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An Electrochemical and Infrared Study of Chloranil in n-Butylpyridinium Chloride:Aluminum Chloride Ionic Liquid

Graham Cheek[1] and R. A. Osteryoung
Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

Key Words: Fused Salts; voltammetry; ESR; potential

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[1] Present address: U.S. Naval Academy
Annapolis, MD 21402

ABSTRACT

The electrochemical behavior of tetrachlorobenzoquinone (chloranil, Q) has been studied in the aluminum chloride-n-butylpyridinium chloride (BuPyCl) ionic liquid system. The reduction of chloranil proceeds in a two-electron step, giving rise to the dianion. Both the electrochemistry and infra-red spectroscopy appear to indicate that, depending on the acidity of the system, chloranil is complexed by $AlCl_3$, initially on the carbonyl oxygen, and on the ring chlorines. The second carbonyl appears to remain uncomplexed. Large shifts in the reduction potential for chloranil are observed as the solvent acidity (mole ratio of $AlCl_3$ to BuPyCl) is varied, indicating the extensive degree of interaction of the solute with the solvent. Cyclic voltammetry indicates the presence of one or as many as three species, depending on the acidity, which are concluded to be in rather slow equilibrium. Nernst plots of the potential of an indicator electrode as a function of the $Q/Q^=$ ratio indicate potentiometric reversibility; at a fixed $Q/Q^=$ ratio, the potential variation as a function of melt acidity indicates a gain of three $AlCl_3$ molecules per $Q^=$ relative to Q, suggesting that it is complexed by 6 $AlCl_3$ molecules in the acid system.

INTRODUCTION

Several studies from this laboratory have shown that the $AlCl_3$:n-butylpyridinium chloride molten salt system is a useful and interesting solvent for electrochemical studies.[1-6] The attractiveness of this solvent is due both to its low melting point and the absence of moisture in the medium. Recent work has shown that $AlCl_3$ complexation of such species as aromatic hydrocarbons,[5] aromatic amines,[4] and 9,10-anthraquinone[6] occurs in the acidic melt, the results indicating that the existence of $AlCl_3$ in this system as $Al_2Cl_7^-$ does not prevent its interaction with basic centers on the molecules studied.[6] Since considerable work has been carried out in the high-temperature $AlCl_3$:NaCl system,[7-11] it is of interest to relate the properties of these $AlCl_3$-based molten salt systems by studying a particular solute in both systems. A previous study of p-tetrachlorobenzoquinone (chloranil) in the $AlCl_3$:NaCl system[9] suggests this compound as a logical choice for the comparison. The electrochemical behavior of chloranil in other solvents, particularly superacid systems such as HF[12] and HF/SbF_5,[13] is also of interest in this regard; in addition, the considerable interest in chloranil as a cathode material for battery systems[14,15] makes a study of chloranil electrochemistry desirable. Comparison with quinone electrochemistry in general[16-19] is also of interest. Finally, a study of both chloranil and 9,10-anthraquinone (AQ) in the present system should reflect any differences in electrochemical characteristics due to the different structures of the two quinones.

EXPERIMENTAL

All experiments were carried out in an argon atmosphere in a Vacuum Atmospheres Corp. drybox, the moisture and oxygen levels of the atmosphere being monitored by appropriate instrumentation;[6] these levels were typically below 2 ppm.

Electrochemical experiments employed vitreous carbon (Atomergic Chemicals Corp., 3 mm diameter sealed in Pyrex) as the working electrode material; other electrodes and cell design were as previously described.[3] Electrochemical instrumentation consisted of either a PAR 173 Potentiostat/Galvanostat, with PAR 179 Digital Coulometer and PAR 175 Universal Programmer, or a Wenking 61RH potentiostat controlled by the PAR 175 Universal Programmer; both systems gave equivalent results. A Tektronix Model 564 storage oscilloscope was used for rapid-scan cyclic voltammetric and chronoamperometric experiments. Potentiometric experiments utilized an Analog Devices Model 311J Electrometer connected to a Fluke Model 8000A Digital Voltmeter.

The preparation and purification of the melt components n-butylpyridinium chloride (BuPyCl) and aluminum chloride, including melt preparation procedure, have been presented previously.[3] Chloranil (denoted in this work as Q; Eastman Chemical Co.) was recrystallized either from benzene or absolute ethanol; agreement of melting point and infrared spectrum served as an indication of purity. Tetrachlorohydroquinone (Eastman) was sublimed under vacuum, m.p. 231-232 °C.

Infrared spectra were obtained on a Perkin-Elmer 467 Grating Infrared Spectrophotometer. It was found that solutions of chloranil in the acidic melt were rapidly decolorized (red color changing to yellow; see Results and Discussion) upon contact with either NaCl or AgCl infrared cell windows; therefore, cells were constructed of polyethylene film (0.9 mil thickness) by securing a piece of the film to each of two NaCl salt plates by means of an O-ring. Spacers were also constructed from the film by using two cork borers of different diameter to cut circular sections with a concentric hole; two of these spacers were used and were secured to one of the polyethylene-covered NaCl plates by heating for approximately 15 minutes in an oven at 80-90°C. These cells gave satisfactory results, the red color remaining unchanged after being in the cell for several hours. Infrared spectra were taken with these cells enclosed in a small container equipped with NaCl windows to assure the absence of moisture and air during the acquisition of spectra. Visible spectra were obtained on a Cary 14 UV-VIS spectrophotometer, while ESR spectra were run on a Varian 4502 ESR Spectrometer.

