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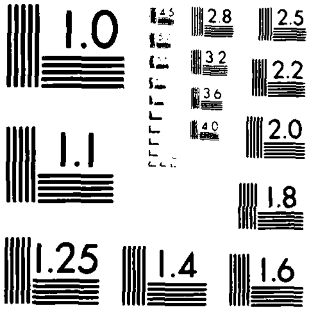

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Iodine, iodine chloride, tetraethylammonium iodide and tetraethylammonium triiodide solutions in aluminum chloride - N-(1-butyl)pyridinium chloride ambient temperature ionic liquids have been studied by u.v. - visible spectrophotometry. The different oxidation states of iodine show a distinct dependence on the solvent acidity. Iodine(+1) exists in the form of ICl in acidic melts and in the form of ICl_2^{1-} in basic $AlCl_3$-BuPyCl mixtures. Molecular iodine does not form strong complexes in acidic or neutral solutions. Triiodide ion is stable

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TECHNICAL REPORT NO.20

Spectrophotometric Studies of Iodine Complexes In An Aluminum Chloride - Butylpyridinium Chloride Ionic Liquid

by

Zenon J. Karpinski and Robert A. Osteryoung

Prepared for Publication

in

Inorganic Chemistry

Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

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ABSTRACT

Iodine, iodine chloride, tetraethylammonium iodide and tetraethylammonium triiodide solutions in aluminum chloride - N-(1-butyl)pyridinium chloride ambient temperature ionic liquids have been studied by u.v. - visible spectrophotometry. The different oxidation states of iodine show a distinct dependence on the solvent acidity. Iodine(+1) exists in the form of ICl in acidic melts and in the form of ICl_2^- in basic $AlCl_3$-BuPyCl mixtures. Molecular iodine does not form strong complexes in acidic or neutral solutions. Triiodide ion is stable in neutral butylpyridinium tetrachloroaluminate, but not in acidic melts. In solutions of iodine or triiodide in basic $AlCl_3$-BuPyCl ionic liquids equilibrium mixtures of I_2Cl^-, I_3^-, ICl_2^- and I^- are formed.

The charge transfer band observed for iodide solutions in neutral and basic melts reveal the formation of iodide ion - butylpyridinium cation ion pairs. Similar bands in pure basic AlCl3-BuPyCl mixtures indicate the association of chloride ion and butylpyridinium cation.

INTRODUCTION

Our electrochemical investigations of iodine in aluminum chloride-N-(1-butyl) pyridinium chloride (BuPyCl) ambient temperature molten salts (1,2) showed that in this solvent iodine and its compounds are involved in extensive acid-base and redox equilibria. Variations in the $AlCl_3$:BuPyCl mole ratio lead to wide changes in Lewis acidity of the medium. Neutral equimolar mixture of $AlCl_3$ and BuPyCl can be made acidic by adding excess $AlCl_3$ or basic with excess BuPyCl. The present study was undertaken to obtain additional information on interactions of iodine in different oxidation states with the ionic solvent. The electrochemical experiments did not directly identify all the iodine species formed in basic $AlCl_3$-BuPyCl ionic liquid (2). They did not indicate the formation of I_2^+ ion in acidic ambient temperature melts although this ion has been postulated on the basis of spectral results for mixtures of I_2 and Cl_2 dissolved in high temperature $AlCl_3$-NaCl molten salts (3).

It was also of interest to seek in this medium, containing high concentration of butylpyridinium cation, charge transfer bands for iodide and chloride ions. Charge transfer, (CT), transitions for alkylpyridinium iodides have been observed in many different solvents (4-7). CT bands have also been reported for myristylpyridinium chloride solutions in chloroform (6). It was assumed (5-7) that these transitions occur for contact ion pairs; a possible contribution of solvent separated ion pairs to ionic association equilibria in these systems was however unclear (6-8). Ionic association equilibria in $AlCl_3$-BuPyCl ionic liquids are different in this respect in that in this medium only contact ion pairs should be formed. Formation of this type of ionic association between butylpyridinium cation and iodide and chloride ions is indicated by charge transfer bands reported herein.

EXPERIMENTAL

The procedures used for purification of $AlCl_3$ (Fluka), synthesis and purification of N-(1-butyl)pyridinium chloride and preparation of the melts were similar to those described previously (9). Iodine (Malinckrodt AR), iodine chloride (Eastman Kodak), and tetraethylammonium iodide (TEAI) (Eastman Kodak) were used as received. Tetraethylammonium triiodide ($TEAI_3$) was prepared according to Chattaway and Hoyle (10) and dried under vacuum.

