule, and 0.9 for the coordinated species. These changes are attributed to the fact that the combination band is closer in frequency to the C ≡ N stretch for the coordinated species by 13 cm^{-1} with respect to the same bands for the unassociated solvent molecule.

IR spectra for the $Mg(ClO_4)_2$ solutions in AN in the C-C stretch region are shown in Fig.3. The band at 918 cm^{-1} (band V) is attributed to the ν_4 C-C stretch mode of the free solvent molecule. However, it should be noted that its intensity appears to be independent of $Mg(ClO_4)_2$ concentration. A new band appears at 939 cm^{-1} (band IV). In previous work[2,3], this band was reported at 936 cm^{-1} and assigned to the C-C stretch of coordinated solvent molecules.

Relative intensities based on integrated band area are shown in Fig. 4 as a function of electrolyte concentration for the four bands discussed above. The slopes of the linear plots are 9.9, 9.4, and 9.1 intensity units L mol^{-1} for bands I, II, and IV, respectively. In the case of band V, the slope is essentially zero, whereas for band III, which corresponds to the negative going band at 2253 cm^{-1}, the slope is -2.4 intensity units L mol^{-1}. In order to insure that concentration dependent effects are not obscured by saturation in the ATR experiments, spectra were collected for AN solutions in carbon tetrachloride over the whole composition range up to pure AN. The results of these experiments which are summarized in Fig. 5 demonstrate that the extinction coefficients for the $C \equiv N$, and C-C stretch bands, and for the combination band are independent of AN concentration. The resulting extinction coefficients are 0.718, 0.328, and 0.132 intensity units L mol^{-1} for the $C \equiv N$ stretch, the C-C stretch, and combination band, respectively. This information may be combined with the extinction coefficient of the negative going band at 2253 cm^{-1} to extract an average coordination number for Mg^{2+}. Since the relationship between intensity and concentration is linear for data obtained at 2253 cm^{-1}, and assuming that the extinction coefficient for the absorption at this frequency is the same for an AN molecule coordinated to Mg^{2+} in an AN solution, and for the same molecule in a carbon tetrachloride solution, one may estimate the coordination number from the ratio of the two extinction coefficients. Thus, since the band at 2253 cm^{-1} decreases by 2.4 intensity units for an increase in Mg^{2+} concentration by 1 M, and the same band increases in intensity by 0.718 units for increase in AN concentration by 1 M in carbon tetrachloride, one concludes that 3.3 molecules of AN are associated with one Mg^{2+} ion on the average. Assuming that the coordination number of Mg^{2+} at least is four in the absence of ion pairing, this result suggests that contact ion pairs are formed to the extent that the average coordination number drops to 3.3. The observation that the coordination number is constant over the range of Mg^{2+} concentrations studied is considered in more detail below.

In order to assign the overlapping bands in the spectrum, spectra were recorded for the deuterated solvent and its solutions with $Mg(ClO_4)_2$ in the $C \equiv N$ and C-C stretch regions (see Fig. 6). For pure d-AN there is one band at 2261 cm^{-1} corresponding to the $C \equiv N$ stretch.[12] In the presence of $Mg(ClO_4)_2$ a new band appears at 2303 cm^{-1} corresponding to the $C \equiv N$ stretch of molecules solvating Mg^{2+}. In the deuterated solvents[12], the C-C stretch (ν_4) appears at 833 cm^{-1}, the CH_3 rock (ν_7) at 847 cm^{-1}, and the CH_3 deformation (ν_6) at 1037 cm^{-1}. No absorption in the pure solvent is seen in the region from 850 to 1000 cm^{-1}. However, in the $Mg(ClO_4)_2$ solutions, a band whose intensity increases with electrolyte concentration appears at 933 cm^{-1}. Since this band cannot be associated with the solvent, it must arise from the perchlorate ions of the electrolyte, and also be present in the spectra recorded in protonated solvent (see Fig. 3).

When one carefully examines the spectra shown in Fig. 3, it is apparent that both bands IV and V have shoulders, the first at lower frequencies and the second at higher frequencies. The spectrum in this region for a $Mg(ClO_4)_2$ concentration of 0.9 M was fitted assuming the presence of four bands with Lorentzian line shapes, the results being shown in Fig. 7. On the basis of the residual, it is apparent that an excellent fit is obtained with bands at 939 (i), 933 (ii), 922 (iii) and 918 cm^{-1} (iv). This procedure was repeated for nine different $Mg(ClO_4)_2$ concentrations and the resulting intensities plotted against electrolyte concentration in Fig. 8. The intensity of the band at 918 cm^{-1} which is attributed to the C-C stretch in free AN decreases with increase in electrolyte concentration as one would expect. On the basis of the extinction coefficient determined in CCl_4, this corresponds to the loss of 2.9 AN molecules per Mg^{2+} ion. This solvation number is somewhat less than that determined using the data at 2253 cm^{-1} but is probably less reliable due to the fact that bands overlap in the region of this absorption. The bands at 939 and 933 cm^{-1} whose intensities increase significantly with Mg^{2+} concentration are attributed to the C-C stretch in coordinated AN and to the Cl-O stretch in perchlorate ion paired with Mg^{2+}, respectively. The band at 922 cm^{-1} is assigned to the C-C stretch in AN molecules which are coordinated to residual water molecules via a hydrogen bond.[1,13] Any residual water in these solutions would predominantly be associated with Mg^{2+} ions as ligands. Thus, the concentration of such a species would increase slightly with increase in electrolyte concentration.

Band positions and shifts due to $Mg(ClO_4)_2$ are summarized in Tables 1 and 2. The assignments for pure solvents are based on early work by Evans and Bernstein.[12] The results in Table I agree well with Raman data reported earlier by Irish et al.[7] for Zn^{2+} and confirm that the spectral shifts for divalent ions are much larger than those for Li^+ and Na^+. Attention is called to the fact that the shift in the $C \equiv N$ stretch frequency is 36 cm^{-1} in AN and 42 cm^{-1} in d-AN. Since the mass effect is cancelled out when frequency shifts are considered, the shifts should be independent of whether or not the solvent is deuterated. The fact that the shift is 6 cm^{-1} smaller for the protonated solvent is attributed to the presence of Fermi resonance for the combination band in this system. Fermi coupling between the ν_2 band and $\nu_3 + \nu_4$ combination band not only leads to a change in the intensity of the ν_2 band but also a shift in their relative positions such that the combination band appears at higher frequencies and the $C \equiv N$ stretch, at lower ones. In the case of the unassociated protonated solvent, the combination band occurs exactly where one would expect it on the basis of the positions of the ν_3 and ν_4 bands indicating little Fermi interaction. However, the $C \equiv N$ band of the protonated species is clearly shifted in the red direction by at least 6 cm^{-1} because on the basis of the mass effect it should appear at a higher frequency than in the deuterated solvent. The spacing between the $C \equiv N$ stretch and combination bands for associated solvent is 27 cm^{-1} whereas it is 40 cm^{-1} for unassociated solvent. On the basis of the corresponding positions of the ν_3 and ν_4 bands, the combination band should appear at 2314 cm^{-1}. The fact that it is seen at 2316 cm^{-1} indicates that Fermi coupling has resulted in a 2 cm^{-1} shift in the blue direction. Since the shift in the ν_2 band brings the combination band closer to the $C \equiv N$ fundamental for associated solvent, Fermi coupling is stronger and a larger red shift for the $C \equiv N$ band would be anticipated with respect to that found for the unassociated solvent. The net result of these interactions is that one cannot consider the blue shift of the C ≡ N stretch frequency observed in the presence of cations as being only an indication of solvent-dipole interaction. Because the combination band is close to the C ≡ N stretch in the protonated solvent, these bands affect one another through Fermi coupling. Since the Fermi resonance is absent in the deuterated solvent, the cation shifts observed in this system give a better indication of the strength of the cation/solvent interaction.