The chemical reaction between chloranil and benzene in the acidic melt involved an initial solution of 156 mM chloranil in a 1.6:1.0 $AlCl_3$:BuPyCl acidic melt (volume - 10.4 ml) at 40°C; upon addition of 1.4 ml of benzene, the color of the melt immediately began to change from red to brown. The rest potential (open-circuit potential) of the quinone solution was monitored at a vitreous carbon electrode (vs. Al reference), the potential falling 400 mV over a period of one hour. Since the rate of potential decrease at this point was rather slow, the reaction mixture was quenched with BuPyCl to produce a 0.8:1.0 basic melt. This solution was centrifuged overnight to produce a clear orange melt containing a brown semisolid precipitate; both fractions were found to give a single broad ESR absorption, the strength of the absorption being somewhat greater in the precipitate than in the melt. This melt was extracted with several 100 ml portions of benzene, yielding only a small amount (approximately 25 mg) of a red-orange solid. The melt was then hydrolyzed by addition of water and extracted with benzene. The mass spectrum for the hydrolyzed melt extract contained peaks at m/e 246, 248, and 250 (relative intensities 1.00:1.26:0.68) and at m/e 288, 290, and 292 (relative intensities 1.00:1.00:0.42); relative amounts of the two groups 1:6. Comparable peaks at m/e 212, 214, and 216 (relative intensities 1.00:0.94:0.25) were also observed and could correspond to loss of C_6H_6 from the system at m/e 288-292 (see Results and Discussion, Chemical Aspects).

RESULTS AND DISCUSSION

General Aspects and Spectroscopy

Investigation of the electrochemical behavior of p-chloranil in the melt as a function of acidity was carried out using cyclic voltammetry; infrared and visible spectroscopy were also used to provide structural information about the species in solution. Cyclic voltammograms for p-chloranil in the melt are presented in Figure 1, the acidity of the melt increasing from the top to the bottom scans. In this series, the potential for reduction of chloranil in the acidic melt is approximately 1.5 V positive of that in the basic melt; this behavior, along with the appearance of the intermediate species observed in the cyclic voltammograms in the neutral melt, is evidence of successive complexation of chloranil by $AlCl_3$ with increasing melt acidity. This type of behavior has been observed for N,N,N',N'-tetramethylbenzidine[4] and, most recently, 9,10-anthraquinone (AQ),[6] both of which show cyclic voltammetric behavior indicating the formation of two successive $AlCl_3$ complexes by interaction of the molecules with $Al_2Cl_7^-$ present in acidic melts, both molecules possessing two electron-rich sites available for complexation. The appearance of three peaks beyond that for reduction of the uncomplexed chloranil in the basic melt (Figure 1, middle scans) suggests the existence of three complexation sites for chloranil; the two unresolved peaks in the acidic melt cyclic voltammogram (Figure 1, bottom scan) apparently are due to reduction of a mixture of tetra- and (mostly) tri-complexed chloranil, $Q(AlCl_3)_4$ and $Q(AlCl_3)_3$, implying the existence of a fourth site of complexation on the molecule. This rather extensive interaction of chloranil with the acidic melt is supported by the increased solubility of chloranil in the acidic melt relative to that in the basic melt; solutions of 50 mM chloranil in the basic melt were saturated at 40°C, whereas solubility in the acidic melt was found to exceed 150 mM. It should be noted that the solubility of AQ in the acidic melt (present as $AQ(AlCl_3)_2$ was found to be much lower than that in the basic melt;[6] evidently, the high solubility of chloranil in the acidic melt is due to its increased degree of complexation, although the orientation of complexation (see below) may be a more important factor in this regard than simple degree of complexation.

The existence of chloranil as the uncomplexed molecule in the basic melt was inferred from the infrared spectrum (Figure 2a) of the chloranil in the 0.8:1.0 $AlCl_3$:BuPyCl melt. In this spectrum, the bands at 1635 and 1585 cm^{-1} are due to the n-butylpyridinium cation; the bands denoted by arrows, at 1692 and 1570 cm^{-1}, are attributed to the carbonyl and double bond stretching modes, respectively, of chloranil.[20] Visible spectroscopic data for chloranil in the basic melt showed the presence of one very weak absorption maximum at 330 nm, just before the onset of background absorption from the n-butylpyridinium cation beyond 300 nm. UV-VIS spectra of chloranil in other solvents[21,22] contain two absorption maxima at 330 nm ($\log a = 2.48$) and 280 nm ($\log a = 4.02$); the absorption observed for chloranil in the basic melt is evidently the longer wavelength absorption. Qualitatively, no color change is observed upon addition of chloranil to the basic melt, the color of both the solid and its basic melt solution being yellow.

The extensive interaction of chloranil with the acidic melt, indicated above by the cyclic voltammetric behavior, is also observed from the infrared spectrum of Figure 2b. In this spectrum, it is evident that the intensity of the carbonyl band at 1692 cm^{-1} has decreased relative to that seen in the basic melt spectrum (considering that the chloranil concentration for the acidic melt spectrum is approximately twice that for the basic melt spectrum) and that a new band has appeared at 1545 cm^{-1}. This new band can be attributed to a chloranil carbonyl bond, the bond order of which has been decreased due to complexation with $AlCl_3$.[6] In contrast to the behavior observed for AQ, in which carbonyl absorption was entirely shifted to the lower frequency due to formation of $AQ(AlCl_3)_2$, the existence of both a shifted and an unshifted carbonyl band in the chloranil spectrum indicates that only one of the carbonyl bonds is complexed by $AlCl_3$. Further complexation of the chloranil molecule by $AlCl_3$ is indicated by the disappearance of the band at 1570 cm^{-1} due to the double bond stretching; this absorption is presumably also shifted by $AlCl_3$ complexation to lower frequencies, lying outside the rather limited absorption window bounded by n-butylpyridinium and polyethylene (see Experimental Section) absorption. Whether this complexation occurs directly by interaction of $AlCl_3$ with the double bond itself, with its rather high π-electron density,[22] or indirectly through the unshared electron pairs of the chlorine substituents, is not clear; however, in either case considerable alteration of the electron density in the double bond would occur. Spectroscopic and physical studies of organochlorine/Lewis acid solutions have indicated the formation of complexes between the Lewis acid and the chlorine substituent[23] and would support $AlCl_3$ complexation of the chloranil ring through the chlorine atoms. The complete absence of the double bond stretching band and the changes in the carbonyl absorption, together with the cyclic voltammetric evidence for formation of a tri-$AlCl_3$ chloranil complex, indicates that one $AlCl_3$ molecule is complexed to each of the two dichloroethylenic moieties in the chloranil ring and at one of the carbonyl oxygens. Further complexation at the remaining carbonyl group would account for the small amount of the tetra-substituted chloranil apparent in the cyclic voltammogram for the acidic melt. However, both the cyclic voltammetric behavior and the infrared spectral evidence indicate that the amount of this $Q(AlCl_3)_4$ complex is relatively small. The increase in solubility of chloranil in the acidic melt relative to that in the basic melt could be explained by considering that complexation of chloranil as proposed above leads to formation of a species possessing a net dipole moment, thereby leading to greater solubility in the polar melt.