Absorption specta were obtained with a Perkin Elmer Model Coleman 750 spectrophotometer using 0.1 cm matched quartz cells (Wilmad). Cells were filled and sealed under a purified argon atmosphere in a Vacuum Atmosphere dry box with an HE 493 Dri Train.

RESULTS

Iodide and chloride ions.

Iodide ion, which in acidic melts does not exhibit any absorption in the accessible u.v. region (1), shows a single absorption band with a maxima at ca 330 nm in neutral and basic solutions (Figure 1). This band was found to obey Beer's law at iodide concentrations from 3 x 10^{-4} to 7 x 10^{-3} mol dm^{-3} and the apparent molar absorptivity at 330 nm was 3 x 10^3 dm^3 mol^{-1} cm^{-1} in the neutral as well as in basic 0.95:1 and 0.75:1 melts (Table I).

Visible or near u.v. absorption bands observed for alkylpyridinium iodides in many different solvents (4-7) have been assigned to charge transfer transitions (4-7) and taken as an evidence for contact ion pair formation (5-7). The observed independence of the apparent molar absorptivity on iodide concentration in butylpyridinium tetrachloroaluminates indicates full association of iodide ions with butylpyridinium cations. It is also interesting to note that the molar absorptivity in the ionic liquid is distinctly higher than in the other solvents where its value varied between 300 and 1600 dm^3 mol^{-1} cm^{-1} (4-7). Since in the ionic liquid only contact ion pairs are formed, the measured value can be regarded as the molar absorptivity of the contact $BuPy^+I^-$ ion pair. Lower values of apparent molar absorptivity observed in the other solvents (4-7) suggest that solvent separated ion pairs are a significant fraction of ionic associations formed there.

Spectra recorded for pure melts at different $AlCl_3$:BuPyCl mole ratios revealed a dependence of the short wavelength "cut off" on the melt composition. In acidic and neutral melts the 'cut offs' were essentially the same; an absorbance equal to 1 at 284 nm for 1.5:1 and at 285 nm for the neutral $AlCl_3$:BuPyCl mole ratios (1.0:1.0) melt (at 0.1 cm pathlengths, the spectra recorded versus air). For basic melt compositions these "cut offs" shifted to 313 nm for 0.95:1, 319 nm for 0.9:1 and to 325 nm for 0.75:1 $AlCl_3$:BuPyCl mole ratios. In acidic and neutral melts the "cut offs" are due to butylpyridinium cation π-π^* transitions (8). In aqueous solutions, maxima of alkylpyridinium cation absorption bands were observed at ca 260 nm (5). The slight difference between 1.5:1 and 1:1 melts results from an increase in $BuPy^+$ concentration which is 3.5 mol dm^{-3} in 1.5:1 and 4.1 mol dm^{-3} in 1:1 melt. In basic melts, however, the $BuPy^+$ concentration increase cannot account for the observed shift of the cut off; $BuPy^+$ concentration in the 0.75:1 melt is 4.45 mol dm^{-3}. On the other hand, an absorbance edge observed between 285 and 310 nm increased when excess BuPyCl was added to the neutral butylpyridinium tetrachloroaluminate (Figure 2). The absorbance at constant wavelength varied linearly with the concentration of "free" chloride (in excess over $AlCl_3$) (Figure 3). This shows that the absorption at these wavelengths is due to charge transfer transitions for a butylpyridinium cation-chloride ion pair, similar to the $BuPy^+...I^-$ association. The proportionality between the absorbance and excess chloride concentration (at 305 nm Beer's law was obeyed in the chloride ion concentration range from 5×10^{-3} to 0.1 mol dm^{-3}) indicates full association of butylpyridinium cation and chloride ion under the conditions employed (large excess of $BuPy^+$).

The charge transfer band observed in the u.v. spectrum of $AlCl_3$-BuPyCl ionic liquid is a good indication of basic melt composition. It is especially useful at very low chloride concentrations, close to the neutral butylpyridinium tetrachloroaluminate. It was found, that at concentrations below ~ 5×10^{-3} mol dm^{-3}, neither chloride nor heptachloroaluminate ions effect the electrochemical window of the molten butylpyridinium tetrachloroaluminate (2) which can be used as a criterion of the neutrality of the solvent (11). However, in u.v. spectra analogous to those shown in Figure 2, 1×10^{-3} mol dm^{-3} excess chloride could be detected (at 290 nm the absorbance value corresponding to 1×10^{-3} mol dm^{-3} chloride was 0.043). This method did not require the preparation of an ideally equimolar neutral melt as the reference solution. Since, as discussed above, spectra of neutral and acidic melts were esentially the same, an acidic melt could be used as the reference.