The differential spectrum (-ΔR/R)) for a 0.24 M $Mg(ClO_4)_2$ solution in AN is shown in Fig. 9 in the perchlorate absorption region (1160-1000 cm^{-1}). The envelope shows the presence of at least five bands, and the spectrum can be easily fitted to five bands with a very low residual as shown in Fig. 9. The band positions are 1 (1125 cm^{-1}), 2 (1103 cm^{-1}), 3 (1089 cm^{-1}), 4 (1056 cm^{-1}) and 5 (1038 cm^{-1}). Band 5 is attributed to the CH_3 rocking mode of the solvent. It remains in the differential spectrum since its intensity is increased by the presence of the electrolyte, probably as a result of interactions between the ClO_4^- anion and the CH_3 group at the electropositive end of the solvent dipole.[4] The total intensities of the bands (2+3) and of bands (1+4) are plotted against electrolyte concentration in Fig. 10. From the slopes of the curve through these data, the intensity of the bands (2+3) varies from 1.6 to 1.8 times that of bands (1+4) over the concentration range investigated. It seems likely that bands 1 and 4 which are approximately equally intense correspond to the A_1 and E modes of the perchlorate ion which arise from the triply degenerate F_2 mode as a result of ion pairing. Bands 2 and 3 are assigned to the same modes but for perchlorate ions which are associated with AN molecules only. The electrostatic interaction between the anion and the positive end of the dipole is weaker than the charge-charge interaction involved in an ion pair. Thus, the splitting is smaller between bands 2 and 3. If the coordination number for AN around Mg^{2+} is four, the solvation number 3·3 determined above corresponds to 70% of the Mg^{2+} ions having formed contact ion pairs with ClO_4^- so that three acetonitrile molecules remain coordinated to the cation. The remaining 30% of the Mg^{2+} ions are surrounded by four AN molecules. This gives a molar ratio of free ClO_4^- to ClO_4^- ion paired with Mg^{2+} of 1.3/0.7 = 1.9. The result is close to the ratio of the intensity of bands (2+3) to that of bands (1+4). This observation gives strong support to the assignment of the perchlorate bands proposed here.

Discussion

It is readily apparent when one compares the present results with those reported earlier in the literature[2,3,14] that much more information is available from the ATR-FTIR spectra. Focussing firstly on the data recorded in the C ≡ N stretch region (Figs. 1 and 2), it is clear that there are two new bands in the presence of the electrolyte, not only one as previously reported.[2,3,14] Perelygin and Klimchuk[14] concluded that the coordination number for Mg^{2+} in AN solutions was six on the basis of the rate of increase in absorption at 2290 cm^{-1} with increase in electrolyte concentration. Since their spectra were poorly resolved, it is highly probable that they were observing the effects of both the C ≡ N stretch and combination bands for the coordinated AN molecules, and thereby obtained a high result. The conclusion reached here that the coordination number for Mg^{2+} is four is supported by data for both the C ≡ N and C-C stretch bands on the basis of independently measured extinction coefficients. It is interesting to note that Mg^{2+} is generally regarded as having a primary solvation sheath containing six molecules in a variety of non-aqueous solvents including methanol, ethanol, AN, dimethylformamide and dimethylsulfoxide.[15] In the case of the alcohols, the solvation number was obtained by NMR spectroscopy, and for the other solvents from IR transmission spectroscopy. Little is known about the coordination chemistry of Mg^{2+} but it seems likely on the evidence available[16] that the coordination number in solution may be either four or six. Infrared studies of larger alkaline earth metal cations in AN show that Ba^{2+} and Sr^{2+} have solvation numbers close to six.[17] The present study suggests that the solvation number for Mg^{2+} should be reexamined in other non-aqueous solvents with the more precise spectroscopic tools available now.

The results obtained here can be used to calculate the ion pairing constant for $Mg(ClO_4)_2$. Assuming that the extinction coefficients for the two perchlorate species contributing to the absorption in the region from 1160 to 1000 cm^{-1} are approximately equal (Fig. 9), one may use the derived intensities shown in Fig. 10 to estimate the ratio of free perchlorate to that bound in ion pairs, $[ClO_4^-]/[Mg(ClO_4)^+]$. On the basis of the curves drawn through the data in Fig. 10, this ratio varies from 1.66 at an electrolyte concentration of 0.04 M to 1.83 at 0.35 M. Assuming that only one ion pairing step is involved with an association constant defined as

$$\frac{[Mg(ClO_4)^+]}{[Mg^{2+}]\,[ClO_4^-]} = K_{as} \tag{1}$$

one may derive an approximate relationship between the stoichiometric electrolyte concentration and the concentration of ion pairs. At fixed ionic strength, the relationship between these quantities is

$$\frac{c_p}{(c_s-c_p)\,(2c_s-c_p)} = K_{as} \tag{2}$$

where c_s is the stoichiometric electrolyte concentration, and c_p, the equilibrium concentration of the ion pair. Solving the resulting quadratic equation in c_p for the case that ion pairing is strong, one finds

$$c_p = \frac{2c_s^2\,K_{as}}{3c_s\,K_{as}+1} \simeq 2c_s/3 \tag{3}$$

This general result confirms our observation that 70% of the Mg^{2+} ions are ion paired. On the basis of the data presented in Fig. 10, the value of K_{as} at an electrolyte concentration of 0.08 M is 23; it falls to a value of 2 for an electrolyte concentration of 0.63 M. The variation in K_{as} with ionic strength is clearly due to a corresponding variation in activity coefficients and because other possible ion pairing steps involving species with more than one perchlorate ion per Mg^{2+} ion were neglected. It is not possible to estimate a true ion pairing constant from the present results because data are not available at a low enough ionic strength where the ratio c_p/c_s departs significantly from 2/3. Studies would have to be carried out from concentrations at least an order of magnitude smaller so that the results could be extrapolated to zero ionic strength. The technique used here is not sufficiently sensitive to operate in such a low concentration range.

The present data can also be used to estimate the average solvation number defined as

$$S = \frac{4[Mg^{2+}] + 3[Mg(ClO_4^-)^+]}{[Mg^{2+}] + [Mg(ClO_4)^+]} \tag{4}$$

Since $[Mg^{2+}]$ is equal to c_s-c_p, it is easily shown that S is equal to 3.3 when $c_p/c_s = 2/3$. Thus, both the experimental data and the simple model used here confirm that the average solvation number for Mg^{2+} in AN is 3.3. We reiterate that the spectral information comes not only from the perchlorate region of the spectrum, but also from the observed decrease in the intensity of the $C \equiv N$ band due to loss of free AN on addition of Mg^{2+} to the system.

