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COBALT (II) HALIDES AS ELECTROLYTES IN ACETONITRILE

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George J. Janz, Arthur E. Marcinkowsky and H.V. Venkatasetty

Rensselaer Polytechnic Institute
Department of Chemistry
Troy, New York

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INTRODUCTION

Although acetonitrile $(D, 35.99, 25°)$ is an excellent solvent for many inorganic substances[1], a recent survey[2] shows that with the exception of the investigations with substituted ammonium salts and some Group I halides

1. G. Kortum, S.D. Gohale, and H. Wilski, Z.physik.Chem. **3**, 286 (1955)

2. G.J. Janz, H.V. Venkatasetty, and F.J. Kelly, " Conductance Data Non-Aqueous Electrolytes", Rensselaer Polytechnic Institute Technical Bulletin (1962) Troy, N.Y.

very limited conductance data for inorganic electrolytes in this solvent have been reported. Relative to the cobaltous halides in anhydrous acetonitrile, Libus[3] has investigated spectrophotometrically the chloro-cobalt (II) complexes both in the absence and presence of excess chloride ions as additional

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3. L. Libus, 7th International Conference on Coordination Chemistry, Abstract 7G3; Stockholm, June, 1962.

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ligands. A series of simultaneous ionization equilibria, with the tetra-hedrally coordinated species $(CoCl_2L_2)^\circ$, $(CoCl_3L)^-$ and the octahedral complex $(CoL_6)^{+2}$, where L is the solvent, was proposed. It is apparent that the solute-solvent interactions in these solutions are other than simple "passive" solvation. The cobaltous halides-acetonitrile solutions thus appear typical of systems in which ion-solvent interactions are an extreme. The present communication reports an investigation of the electrical conductance for $CoCl_2$ and $CoBr_2$ from 10^{-4} to 0.1 mol l^{-1} over the temperature range 0°-35°C. The techniques of spectrophotometry and electrical transport were used to gain additional information on the structural nature of the solvent-solute interactions in these solutions. The measurements have been limited to the properties of $CoCl_2$ and $CoBr_2$ as electrolytes in CH_3CN since the results of exploratory measurements with CoI_2 indicated a slow decomposition reaction (formation of free I_2) in this solvent system.

EXPERIMENTAL

As described in the studies of the hydrogen halides in acetonitrile[4], care was taken to ensure that anhydrous conditions were maintained through-

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4. G.J. Janz and S.S. Danyluk; J. Am. Chem. Soc. 81, 3846, 3850, 3854 (1959)

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out all phases of the investigations reported in this work. Details need

not be described and it will be sufficient to note that glassware, dilution

flasks, transfer techniques, conductance cells were designed as closed

systems to permit the use of storage and transfer techniques under inert

atmospheres (purified N_2, dried through H_2SO_4 and $Mg\ (ClO_4)_2$ traps); grease-

free stopcocks were used, and when systems were opened to the room atmos-

phere the apparatus exits were guarded with $Mg\ (ClO_4)_2$ tubes; " dry-box"

techniques were used for weighings.

Acetonitrile: The starting material, a technical grade acetonitrile

(Eastman Organic Chemicals), was purified by the repeated chemical drying

and distillation techniques used previously in this Laboratory[4]. The

physical constants of the anhydrous purified solvent were: b. 81.7C° (759.7mm);

d. (25°C) 0.7768; $n^D_{25°C}$, 1.3439; $\eta_{25°C}$, 0.3594 cp; specific conductance,

$6-10 \times 10^{-8}$ ohm^{-1} cm^{-1} (25°C).