Upon addition of chloranil to the acidic melt, or upon making a basic melt containing chloranil acidic, the melt becomes a red-orange color, with an absorption maximum at 500 nm (shoulder at 480 nm) having an apparent molar absorptivity (ε) of approximately 900 M^{-1} cm^{-1}; this color change is reversible, addition of BuPyCl to form a basic melt causing the melt color to change from red back to yellow. This spectrum compares favorably with that reported for the chloranil anion radical in various solvents (maximum at 450 nm, shoulder at 430 nm, $\varepsilon = 9000$ M^{-1}),[24,25] indicating some spontaneous reduction of chloranil by the melt. The presence of the chloranil anion radical was confirmed by ESR spectroscopy of a 5 mM solution of chloranil in the 1.2:1.0 $AlCl_3$:BPC melt, which showed a strong signal consisting of a single absorption; the absorption appeared to be broadened by unresolved chlorine (and possibly aluminum) hyperfine splitting. Comparing the observed and literature values for molar absorptivity of the anion radical, these results indicate that approximately 10% of the chloranil in the acidic melt exists as the anion radical. Similar ESR results have been obtained for chloranil in the $AlCl_3$:NaCl system, the spectrum being observed for a solidified sample.[9] Solutions of chloranil in the neutral $AlCl_3$:NaCl molten salt at 175°C were also found to have a red color[9]; it appears, therefore, that a certain amount of semiquinone (anion radical) formation is occurring in both the high-temperature ($AlCl_3$:NaCl, 175°C) and the low-temperature ($AlCl_3$:BuPyCl, 40°C) tetrachloroaluminate systems. In the present system, the anion radical would, of course, exist as a highly-complexed species, which may account for the bathochromic shift observed for the visible absorption compared to the literature values. Although the uncomplexed anion radical has been found to absorb in the infrared at 1530 cm^{-1}[26] (occurring at nearly the same position as postulated above for the complexed carbonyl bond), the complexation of the anion radical in this case would probably shift the value to even lower frequencies; in either case, its contribution to the infrared spectrum at this frequency, and therefore to the interpretation given above, should be rather small, since the relative amount of anion radical is fairly low.

The visible spectrum of chloranil in the acidic melt also shows an absorption at 330 nm which is much stronger than that due to the anion radical (molar absorptivity = 10,000 M^{-1} cm^{-1}; location of maximum near melt background absorption prevented accurate measurement). This molar absorptivity value compares favorably with that reported for chloranil, in various solvents, at 280 nm.[21] Although chloranil also has a weak absorption near 330 nm in these solvents and in the basic melt, the strength of this absorbance in the acidic melt suggests a bathochromic shift of the major chloranil absorption to 330 nm upon complexation, an effect similar to that observed for AQ complexation.[6]

Electrochemical Behavior in Basic Melt

The reduction of chloranil in the basic melt, as seen in Figure 1, is characterized by a single broad cyclic voltammetric peak; the peak potential for this reduction is shifted positively with respect to those observed for benzoquinone and AQ (-245 and -550 mV, respectively, vs. 2:1 $AlCl_3$:BuPyCl reference melt),[6] an effect due to the electron withdrawing nature of the chlorine substituents. Coulometric reduction at -0.3 V produced a colorless melt and gave an n-value of 1.91, indicating a two-electron process; the somewhat low value indicates that some spontaneous reduction (approximately 5%) of chloranil by the melt may be taking place. An ESR spectrum of 6 mM chloranil in the basic melt showed only a very small amount (near background noise level) of radical present, an observation in accordance with the fact that no red color (see above) is observed for chloranil in the basic melt. The above formation seems to indicate that most of the chloranil reduced by the basic melt exists in the dianion form.

The absence of an oxidation peak on the reverse scan in the immediate vicinity of the reduction process in Figure 1 indicates, as in the case of AQ in the basic melt[6] and quinone reduction in solvents containing proton donors,[18,27] that a rather extensive interaction (complexation) of the reduction product is taking place. Increase of temperature to 100°C and scan rate to 20V/second did not produce any changes in the general appearance of the cyclic voltammogram (except for changes in peak current), showing that this complexation is very rapid and complete. The most likely mechanism for this complexation involves displacement of chloride from $AlCl_4^-$ by the reduced quinone species (anion radical or dianion) as found for AQ reduction.[6] This complexation would probably lead to an ECE mechanistic pathway for the electrochemical process, since a complexed anion radical should undergo reduction at a more positive potential than that for the initial reduction:[28]

$$Q + 1e^- = Q^{\cdot-} \qquad [1]$$

$$Q^{\cdot-} + AlCl_4^- = Q^{\cdot-}(AlCl_3) + Cl^- \qquad [2]$$

$$Q^{\cdot-}(AlCl_3) + 1e^- = Q^{=}(AlCl_3), \qquad [3]$$

with probable further complexation of the dianion. Rapid and complete formation of a complexed anion radical at the electrode surface would encourage the ECE pathway while making homogeneous reactions in solution (e.g., disproportionation of anion radicals) less likely.[29]

It can be seen from Figure 1 that subsequent oxidation of the electrochemically produced dianion must occur at potentials more positive than +0.8 V, at which potential oxidation of chloride (anodic background process) begins, since no oxidation peak is observed on the return sweep in the cyclic voltammogram. Since chloride oxidation intervenes between the redox processes of the chloranil couple and would therefore be near the standard potential of the chloranil couple, some oxidation of chloride by chloranil would be expected. Due to this behavior, stable potentials for coulometrically produced quinone/dianion mixtures could not be obtained, thereby precluding the potentiometric studies carried out for AQ.