Very little information is available from the literature regarding ion pairing for the present system. Libus and Strzelecki[18] measured the conductivity of $Mg(ClO_4)_2$ solutions in acetonitrile but limited their study to dilute solutions so that analysis to obtain an ion pairing constant was not possible. Perelygin and Klimchuk[14] estimated K_{as} to be 7.2 on the basis of their data in the perchlorate region of the IR transmission spectrum for concentrations up to 0.43 M $Mg(ClO_4)_2$. However, it is difficult to accept that K_{as} as defined by eq. (1) would be independent of ionic strength because of the variation in activity coefficients. If one estimates these quantities on the basis of extended Debye-Huckel theory, values of the true association constant of the order of 200 are obtained. Such a result seems reasonable when it is compared with data for the true equilibrium constants for ion pair formation in the alkali metal perchlorates.[19] These constants vary from 10 for $LiClO_4$ to 22 for $CsClO_4$.

The present data also allow one to estimate the Fermi coupling coefficient W for interaction between the ν_2 $C \equiv N$ stretch band and the $\nu_3 + \nu_4$ combination band for AN coordinated to Mg^{2+}. This quantity is given by the equation[20]

$$W = \frac{R^{1/2}\Delta}{(R+1)} \qquad (5)$$

where R is the ratio of integrated intensities (peak areas) for the doublet and Δ, the frequency separation. On the basis of the present results, W is equal to 13.5 cm^{-1} for coordinated AN. From previous work[20], the corresponding quantity for free acetonitrile is 12.5 cm^{-1}. Thus, the combination and fundamental modes of the coordinated species are significantly more strongly coupled through Fermi interaction than the free molecule. This was confirmed by the spectral details for the appropriate bands described above. The net result is that the shift in the $C \equiv N$ stretch upon coordination is significantly less than it would be in the absence of Fermi resonance. It also follows that correlations such as those used by Kecki[8] do not give a true representation of the effect of the cation on the charge density in the C ≡ N bond. On the other hand, if one uses deuterated acetonitrile, the problem with Fermi resonance disappears and the polarizing effect of the cation can be studied in the absence of other complications.

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References

1. Irish, D.E.; Brooker, M.H. Adv. Infrared and Raman Spectroscopy, 1976, 2, 212.
2. Perelygin, I.S. in Ionic Solvation, G.A. Krestov, editor, Nauka, Moscow (1987) Chap.3.
3. Perelygin, I.S. Opt. Spektros. 1962, 13, 198.
4. Coetzee, J.F.; Sharpe, W.R. J. Solution Chem. 1972, 1, 77.
5. Chang, T.G.; Irish, D.E. J. Solution Chem. 1974, 3, 161.
6. Sze, Y.K.; Irish, D.E. J. Solution Chem. 1979, 8, 395.
7. Irish, D.E.; Hill, I.R.; Archambault, P.; Atkinson, G. J. Solution Chem. 1985, 14, 221.
8. Izdebska, B.; Kecki, Z. Polish. J. Chem. 1978, 52, 1531.
9. Wickenden, A.E.; Krause, R.A. Inorg. Chem. 1965, 4, 404.
10. Faguy, P.W.; Fawcett, W.R.; Patrick, D.L. J. Chem. Soc. Far. Trans. 1991, 87, 2961.
11. Gutmann, V. Coord. Chem. Rev., 1976, 18, 225.
12. Evans, J.C.; Bernstein, H.J. Can. J. Chem. 1955, 33 1746.
13. Sze, Y.K.; Irish, D.E. Can. J. Chem. 1975, 53, 427.
14. Perelygin, I.S.; Klimchuk, M.A. Zhur. Fiz. Khim. 1973, 47, 2025.
15. Marcus, Y. Ion Solvation, John Wiley, New York (1985) Chap. 4.
16. Cotton, F.A.; Wilkinson, G. Advanced Inorganic Chemistry, 4th edition, John Wiley, New York (1980) Chap. 8.
17. Fawcett, W.R.; Liu, G., unpublished results.
18. Libus, W.; Strzelecki, H. Electrochim. Acta 1971, 16, 1749.
19. Kay, R.L.; Hales, B.J.; Cunningham, G.P. J. Phys. Chem. 1967, 71, 3925.
20. Bertran, J.F.; La Serna, B.; Doerffel, K.; Dathe, K.; Kabish, G. J. Molec. Structure, 1982, 95, 1.

Table I. Summary of band positions and shifts for $Mg(ClO_4)_2$ solutions in acetonitrile

Band Assignment	Band Position/cm^{-1}		Shift
	CH_3CN	$CH_3CN\text{-}Mg^{2+}$	
Combination band ($\nu_3+\nu_4$)	2293	2316	23
$C \equiv N$ stretch (ν_2)	2253	2289	36
CH_3 symmetrical stretch (ν_3)	1375	1375	0
C-C stretch (ν_4)	918	939	21

Table II. Summary of band positions and shifts for $Mg(ClO_4)_2$ solutions in deuterated acetonitrile

Band Assignment	Band Position/cm^{-1}		Shift
	CD_3CN	CD_3CN-Mg^{2+}	
C≡N stretch (ν_2)	2261	2303	42
CD_3 symmetrical stretch (ν_3)	1103	1103	0
CD_3 asymmetrical stretch ν_6)	1037	1037	0
CD_3 rocking (ν_7)	847	*	-
C-C stretch (ν_4)	833	853	20

* This band cannot be clearly seen due to superimposition by the coordinated C-C stretch band at 853 cm^{-1}.

Figure Legends

Figure 1. IR spectra in the $C \equiv N$ stretch region (2340 to 2230 cm^{-1}) for acetonitrile (AN) containing various concentrations of $Mg(ClO_4)_2$ in the range 0 to 0.9 M. The spectra have been shifted vertically with increasing concentration for clarity.

Figure 2. Difference IR spectra in the $C \equiv N$ stretch region (2340 to 2230 cm^{-1}) for $Mg(ClO_4)_2$ solutions in acetonitrile with respect to the spectrum for pure acetonitrile. The spectra have been shifted vertically for clarity.

Figure 3. IR spectra in the C-C stretch region (960 to 900 cm^{-1}) for acetonitrile containing various concentrations of $Mg(ClO_4)_2$ in the range 0 to 0.9 M. The spectra have been shifted vertically with increasing concentration for clarity.

Figure 4. Variation in the integrated intensity for bands I, II, III, IV, and V (see Figs. 1 and 3) with concentration of $Mg(ClO_4)_2$. The bands are designated as follows I (2316 cm^{-1}) (●), II (2289 cm^{-1}) (▲), III (2253 cm^{-1}) (■), IV (939 cm^{-1}) (◆), and V (918 cm^{-1}) (▼).

Figure 5. Variation in integrated intensity of these bands for acetonitrile dissolved in carbon tetrachloride with acetonitrile concentration. The bands are the $C \equiv N$ stretch (◆), the C-C stretch (●), and combination (▲).

Figure 6. IR spectra for deuterated acetonitrile and its solutions with $Mg(ClO_4)_2$ in the $C \equiv N$ stretch (2360 to 2200 cm^{-1}) and C-C stretch regions (1060 to 800 cm^{-1}). The three curves from the bottom up are for pure CD_3CN, 0.1 M and 0.5 M $Mg(ClO_4)_2$ in CD_3CN.