Iodine, iodine chloride and triiodide ion.

For solutions of iodine in neutral butylpyridinium tetrachloroaluminate a broad absorption band with a maxima at ca 480 nm ($\varepsilon_{I_2}^{480}$ = 800 dm^3 mol^{-1} cm^{-1}), identical to one previously observed in acidic solutions containing iodine (1), was found. A difference between the position of this band for iodine solution in liquid butylpyridinium tetrachloroaluminate and in CCl_4 ($\varepsilon_{max}^{I_2}$ = 517 nm (12)) reflects some weak intermolecular interactions between iodine molecules and solvent ions; nevertheless iodine in neutral as well as acidic $AlCl_3$-BuPyCl mixtures does not form strong complexes and is dissolved in the form of I_2 molecules.

Spectra obtained for iodine solutions in basic $AlCl_3$-BuPyCl ionic liquids (Figure 4) indicated the formation of polyhalogen ions; the uncomplexed iodine band at 480 nm was not observed. The dependence of the spectra on concentration of iodine and melt composition indicated equilibria involving chloride ion. The solvent "cut off" did not allow a direct observation of polyhalogen ion absorption maxima at wavelengths shorter than 320 nm. Only the band at ca 365 nm due to triiodide ion (vide infra) could be observed (Figure 4). Its formation in solutions of iodine dissolved in basic $AlCl_3$-BuPyCl melts shows that I_2 is involved in some redox reaction. Reversible changes of the spectra at varying melt compositions, an independence of the spectra on time, and the fact that more than 90% of the amount of iodine initially added to a basic melt could be observed by rotating disc voltammetry after the melt was made acidic by $AlCl_3$ addition (2), showed that the possible reactions of iodine, reduction by chloride ion and/or solvent impurities as well as the reaction with the organic cation could not account for the observed reaction. On the other hand, electrochemical experiments showed the presence of iodine (+1) as well as iodide in the solutions of iodine in basic melts (2), thus indicating that the redox reaction involving iodine is the disproportionation equilibrium

$$I_2Cl^- + Cl^- = ICl_2^- + I^- \qquad (1)$$

Triiodide ion is formed in the consecutive equilibrium:

$$I_2Cl^- + I^- = I_3^- + Cl^- \qquad (2)$$

Similar equilibria have been reported for I_2Cl^- solutions in acetonitrile (13), and in water (14) and recently for I_2/CsCl-LiCl melts (15). Since in the acidic melts the iodine disproportionation equilibrium is shifted far to the left (1), the addition of $AlCl_3$ to the equilibrium mixture of polyhalogen ions existing in the solution of iodine in basic $AlCl_3$-BuPyCl melt causes the formation of molecular iodine.

Iodine chloride reacts with the acidic melt and is partly reduced to iodine (1), so the spectra obtained for ICl solutions in acidic $AlCl_3$-BuPyCl melts consisted of bands due to ICl as well as I_2. Since the molar absorptivity of iodine is five times larger than the absorptivity of iodine chloride (16), and the two bands appear in the same wavelength range (the ICl band maximum was reported to be at 343 to 466 nm depending on solvent used (16)), only one very broad band was observed. The maximum of this band shifted from ca 450 to 490 nm (in 2:1 $AlCl_3$:BuPyCl melt) over a period of 24 hours reflecting the progress of the reaction

$$2\ ICl = I_2 + Cl_2 \qquad (3)$$

The spectra recorded for ICl solutions in acidic $AlCl_3$-BuPyCl mixtures were different than the spectrum reported for equimolar mixture of iodine and chlorine dissolved in the 2:1 $AlCl_3$-NaCl melt (3). No band in the 600-800 nm region was observed; thus there was no evidence for the I_2^+ ion formation under the employed conditions. For ICl_2^- ion two absorption bands were reported (12,13,14,15), the main one at ca. 230 nm ($\varepsilon^{230}_{ICl_2^-}$ = ca. $5.5 \times 10^4\ dm^3\ mol^{-1}\ cm^{-1}$) and the second, much less intense band at ca 340 nm ($\varepsilon^{340}_{ICl_2^-}$ = ca. $300\ cm^3\ mol^{-1} cm^{-1}$). The spectra obtained for iodine chloride solutions in basic $AlCl_3$-BuPyCl melts indicated the formation of ICl_2^-; however only the less intense band at 338 nm could be observed. Additionally, for the latter solutions a small maximum at ca. 420 nm was evident. This band decreased at higher chloride concentrations; it probably reflected the presence of the small equilibrium concentrations of molecular ICl in the solution.