Cobaltous Halides: Anhydrous $CoCl_2$ was prepared in an ancillary

apparatus from the hexahydrate (Fisher Certified Reagent Grade) by heating

in an HCl gas atmosphere as follows: The hydrate, in a porcelain boat,

was charged in a horizontal vycor tube furnace (1" dia.) and warmed to 60°C

using a continuous $HCl-N_2$ gas flow (1:1 mol ratio, 70-100 ml m^{-1}; the N_2

speeds the water " sweep-out" from the reactor zone). This was continued

until visible evidence of moisture evolution was no longer noted. This

procedure was repeated using a temperature increment of 20-25°C for each

step until 400°-450°C was reached. After several hours at this final

temperature, the sample was cooled en situe to 200°C at which point the

HCl flow was cut off but the dry N_2 sweep was continued. The hot sample was

moved into a pre-dried receiving flask at the end of the vycor furnace tube,

and transferred to the manifold of a vacuum-gas transfer assembly. By successive evacuation and dry gas " purges " as the sample was reheated from 25°C to 150°C, the final traces of HCl were removed from the anhydrous $CoCl_2$ thus prepared. The anhydrous salt is very hydroscopic and is a sky-blue color, completely soluble in anhydrous CH_3CN (no traces of insoluble oxides). It was stored in a P_2O_5 desiccator and all direct transfers of the salt were in a controlled atmosphere " dry-box". Anhydrous $CoBr_2$ was prepared using a quite similar procedure, with an $HBr-N_2$ gas sweep to remove the water from the hydrate. The anhydrous salt likewise is very hydroscopic; it is a light green color. The samples thus pre-pared were stored and used in the manner described for the anhydrous chloride. While simple heating of the hexahydrates in air at 130° for prolonged periods has been reported as adequate for the preparation of the anhydrous cobaltous halides[5,6], this technique was judged inadequate for the preparation of anhydrous cobaltous halides of reproducible purity.

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5. K.H. Gayner, and L.J. Woontner; J. Am. Chem. Soc. 74, 1436 (1952)
6. S. Buffagni and T.M. Dunn; J. Chem. Soc. (London) (1962)

Oxides, and possibly small amounts of $(CoOH)^+$ attributed to hydrolysis in variable amounts, could not be ruled out as impurities in the specimens prepared with less rigorous control.

Saturation Solubilities: The saturation solubility for anhydrous $CoCl_2$ in CH_3CN was determined by temperature equilibration (5 hours) of hot saturated solutions to the desired temperatures, and EDTA analysis[7] of the supernatant liquids. During equilibration the samples were shaken periodically; prior to removal of aliquots for analyses, the solutions were

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7. G. Schwarzenbach: Complexometric Titrations; Interscience Publ. Co. New York (1954)

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left undisturbed for an hour; glass wool filters at the pipette tips were used in the sampling process. The saturation solubilities for $CoCl_2$ in CH_3CN at 0°, 25° and 35°C thus found are 0.226_8, 0.589_5 and 0.935_0 mol 1^{-1} respectively. From these data the heat of solution in this temperature interval may be estimated as 6.8 ± 0.1 kcal mol 1^{-1} for the saturated solutions.

Crystalline Substrates: Crystalline substrates from the chloride and bromide-acetonitrile systems were prepared simply cooling hot solution to 0°C. The supernatant liquids were decanted, and the crystalline substrates were filtered dried at 25°C. The results for gravimetric halide analyses were as follows:

Substrate (g)	AgX(g)	Molar Ratio (CoX_2:CH_3CN)
(a) $CoCl_2$ crystalline substrate		
0.8080	0.8947	1:3.14
0.6871	0.7678	1:3.09
1.6847	1.8347	1:3.20
1.7379	1.9055	1:3.20
(b) $CoBr_2$ crystalline substrate		
0.4224	0.4533	1:3.12
0.4783	0.5127	1:3.20
0.9822	1.0486	1:3.24

The crystalline substrates may accordingly be designated by the general formula $[CoX_2 \cdot 3CH_3CN]_x$. The color of both these "solvated" crystalline salts is a sky-blue; the colors of anhydrous $CoCl_2$ and $CoBr_2$ are, respectively, sky blue and green. The crystalline substrates are unstable when exposed to the room atmosphere, turning the typical pink of hydrated cobaltous salts.

The magnetic susceptibilities of the crystalline substrates $(CoX_2 \cdot 3CH_3CN)_x$, were determined in the conventional manner using a Gouy Balance and $Hg[Co(SCN)_4]$ for the susceptibility calibration[8]. The

8. B.N. Figgis and R.S. Nyholm, J. Chem. Soc. (London) 1958, 4190

susceptibilities, $_{m}$, for the chloride and bromide were, respectively, 90.75×10^{-6} and 41.58×10^{-6} cgs units.