Figure 7. IR spectrum for 0.9 M $Mg(ClO_4)_2$ in acetonitrile in the C-C stretch region (960 to 900 cm^{-1}) with four fitted bands and residual.

Figure 8. Variation in integrated intensity of the four bands in the 960 to 900 cm^{-1} region (see Fig. 7) with $Mg(ClO_4)_2$ concentrations. The bands are designated as follows: i (●), ii (▲), iii (◆), and iv (▼).

Figure 9. Differential absorption spectrum (-ΔR/R) for 0.24 M $Mg(ClO_4)_2$ in acetonitrile in the perchlorate region (1150 to 1000 cm^{-1}) with the five fitted bands and residual.

Figure 10. Variation in integrated intensity for bands (2+3) and bands (1+4) in the perchlorate region (see Fig. 9) with $Mg(ClO_4)_2$ concentration. The bands are designated as (♦) for (2+3) and as (●) for (1+4).

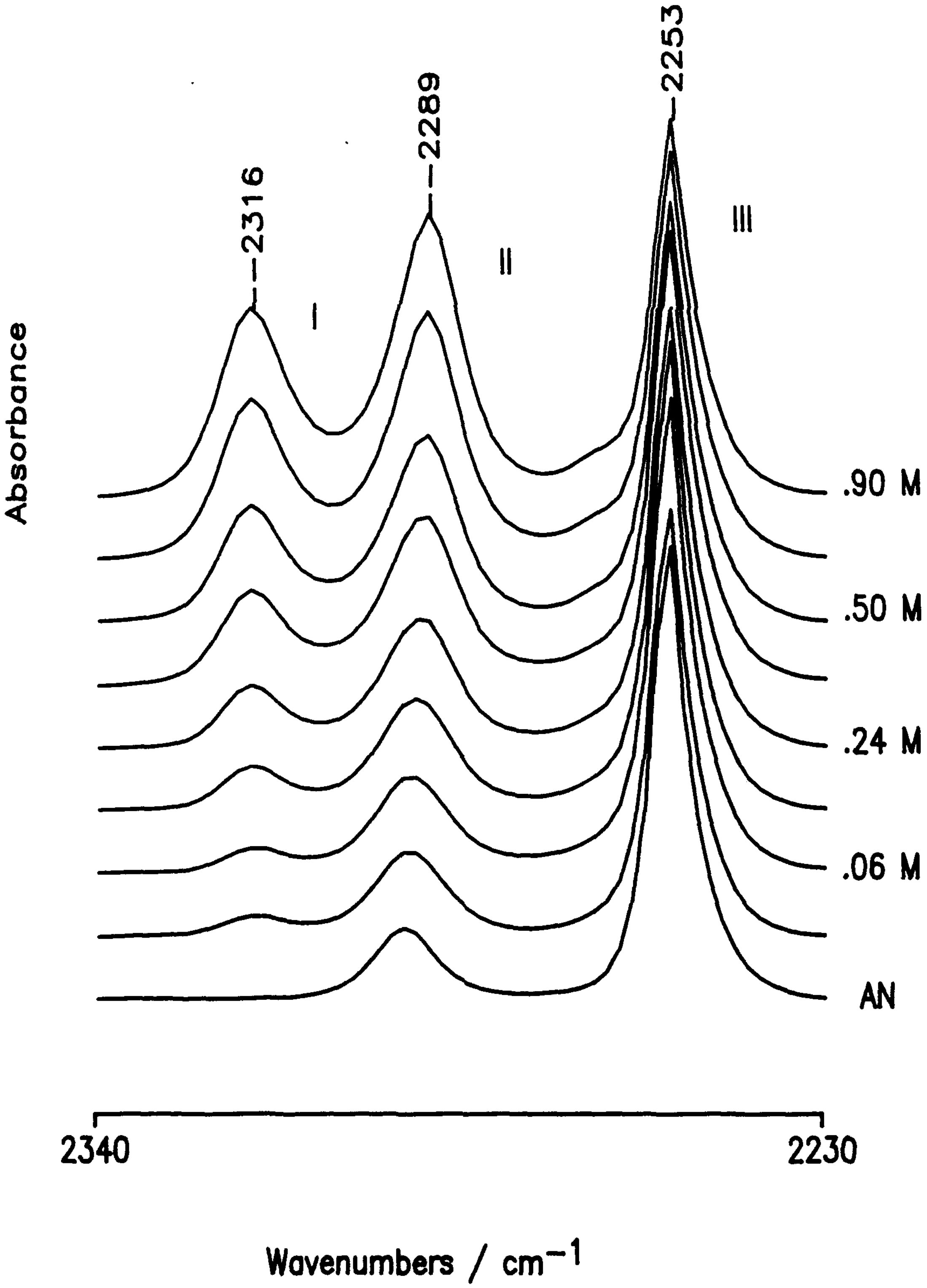


Fig 1. Fawcett and Liu

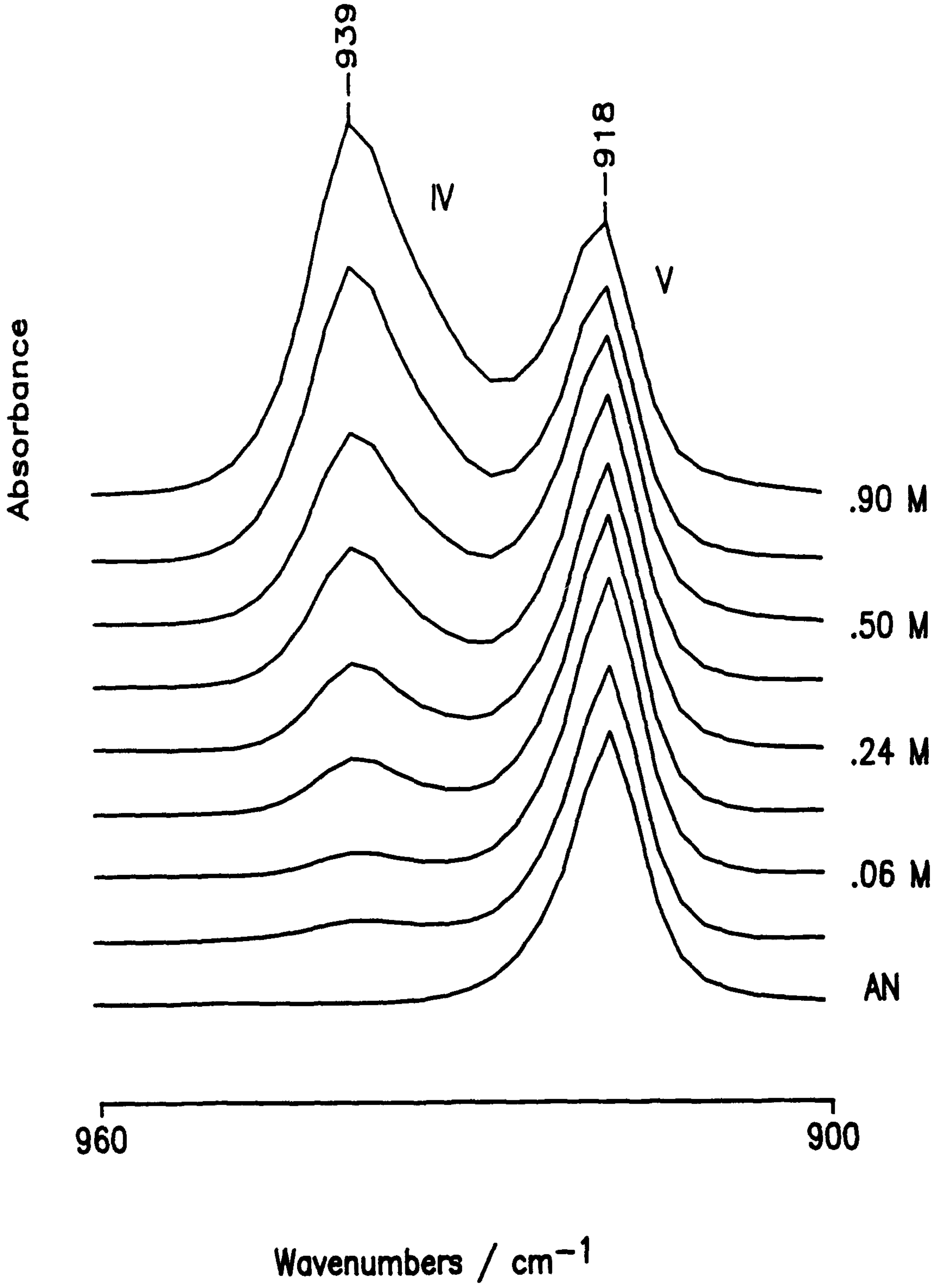
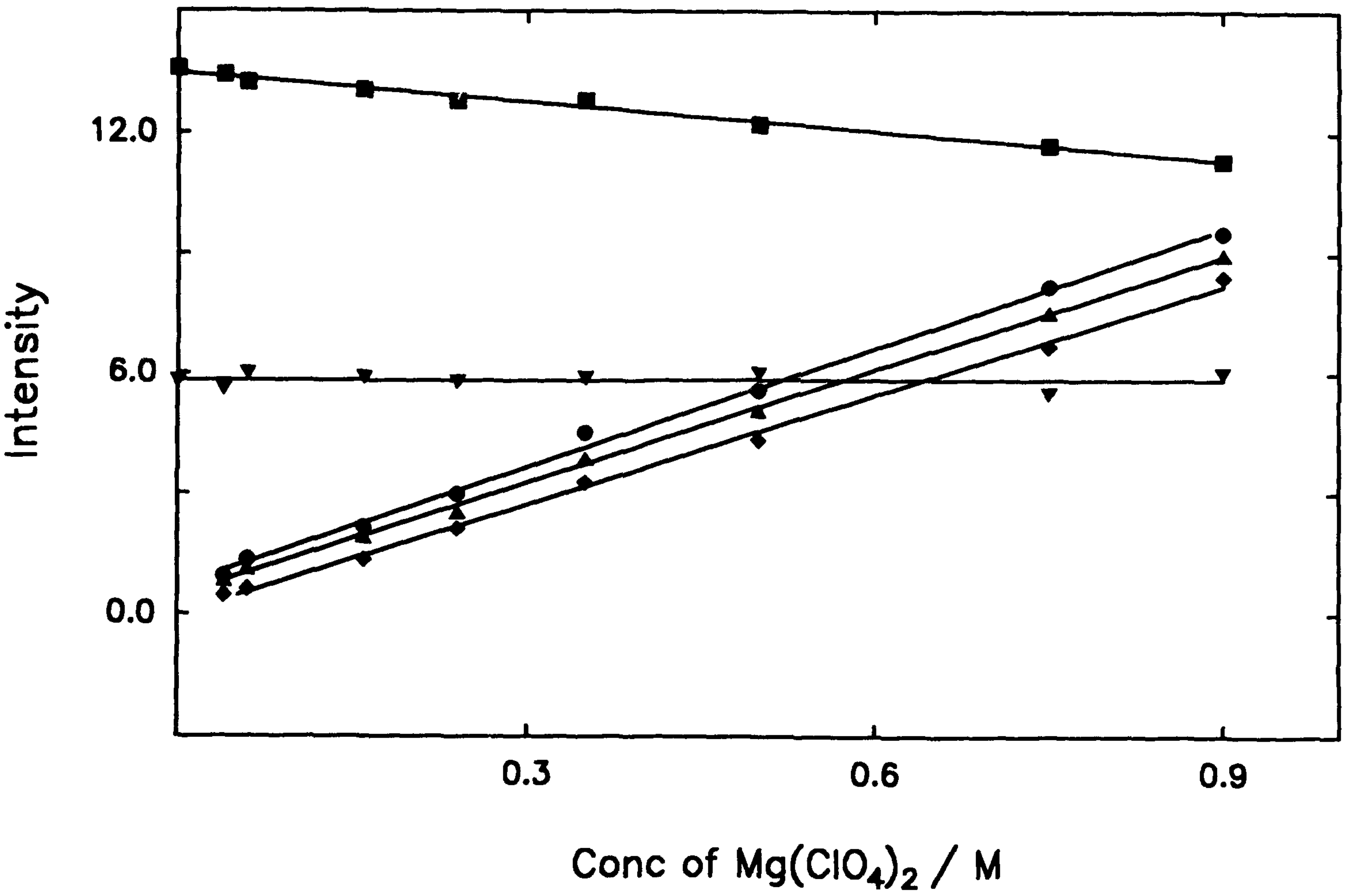
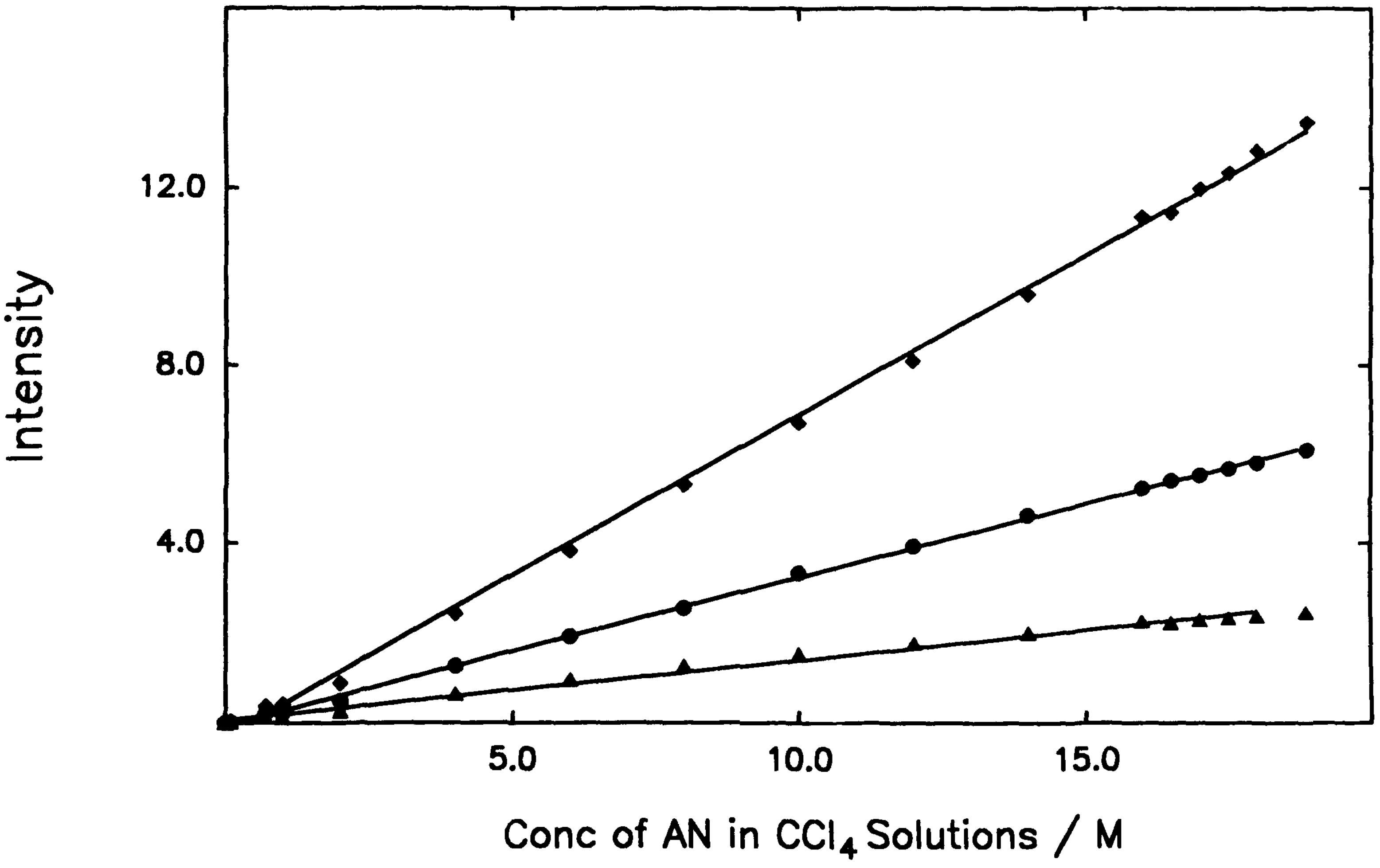