The spectra obtained for $TEAI_3$ solutions at melt compositions close to the neutral (as judged by the electrochemical window of the solvent (11)), were qualitatively similar to the spectra recorded in acetonitrile, with two absorption maxima at 295 and 365 nm. However, apparent molar absorptivities were found to be very sensitive to small additions of $AlCl_3$ and BuPyCl to the solution. These variations reflect changes in the conditional stability of I_3^- ion, which result from acid-base interactions of iodide with $AlCl_3$(1) or iodine with chloride ion (vide supra). Even at concentrations of Cl^- or $Al_2Cl_7^-$ ions below 5 x 10^{-3} mol dm^{-3}, which did not affect the electrochemical window of the solvent, the apparent molar absorptivity of I_3^- distinctly changed. When the melt composition was adjusted to a true "neutral" state, however, the molar absorptivity of I_3^- in neutral butylpyridinium tetrachloroaluminate ($\varepsilon^{365}_{I_3^-}$ = 2.25 x 10^4 dm^3 mol^{-1} cm^{-1}) agreed well with literature data (5,13). The value of the I_3^- ion molar absorptivity in neutral butylpyridinium tetrachloroaluminate confirmed the high stability of I_3^- ion observed in electrochemical experiments (2).

Shapes of the spectra recorded for $TEAI_3^-$ solutions in basic solvent compositions were dependent on triiodide and/or chloride ion concentrations (Figure 5). These variations were consistent with the reaction described by equilibrium 2. Thus reactions 1 and 2 lead to the formation of the equilibrium mixtures of all the ions: I_2Cl^-, ICl_2^-, I_3^-, I^- and Cl^- in basic $AlCl_3$-BuPyCl ionic liquids. In triiodide solutions reaction 2 is followed by reaction 1 (the presence of ICl_2^- and I^- ions in triiodide solutions in basic $AlCl_3$-BuPyCl melts was observed in electrochemical experiments (2)). On the other hand, in iodine solutions iodide ion formed in reaction 1 reacts with I_2Cl^- ion according to equilibrium 2.

DISCUSSION

U.v.-visible spectrophotometric studies characterized the species formed by iodine in different oxidation states at widely varied acidities of the $AlCl_3$-BuPyCl ionic liquid. The summary of these results, which are in agreement with electrochemical experiments (1,2), is shown in Table 1. The variety of species formed at different solvent acidities reflects characteristic features of the acid-base interactions in chloroaluminate molten salts. The ionic nature of the solvent promotes strong interactions between Lewis acids and chloride ion in basic melt compositions and between Lewis bases and heptachloroaluminate ion present in acidic melts. At the same time the high stability of triiodide ion in neutral butylpyridinium tetrachloroaluminate indicates relatively weak intermolecular interactions in this solvent.

Charge transfer transitions observed for butylpyridinium cation - iodide and butylpyridinium cation - chloride ion pairs indicate a high degree of association between these ions in basic $AlCl_3$-BuPyCl ionic liquids. The results obtained in the solutions containing a large excess of $BuPy^+$ over Cl^- and I^- did not allow a quantitative analysis of the association equilibria. Qualitatively, however, the results observed for basic $AlCl_3$-BuPyCl mixtures agreed with the conclusions drawn from the analysis of the conductivity measurements for ambient temperature chloroaluminate ionic liquids (18). The proportionality between the absorbance at 305 nm and chloride ion concentration observed up to 0.1 mol dm^{-3} indicates that at formal concentrations of butylpyridinium cation up to 4 mol dm^{-3}, at least 90% of the chloride is involved in the charge transfer transition, thus is associated with $BuPy^+$ cation (accuracy of the measurements was arbitrarily assumed to be ±10%). This gave an estimated value for the association constant

$K = \frac{[BuPy...Cl^-]}{[BuPy^+][Cl^-]} > 2.3$, which favorably compares with the value of the association constant for a similar low temperature chloroaluminate system, aluminum chloride - imidazolium chloride, which was estimated as 2 (18). The ionic association of butylpyridinium cation with chloride ion has been indicated by NMR (19,20,21) and FTIR (22) studies of $AlCl_3$:BuPyCl melts.