Normal pulse voltammetric investigation of the chloranil reduction process resulted in a voltammogram characterized by a pronounced maximum; the extent of this maximum decreased upon raising the temperature of the solution or stirring the solution. Both of these procedures would lead to improved mass transport near the electrode surface; therefore, it appears that the maximum is due to a depletion effect,[30] following reduction at the electrode during pulses, caused by the high viscosity of the melt. This behavior is to be expected since it is not possible to re-establish the initial quinone concentration at the electrode surface by oxidation between pulses of quinone reduced during the pulses, the potential necessary for this being beyond the background potential limit.

Electrochemical Behavior in Neutral Melt

As mentioned previously, the peaks appearing at increasingly positive potentials in the neutral melt (Figure 1, middle scans) indicate the stepwise complexation of chloranil as the concentration of $Al_2Cl_7^-$ increases. It is assumed that each reduction peak corresponds to a two-electron process, since the melt is very reactive to the reduced species, favoring further reduction, as found in the basic and acidic (see below) melts. Also evident in Figure 1 is a corresponding positive shift of the oxidation peaks, involving oxidation of variously complexed dianions. The degree of complexation of these dianions may be deduced from the proximity of the oxidation peaks to the reduction peaks, with some of which they apparently form quasireversible couples. By this reasoning, the middle scan in Figure 1 depicts the oxidation of the complexed dianions $Q(AlCl_3)_2^{=}$, $Q(AlCl_3)_3^{=}$, and $Q(AlCl_3)_4^{=}$.

Because several reduction peaks are observed in the neutral melt cyclic voltammograms (200mV/second), it is evident that the rate of interconversion of the corresponding quinone species upon reduction of the more highly complexed species is rather slow. The phenomenon of interest here involves the depletion at the electrode surface of a particular quinone complex as it is reduced; in response to this lowering of concentration, less highly complexed chloranil molecules will undergo further complexation, by interaction with $Al_2Cl_7^-$ in solution, in an attempt to restore equilibrium among the complexes. An enhanced reduction current at the potential of reduction of the higher complex would then result from this process. Lowering the scan rate in cyclic voltammograms in the neutral melt to 20 mV/second resulted in a moderate relative increase of reduction current for the higher complexes, showing qualitatively that the rate of interconversion among the complexes is somewhat faster than that for the AQ system, for which the effect was found to be very small. A more quantitative investigation was carried out using normal pulse voltammetry in a melt containing chloranil species in approximately the same proportions as seen in the cyclic voltammogram of Figure 1 (third scan, containing $Q(AlCl_3)$, $Q(AlCl_3)_2$, and $Q(AlCl_3)_3$). An initial potential of +2.0 V was chosen in order to avoid depletion effects (so that all chloranil species are re-oxidized between pulses), while a pulse width ranging from 10 msec to 1 sec established the time frame for the experiment. Figure 3 presents a plot of log i vs. log τ (i = normal pulse voltammetric plateau current, τ = pulse width) for the three species mentioned above. Comparing the slopes of these curves with the value -0.50 expected for diffusion only, one notes that the lower slope observed for the highest complex (-0.35) indicates a slower rate of current decrease than for diffusion alone, implying some formation of this complex from lower complexes. Accordingly, the slope values for the $Q(AlCl_3)_2$ and $Q(AlCl_3)_1$ complexes are -0.75 and -0.58, respectively, indicating an accelerated decrease in concentration of these species as they convert to higher complexes. Finally, the total current for all three complexes was found to be diffusion-controlled, as seen from its slope of -0.50. As in the AQ system,[6] the reason for this rather slow rate of equilibration is not entirely clear, but again may involve the unbuffered nature of the neutral melt. Further complexation of the quinone species upon reduction would also reduce the $Al_2Cl_7^-$ concentration in solution, altering acidity at the electrode surface.

In the course of obtaining the cyclic voltammograms, it was noticed that the red color characteristic of the semiquinone appeared after the formation of the second chloranil-$AlCl_3$ complex ($Q(AlCl_3)_2$), indicating some disproportionation of this complex with the small amount of dianion formed in the basic melt (from which the series of the cyclic voltammograms in Figure 1 was initiated). This disproportionation is evidently unfavorable for uncomplexed chloranil in the basic melt and the $Q(AlCl_3)_1$ complex in the neutral melt, as is clear from the wide separation in potential for the reduction of the first chloranil complex and the closest dianion oxidation process; the dianion here appears to be the most stable reduced form. With increasing complexation, to the $Q(AlCl_3)_2$ complex, the potentials of the redox process become much closer, apparently enough to favor the existence of some amount of anion radical.

Electrochemical Behavior in Acidic Melt

As seen from Figure 1, increasing the melt acidity to produce a 1.2:1.0 $AlCl_3$:BuPyCl melt causes another small unresolved peak to appear at slightly more positive potential in the chloranil cyclic voltammogram, apparently due to formation of a small amount of a higher chloranil complex $Q(AlCl_3)_4$. Cyclic voltammetry of tetrachlorohydroquinone in a melt of the same acidity, employing an initial positive scan, was identical to that of chloranil in Figure 1 (initial negative scan), indicating that these species form a two-electron couple in the melt. (Addition of tetrachlorohydroquinone to the melt results in replacement of the protons with $AlCl_3$, producing the complexed dianion. Similar behavior has been observed upon addition of tetrachlorohydroquinone to the $AlCl_3$:NaCl melt[9] and of anthrahydroquinone to the $AlCl_3$:BPC melt[6]). The separation in potentials for the reduction and oxidation process again appears to be due to further complexation of chloranil upon reduction, this complexation being irreversible at the temperature (40°C) and scan rate (200 mV/second) employed. As the temperature was increased to 120°C and scan rate lowered to 5 mV/second, the oxidation peak underwent a considerable shift to more negative potential, with some slight positive shift of the reduction peak (the two components of which merged to form a single reduction peak), giving a cyclic voltammogram characteristic of a two-electron quasireversible system (equal anodic and cathodic peak currents; E_p = 55 mV, compared to 37 mV for a reversible two-electron system at 120°C). This behavior indicates a marked increase in the kinetics for the complexation steps associated with dianion formation at the higher temperature, giving rise to nearly reversible behavior.