Fig. 3. Fawcett and Liu.



Intensity
12.0
6.0
0.0
0.3
0.6
0.9
Conc of $Mg(ClO_4)_2$ / M



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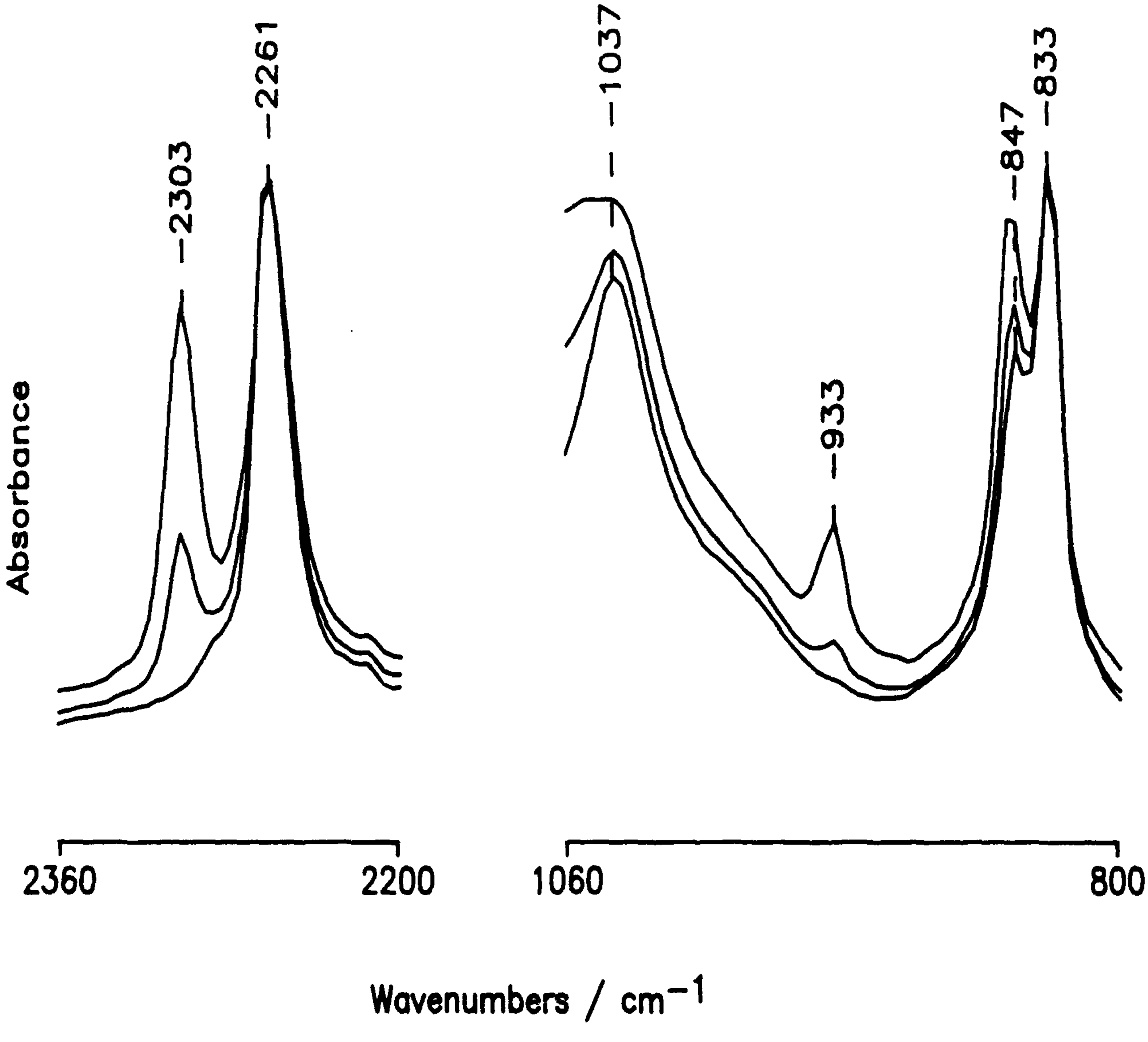