For solutions of iodine and $TEAI_3$ in basic $AlCl_3$-BuPyCl ionic liquids the spectrophotometric studies confirmed polyhalogen equilibria deduced from the electrochemical results (2). In particular, the formation of I_3^- in iodine solution, expected from the values of equilibrium constant for reactions 1 and 2 estimated in the electrochemical studies (2), was directly observed. Attempts to obtain more accurate estimates of the equilibrium constants for reactions 1 and 2 from the spectral data were unfortunately unsuccessful. Spectra recorded for I_2 and $TEAI_3$ solutions in basic $AlCl_3$-BuPyCl mixtures were limited to a narrow range of wavelengths and consisted of overlapping bands of all ions involved in the polyhalogen equation, i.e., ICl_2^-, I_2Cl^-, I_3^- and I^-. Additionally a spectrum for I_2Cl^- ion could not be obtained separately, thus molar absorptivity values for this ion were uncertain. However, the spectra obtained for iodine and triiodide solutions at low chloride concentrations (Figures 4 and 5) confirmed the approximate values of the equilibrium constants for reactions 1 and 2. Concentrations of I_3^- ions calculated from these equilibria agreed reasonably well with the I_3^- concentrations estimated from the absorbance measured of 365 nm.

CREDIT

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REFERENCES

1. Karpinski, Z. J.; Osteryoung, R. A. J. Electroanal. Chem., 1984, 164, 281.

2. Karpinski, Z. J.; Osteryoung, R. A. J. Electroanal. Chem., in press.

3. Tanemoto, K.; Mamantov, G.; Marassi, R.; Begun, G. M. J. Inorg. Nucl. Chem., 1981, 43, 1779.

4. Kosower, E. M. J. Am. Chem. Soc., 1958, 80, 3253.

5. Kosower, E. M.; Skorcz, J. Z. J. Am. Chem. Soc., 1960, 82, 2195.

6. Ray, A.; Mukerjee, P. J. Phys. Chem., 1966, 70, 2138.

7. Mackay, R. A.; Poziomek, E. J. J. Am. Chem. Soc., 1970, 92, 2432.

8. Smid, J. "Ions and Ion Pairs in Organic Reactions", p. 95, Szwarc, M. Ed., Interscience, 1972.

9. Robinson, J.; Osteryoung, R. A. J. Am. Chem. Soc., 1979, 101, 323.

10. Chattaway, F. D.; Hoyle, G. J. Chem. Soc., 1923, 123, 654.

11. Lipsztajn, M.; Osteryoung, R. A. J. Electrochem. Soc., 1983, 130, 1968.

12. Keefer, R. M.; Allen, T. L. J. Chem. Phys., 1956, 25, 1059.

13. Popov, A. I.; Swensen, R. F. J. Am. Chem. Soc., 1955, 77, 3724.

14. Cason, D. L.; Neumann, H. M. J. Am. Chem. Soc., 1961, 83, 1822.

15. Child, Jr., W. C.; Papatheodorou, G. M. J. Phys. Chem., 1983, 87 271.

16. Bucles, R. E.; Mills, J. F. J. Am. Chem. Soc., 1954, 76, 4845.

17. Popov, A. I.; Jessup, J. N. J. Am. Chem. Soc., 1952, 74, 6127.

18. Lipsztajn, M.; Osteryoung, R. A. in preparation.

19. Tauselle, F.; Popov, A. Polyhedron, 1983, 2, 889.

20. Wilkes, J. S.; Pflug, J. L.; Levisky, J. A.; Hussey, C. L.; Fannin, Jr., A. A.; King, L. A., Frank J. Seiler Research Laboratory, FJSRL-TR-82-0005, U.S. Air Force Academy, CO.

21. Wilkes, J. S.; Levisky, J. A.; Pflug, J. L; Harvy, C. L.; Schoeffler, T. B. Anal. Chem. 1982, 54, 2379.

22. Tait, S.; Osteryoung, R. A. Inorg. Chem, in press.

Table 1

Apparent molar absorptivity of TEAI band at 330 nm in $AlCl_3$-BuPyCl melt.