Coulometry at +1.5 V resulted in an n-value of 1.70 for chloranil reduction, which, assuming intrinsically two-electron behavior for the chloranil system as evidenced above, indicates spontaneous reduction of chloranil by the melt. As in the basic melt, a colorless solution resulted after the exhaustive reduction. Oxidation of this solution at +2.1 V gave an n-value of 2.0, although background currents were somewhat higher than at +1.5 V. The nature of the reductant in the spontaneous reduction as observed both in the $AlCl_3$:NaCl[9] and $AlCl_3$:BuPyCl systems[6] suggests that oxidation of chloride (as $Al_2Cl_7^-$ or $AlCl_4^-$) to chlorine may be involved. The amounts of the species (i.e., dianion and anion radical) produced by this spontaneous reduction may be estimated by assuming that the molar absorptivity of the anion radical is the same in the acidic melt as in other solvents; as given previously, this leads to a value of about 10% of total chloranil present as the anion radical. Assuming that the remainder of the reduced product is the dianion, from the coulometric n-value its percentage of total chloranil must also be about 10%, since reduction to the dianion involves two electrons, or $n = 1.70 = 2.00 - 0.10 - 2(0.10)$.

A potentiometric analysis of the chloranil systems was carried out by stepwise coulometric oxidation of an exhaustively-reduced chloranil solution (in order to avoid as much as possible the effects of spontaneous reduction of chloranil). This procedure gave stable potential readings and a slope of 33 mV/decade $Q/Q^{=}$ (Figure 4); comparing this value with 31 mV/decade for a reversible two-electron system at 40°C, it appears that the chloranil system is potentiometrically reversible. Some deviation from linearity at higher $Q/Q^{=}$ values is apparent, probably the result of increasing importance of the spontaneous reduction process at higher positive potentials.

The extent of complexation of chloranil upon reduction was also studied potentiometrically, using the equation

$$Q(AlCl_3)_p + m\ Al_2Cl_7^- + 2e^- = Q(AlCl_3)^{=}_{p+m} + m\ AlCl_4^- \qquad [4]$$

(where p is the complexation number of chloranil in the acidic melt, at least 3 as given previously, and m is the additional number of $AlCl_3$ molecules complexing the dianion upon reduction) and the corresponding Nernst equation

$$E = E + \frac{RT}{2F} \ln \frac{Q(AlCl_3)_p}{Q(AlCl_3)_{p+m}} + \frac{RT}{2F} \ln \left(\frac{[Al_2Cl_7^-]}{[AlCl_4^-]}\right)^m . \qquad [5]$$

A slightly acidic melt containing equimolar amounts of chloranil and its dianion was made progressively more acidic by additions of $AlCl_3$; the resulting slope of the Nernst plot (Figure 5) was found to be

87 mV/decade $Al_2Cl_7^-/AlCl_4^-$, indicating that $m = 87 \div 31 = 2.8$. The chloranil dianion, then, is apparently complexed by approximately six $AlCl_3$ molecules. For the case of AQ in the acidic melt, a similar analysis showed the AQ dianion to be complexed by four $AlCl_3$ molecules, or two per oxygen anion.[6] If this two-fold complexation of oxygen anions also applies for the chloranil dianion, the above observation is consistent with the postulate that only one of the chloranil (oxidized species) carbonyl groups is appreciably complexed by $AlCl_3$ in the acidic melt; upon reduction, interaction with three $AlCl_3$ molecules would result in doubly complexed oxygen anions.

Solvent System Comparison of Chloranil Electrochemistry

At this point it is of some interest to survey the electrochemical behavior of chloranil in other solvents in order to place the present work in some perspective. In nonaqueous solvents such as acetonitrile, dimethylformamide, and dimethylsulfoxide, the electrochemical reduction of chloranil has been found to proceed by two successive one-electron steps, indicating the lack of interaction (complexation, protonation) of the reduced species with the solvent/supporting electrolyte system.[31,32] The half-peak potential $E_{p/2}$ for chloranil reduction in the basic melt is +0.05 V + 0.060 V = +0.110 V vs. SCE (since the aluminum reference electrode is 60 mV positive of the SCE)[5] and is thus somewhat positive of the potentials for the first reduction process of chloranil of +0.01, -0.02, and + 0.07 V in the three solvents mentioned above.

Comparing the electrochemical characteristics of chloranil in the neutral $AlCl_3$:NaCl[9] and the acidic $AlCl_3$:BuPyCl molten salt systems, one notes the similarity in cyclic voltammetric behavior for chloranil reduction in the two melts as the temperature of the $AlCl_3$:BuPyCl melt is raised, both involving quasireversible two-electron systems composed of chloranil and its complexed dianion. In addition, both melts seem to stabilize the chloranil anion radical, generated spontaneously in the melts, to some extent, as shown by the visible and ESR spectroscopic results. The main difference between the two systems becomes apparent as the melts are made increasingly basic; in the $AlCl_3$:BuPyCl system, a series of complexes is observed, involving large shifts (-1.5 V) in potential, while in the $AlCl_3$:NaCl system a cathodic shift of only -0.5 V was found, with an increase in the stability of the electrogenerated anion radical. No series of chloranil complexes was observed in this system. This behavior reflects the higher levels of acidic species (principally as $Al_2Cl_7^-$) in the $AlCl_3$:NaCl system, even with a molar excess of chloride (basic melt), compared to the $AlCl_3$:BuPyCl system.[2,33]

Work in other superacid systems also reveals some relationship to the present study. Reduction of chloranil in HF/H_2O mixtures has been found to involve a single two-electron process, in contrast to the behavior of other quinones in this medium, which showed successive one-electron steps at higher acidities.[12] The difference in behavior was attributed to the instability of the semiquinone. In the basic medium 0.15M KF/HF,[13] the observation of the same type of behavior (single two-electron process, occurring at approximately the same potential) suggests that chloranil is not protonated in these media.

In the acidic HF/SbF_5 system, however, marked changes in chloranil electrochemistry occur, involving a positive shift for reduction of 700 mV, with the reduction process now consisting of two successive one-electron reductions.[13] Together with a color change to violet and a greatly increased solubility, this is cited as evidence for protonation of chloranil, the stability of the electrogenerated semiquinone being attributed to its protonation upon reduction to $QH_2^{+\cdot}$. Potentiometric evidence, similar to that given above for chloranil in the $AlCl_3$:BuPyCl system, indicates that the final reduction product is QH_4^{2+}. Thus, extensive interaction of chloranil with $Al_2Cl_7^-$ in the melt, both before and after reduction, seems to have its parallel in another superacid system.