Fig 6. Fawcett and Liu

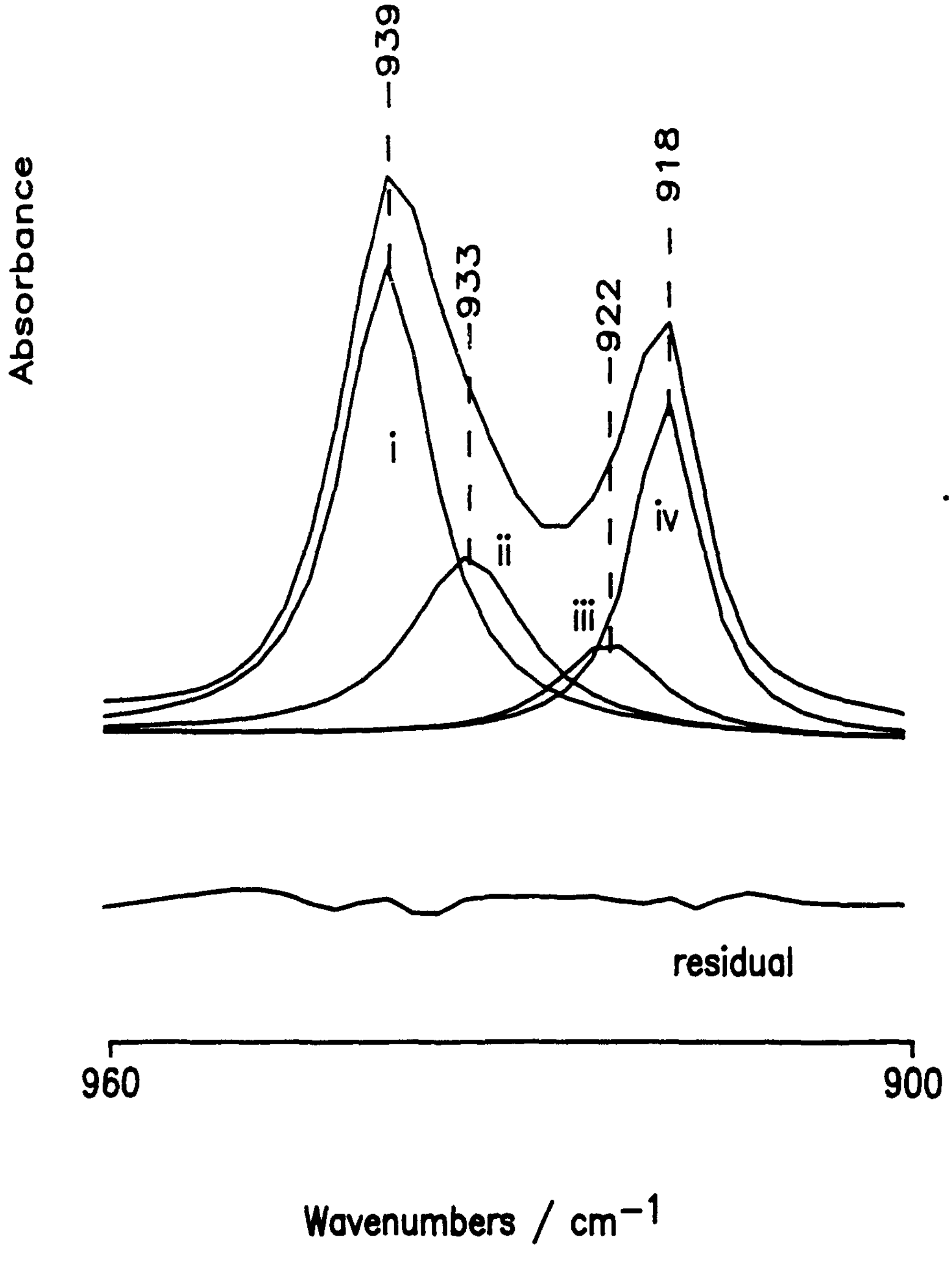
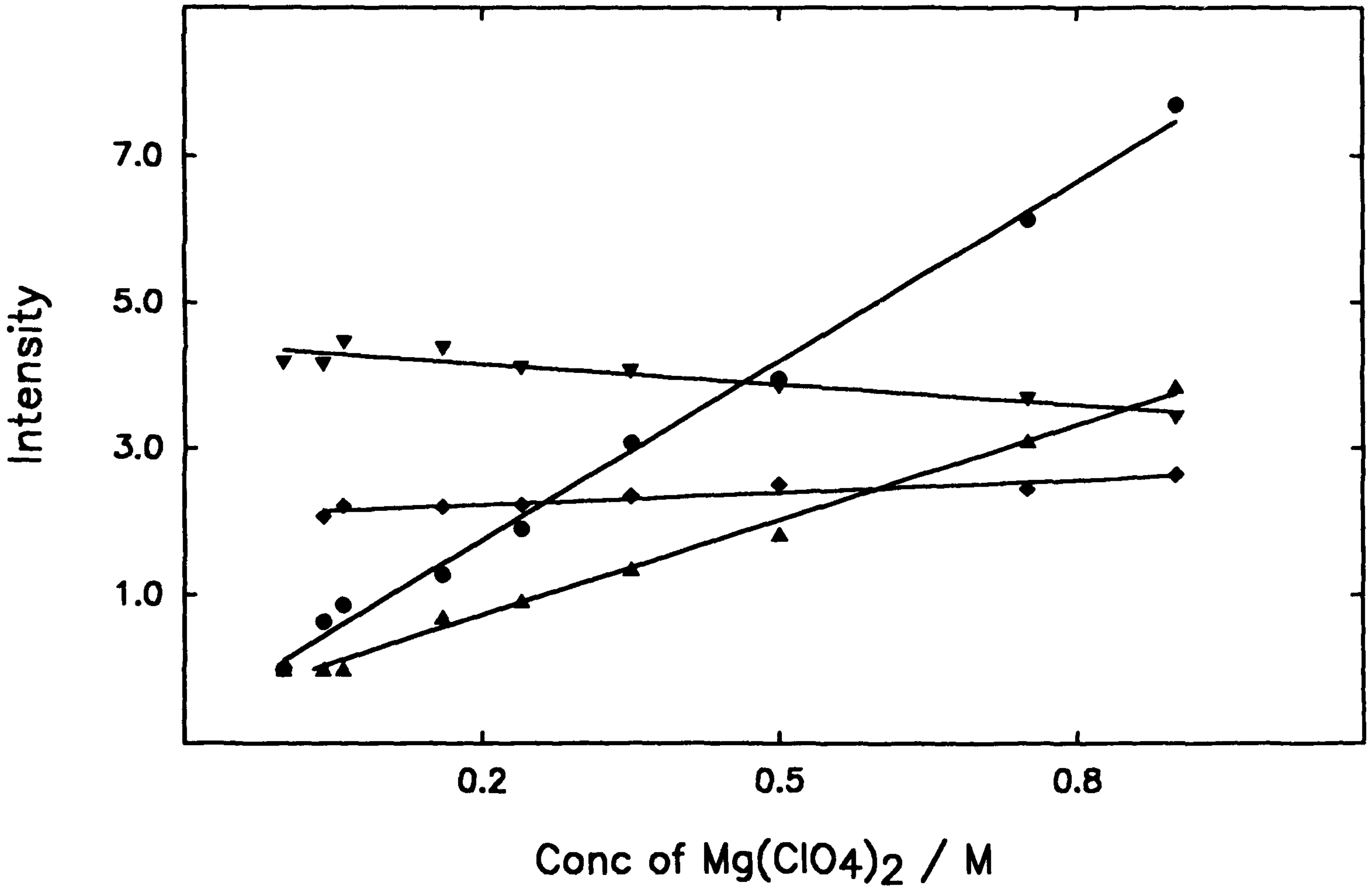


Fig 7. Fawcett and Liu.