Melt composition N_A/N_B	TEAI concentration x 10^3 mol dm^{-3}	ϵ x 10^{-3} dm^3 mol^{-1} cm^{-1}
1:1	3.7	2.97
0.95:1	0.85	2.85
0.95:1	1.99	3.04
0.95:1	4.65	2.99
0.95:1	7.7	2.98
0.75	1.8	2.95
0.75	5.9	3.05

N_A - Number of moles of $AlCl_3$

N_B - Number of moles of BuPyCl

TABLE 2

Iodine species at different $AlCl_3$-BuPyCl ionic liquid compositions.

Iodine oxidation state	Melt composition Acidic	Neutral	Basic
+1	ICl	ICl	ICl_2^-
0	I_2	I_2	I_2Cl^-
-0.33	---	I_3^-	I_3^-
-1	$AlCl_3I^-$, $Al_2Cl_6I^-$	$I^-(BuPy^+...I^-)$	$I^-(BuPy^+...I^-)$

FIGURE CAPTIONS

Fig. 1. Absorption spectra of tetraethylammonium iodide solution in 0.95:1 $AlCl_3$:BuPyCl melt. C_{TEAI}: (1) 4.65; (2) 1.99; (3) 0.85 mM.

Fig. 2. Absorption spectra of butylpyridinium chloride added to neutral butylpyridinium tetrachloroaluminate. Excess of BuPyCl; (1) 18; (2) 11; (3) 5.4 mM.

Fig. 3. Absorbances at constant wavelength measured for spectra shown in Fig. 2 plotted against chloride concentration. Wavelength: (1) 290; (2) 295; (3) 300; (4) 305 nm.

Fig. 4. Absorption spectra of iodine in 0.95:1 $AlCl_3$-BuPyCl melt. C_I: (1) 3.5; (2) 1.68; (3) 0.85 mM.

Fig. 5. Absorption specta of tetraethylammonium triiodide in 0.95:1 $AlCl_3$-BuPyCl melt. C_{TEAI_3}: (1) 1.89; (2) 1.42; (3) 0.85; (4) 0.35mM.