Finally, the observed electrochemical stability of the chloranil anion radical in the HF/SbF_5 system suggests an alternative interpretation of the presence of the two unresolved peaks in the cyclic voltammogram for chloranil in the acidic $AlCl_3$:BuPyCl melt (existence of $Q(AlCl_3)_3$ and some $Q(AlCl_3)_4$; that is, these peaks could also be due to partially resolved successive one-electron reduction steps for the $Q(AlCl_3)_3$ complex. A choice between these two interpretations is difficult because of the closeness of the peaks; a more certain knowledge of the relative peak heights would be necessary to make the distinction.

Chemical Aspects

From the data presented in the Experimental section, it is apparent that the complexation of chloranil in the acidic melt leads to interesting chemical behavior in connection with the spontaneous reaction observed upon addition of benzene to an acidic melt containing chloranil. The principal aspect of this reaction involves reduction of chloranil, as inferred from the mass spectrum of the hydrolyzed melt extract, indicating tetrachlorohydroquinone as the major species isolated (peaks at m/e 246, 248, and 250 with relative intensities 1.00:1.26:0.68), and from the drop in potential observed at the monitoring electrode. The ESR spectrum also gives evidence of reduction to the anion radical, although it is difficult to determine the amount of this species relative to that of the dianion. Comparison of this ESR spectrum with that for chloranil in the acidic melt presented previously indicated roughly comparable intensities, suggesting that the concentration of anion radical is fairly small (low millimolar levels) given that the original chloranil concentration, before benzene addition, was 156 mM. The above mass spectrum also contains peaks at m/e 288, 290, and 292 with relative intensities 1.00:1.00:0.42, indicating a species containing three chlorine atoms),[34] consistent with the presence of trichlorophenylhydroquinone in the hydrolyzed melt extract; the amount of this species appeared to be approximately 17% that of the tetrachlorohydroquinone. This result indicates that some Friedel-Crafts substitution of phenyl for chlorine has occurred prior to reduction. Since only one chlorine was substituted in this manner, it is evident that the Friedel-Crafts pathway is not very competitive with respect to reduction; however, the fact that some substituted product is obtained lends some support for the complexation of the chloranil chlorine substituents by $AlCl_3$ as proposed earlier.

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Figure Captions

1. Cyclic voltammograms of p-chloranil in 0.8:1.0 basic melt (a), in neutral melt, acidity adjusted by small coulometric additions of $AlCl_3$ (b,c,d); in 1.2:1.0 acidic melt (e). Scans recorded at 40°C, 200 mV/sec scan rate, total p-chloranil concentration 3.8 m*M*.

2. Infrared spectra of p-chloranil in (a) 0.8:1.0 basic melt, chloranil concentration = 50 m*M*; (b) 1.2:1.0 acidic melt, chloranil concentration = 110 m*M*. Arrows indicate bands due to chloranil species; other bands are due to n-butylpyridinium cation.

3. Plot of log ($i/\mu A$) vs. log (τ/msec) for normal pulse voltammetric data in neutral melt containing total chloranil concentration of 4.0 m*M*; distribution of species is similar to that shown in Figure 1, third scan. τ values are given for times corresponding to the middle of the sampling interval (75-99% of pulse width). Scan rate = 5 mV/sec; interval between pulses = 10X pulse width. Plot labels indicate current responses due to (a) $Q(AlCl_3)_3$, (b) $Q(AlCl_3)_2$, (c) $Q(AlCl_3)_1$ (with small amount of uncomplexed Q), and (d) total current. Slopes: (a) -0.35, (b) -0.75, (c) -0.58, (d) -0.50.

4. Nernst plot obtaining by coulometrically varying $[Q]/[Q^=]$ ratio, starting from exhaustively reduced solution. Melt composition: 1.2:1.0 acidic melt. Total chloranil concentration = 7.2 m*M*.