7.0
5.0
3.0
1.0
Intensity
0.2
0.5
0.8
Conc of Mg(ClO4)2 / M

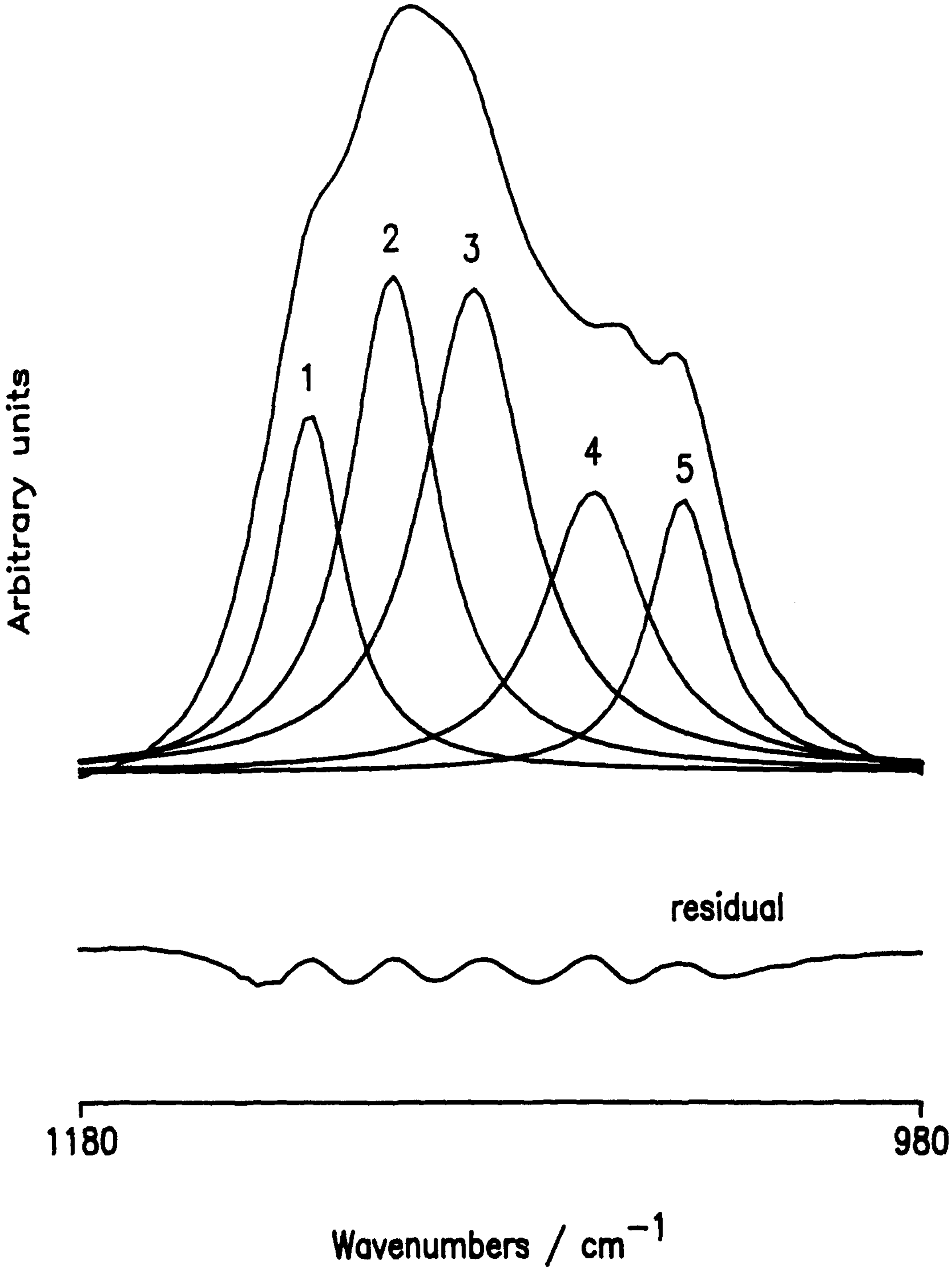
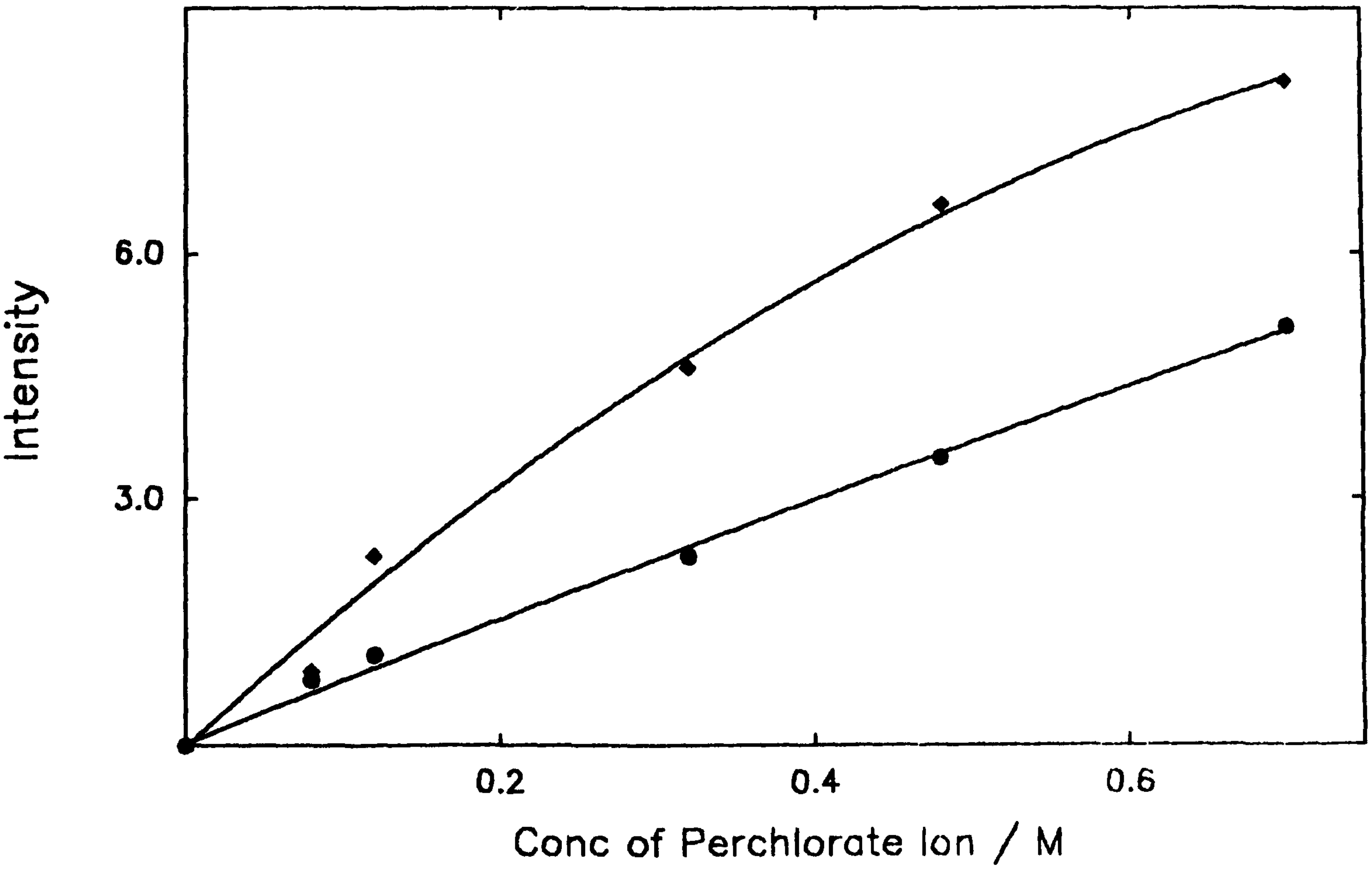


Fig 9. Fawcett and Liu



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