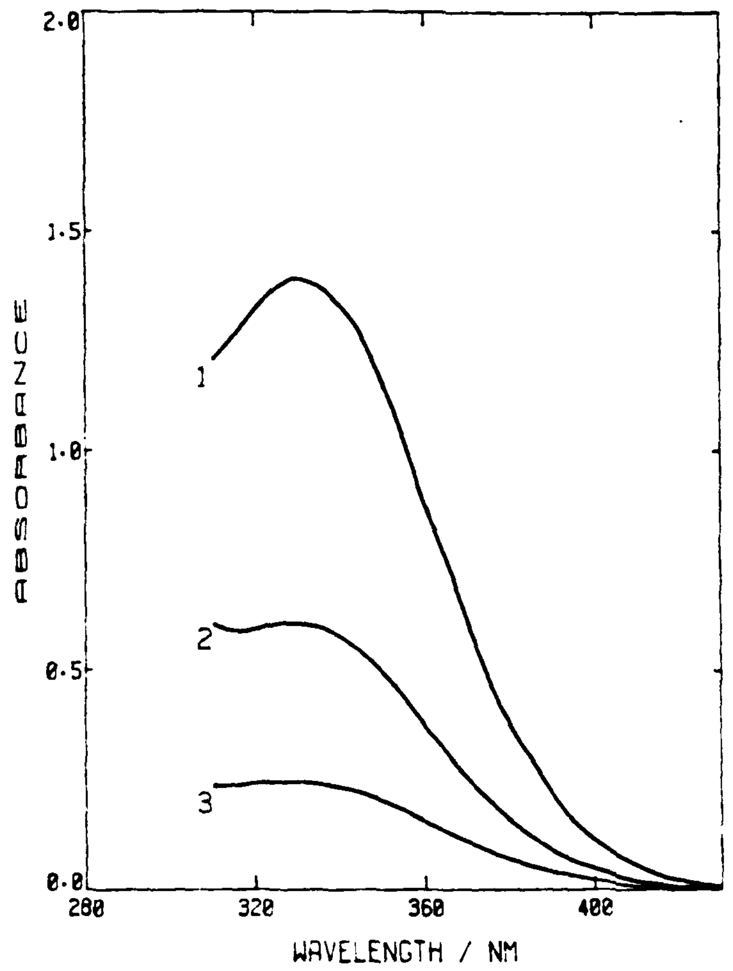


FIGURE 1

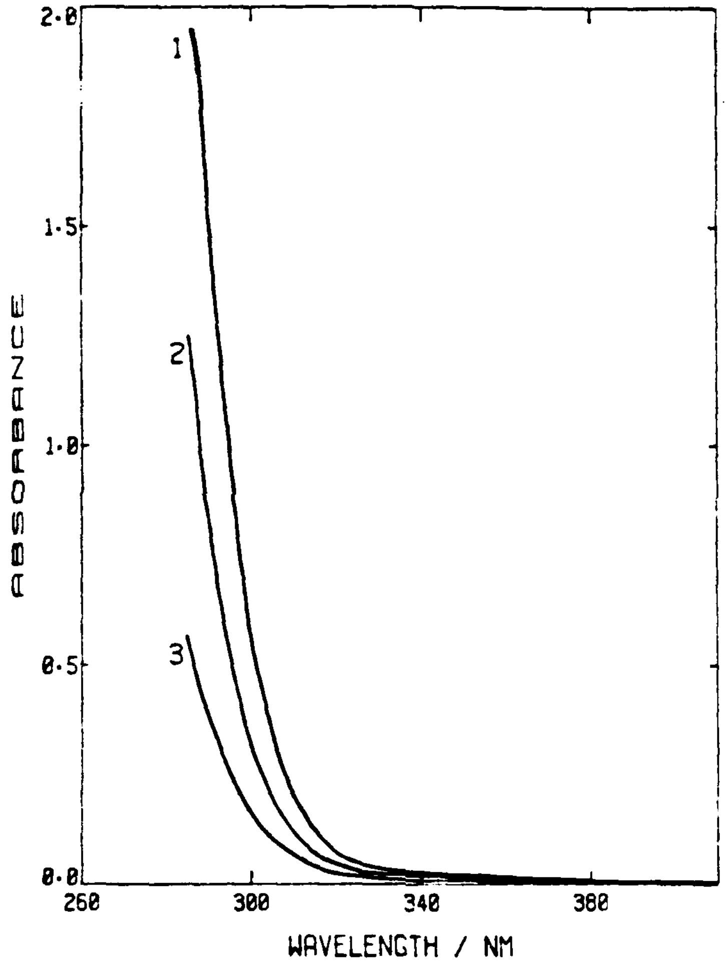
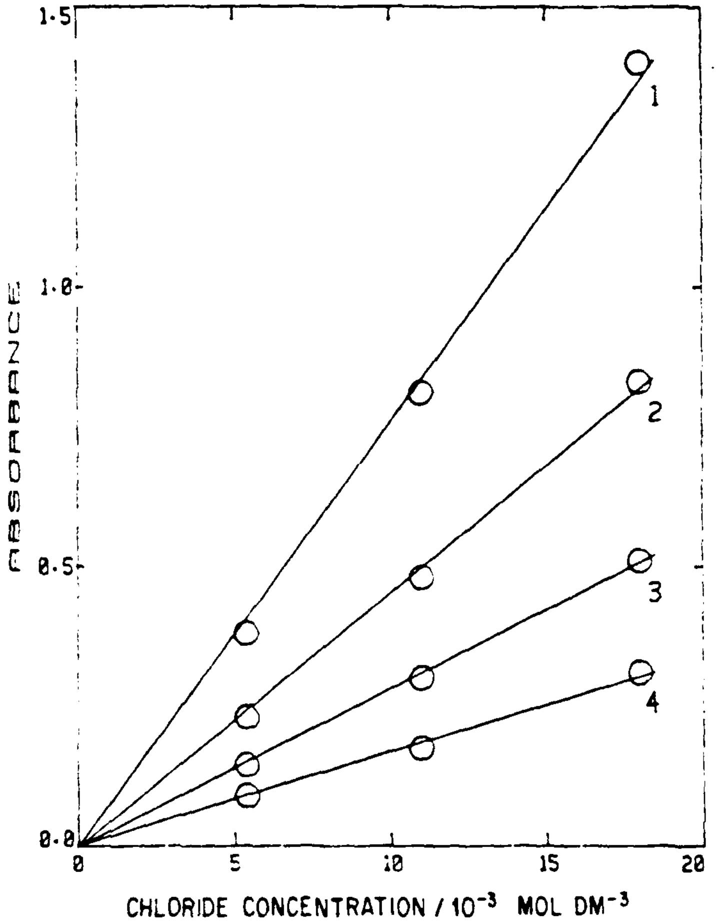