5. Nernst plot obtained by varying acidic melt composition with addition of $AlCl_3$. $[Q] = [Q^=] = 3.6$ m*M*.

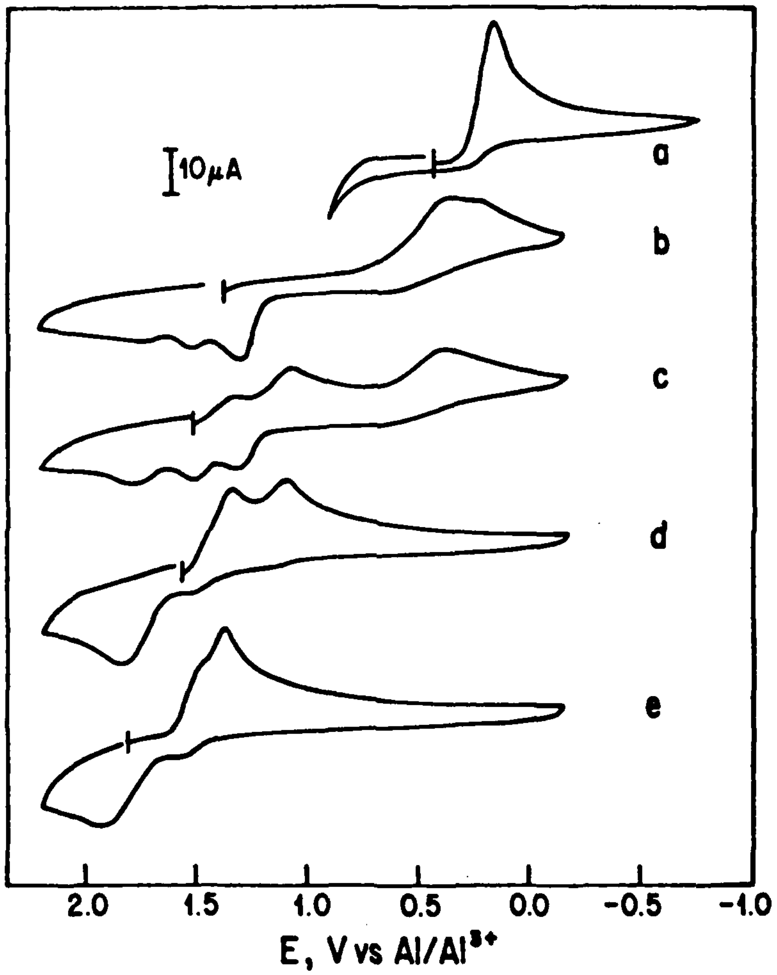

Figure 1

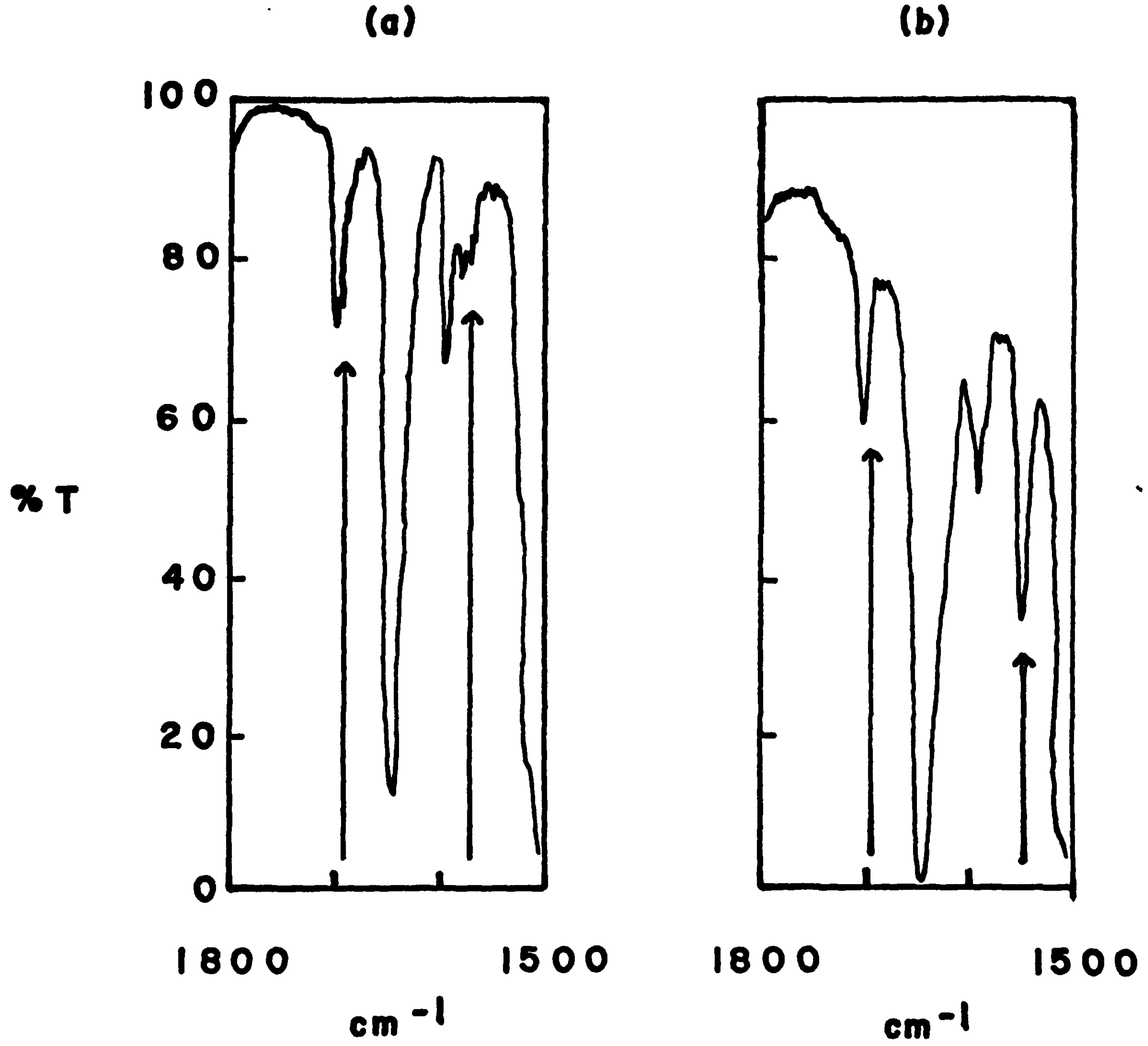

Figure 2

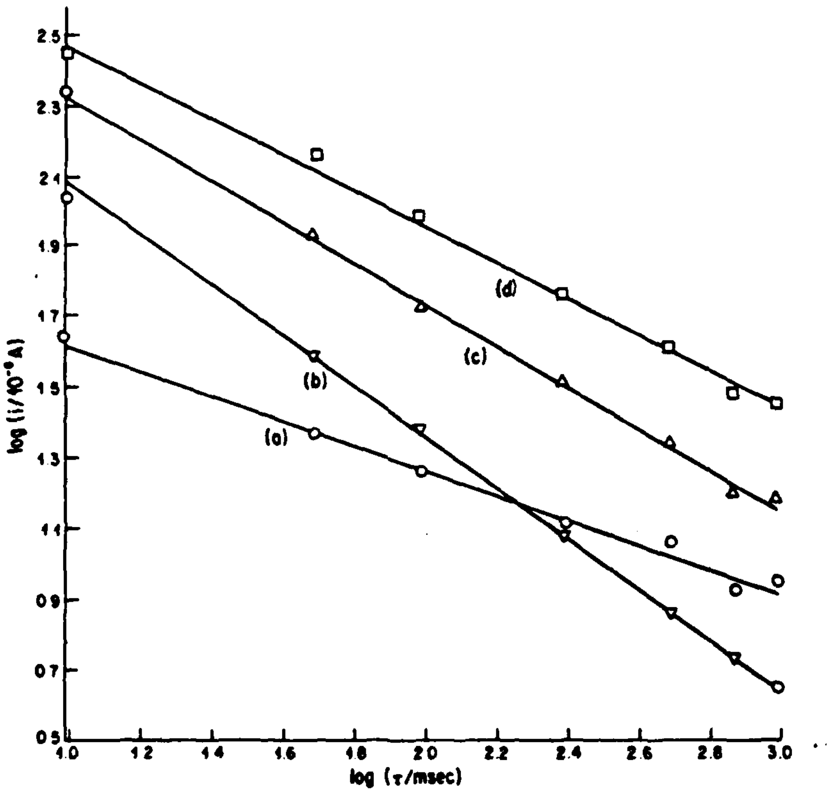
log (i/10⁻⁶A)
2.5
2.3
2.1
1.9
1.7
1.5
1.3
1.1
0.9
0.7
0.5
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
log (τ/msec)
(a)
(b)
(c)
(d)

Figure 3

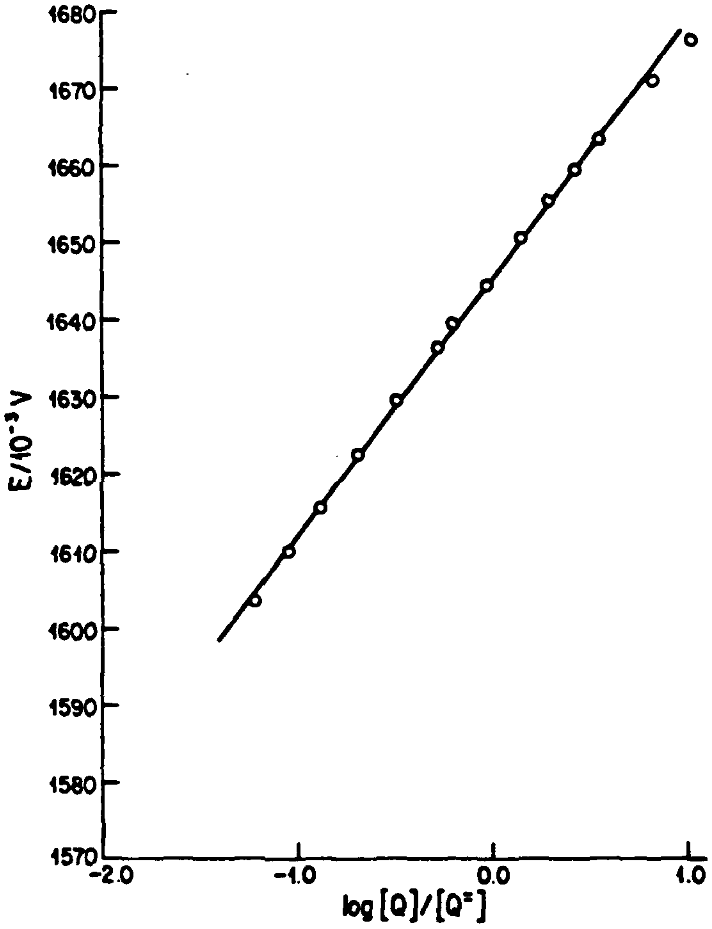
1680
1670
1660
1650
1640
1630
1620
1610
1600
1590
1580
1570
E/10⁻³ V
-2.0
-1.0
0.0
1.0
log [Q]/[Q⁼]

Figure 4

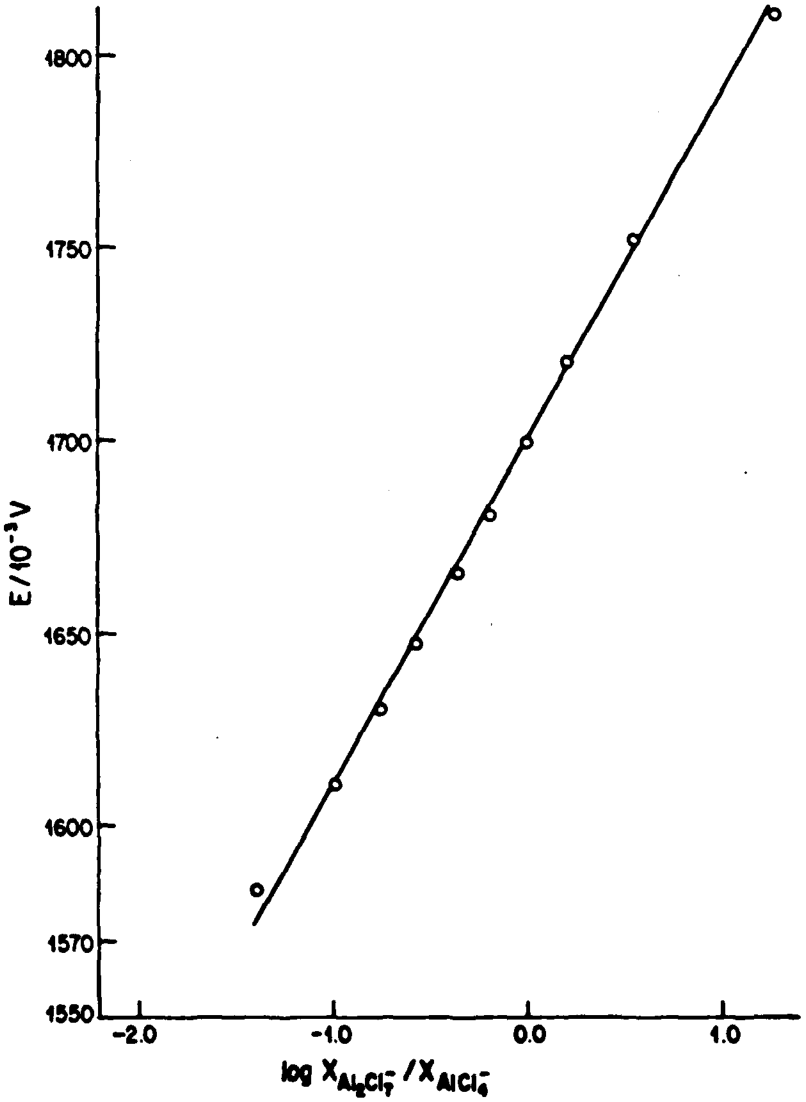
1800
1750
1700
1650
1600
1570
1550
E/10⁻³ V
-2.0
-1.0
0.0
1.0
log X_{Al₂Cl₇⁻} / X_{AlCl₄⁻}

Figure 5

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