FIGURE 2



ABSORBANCE
1.5
1.0
0.5
0.0
0
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CHLORIDE CONCENTRATION / 10⁻³ MOL DM⁻³

FIGURE 3

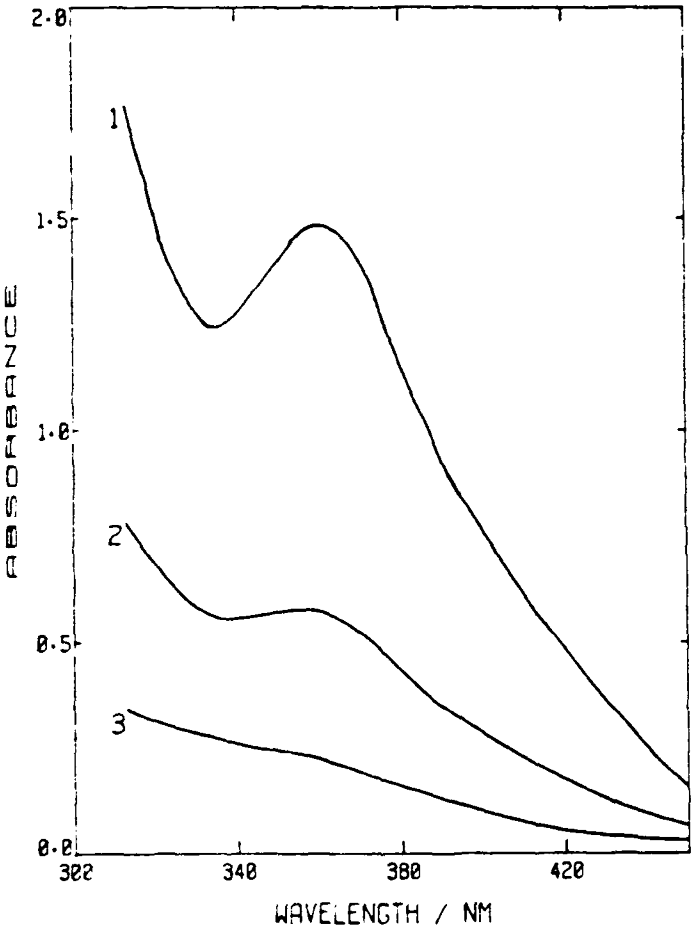

FIGURE 4

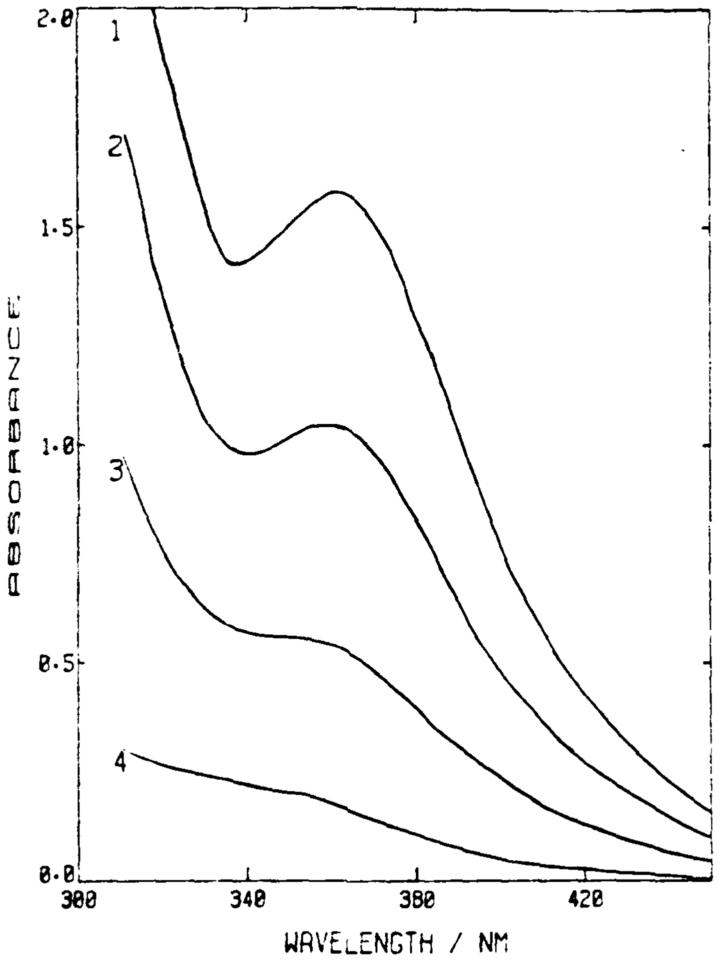

FIGURE 5

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