Spectrophotometry: All measurements were made with a Beckmann DU spectrophotometer in a dry nitrogen atmosphere. A set of matched 1 cm quartz cells were used to investigate the spectra of $CoCl_2$ and $CoBr_2$ in anhydrous CH_3CN solutions at 10 mu intervals from 500-720 mu. The measurements were reproducible to ± 0.02 optical density units. Measurements were restricted to the range $1 \times 10^{-4} - 6 \times 10^{-3}$ mol l^{-1} owing to the high absorption of these solutions. In Figure 1 are illustrated the molar extinction coefficients vs conc. relation for two comparable concentrations of $CoCl_2$ and $CoBr_2$ respectively. For $CoCl_2$ in CH_3CN there are four peaks of which the 570, 610 and 680 are quite intense, with the latter being the peak of maximum absorption (cf. aqueous spectra, 510 mu, max. absorption). For $CoBr_2$ there are also three quite intense peaks at 590, 640 and 690 mu, with the latter the maximum absorption point.

A graphical analysis of the spectrophotometric extinction coefficient vs. conc. for seven arbitrarily chosen wave lengths in this region showed that these data could be expressed by straight line functions of the type:

$$E_0 = D_0/c_0 = a \pm bc_0 \tag{1}$$

or

$$D_0 = ac_0 \pm bc_0^2 \tag{2}$$

where $\underline{a}$ is the intercept, $\underline{b}$ the slope ($\pm$), and c_0 the initial CoX_2 concentrations.

Conductance: The Jones conductance bridge and accessories, constant temperature baths ($\pm 0.01°C$) were those used in the preceding investigations[4] and need not be described again. Four conductance cells, with cell constants (cm^{-1}) 1.129, 0.9848_5, 0.1765, and 0.05365, respectively, were used as required. Four independent stock solutions of each solute were used; an aliquot of the stock solution was used for only four dilutions to minimize cumulative errors. The stock solutions were prepared analytically by weight (corrected to vacuo), and the concentrations were checked with EDTA analyses The results for the concentration range 10^{-4} to 0.1 eq. 1^{-1}, for the temperatures 0°, 25° and 35°C are listed in Table 1 at rounded $C^{\frac{1}{2}}$ values taken from a large scale graphical analysis (± 0.01 conductance units) of the several independent dilution runs.

To gain additional information, the conductance measurements were extended for $CoCl_2$ as follows: (i) the temperature dependence of conductance for a fixed concentration was examined from -50° to 75°C; (ii) the water effect on conductance/of added Cl^- ions (as tetra-ethyl ammonium chloride) and (iii) the effect were investigated. The results are given in Tables 2-4, respectively.

Transference: A modified Hittorf-type cell especially suitable for radio-active tracer techniques[9] was used for a limited series of transference measurements with $CoCl_2$-CH_3CN solutions at 25°C. Radioactive $CoCl_2$ was prepared using one m curie of Co^{60} as $CoCl_2$ and 15 g $CoCl_2 \cdot 6H_2O$ in aqueous solution. The anhydrous "active" $CoCl_2$ was prepared from this mixture in the conventional manner with due shielding safety precautions.

9. A.P.P. Brady, J. Am. Chem. Soc. 70, 911 (1948)

Silver and silver chloride electrodes as anode and cathode in the transport cell, and a calibrated precision constant current source (Sargent Co.) completed the assembly. The radiotracer analysis were made with a scintillation

counter calibrated for Co^{60} decay with standardized $CoCl_2-CH_3CN$ solutions, the results being corrected for background scattering and diffusion effects (for equivalent periods of time corresponding to the electrolysis experiments). For simple electrolytes and conventional gravimetric analyses, the modified Hittorf-type cell gave values that agreed within $\pm 5\%$ of the accepted literature values (eg. 0.02 mol 1^{-1} NaCl, 25°C; t_+ 0.41(found), 0.390 (lit.). The results for a series of four experiments at $25° \pm 0.02°C$ with 0.067 mol 1^{-1} $CoCl_2$ may be summarized as follows:

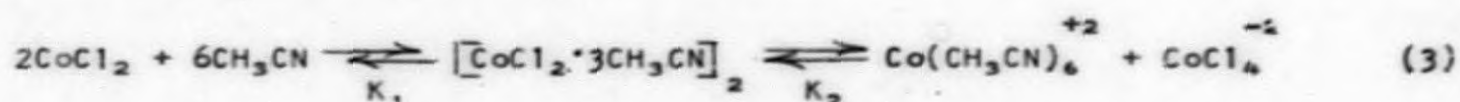| t(sec)	11,951	8,314.5	10,955	10,676
coulombs passed	5.95×10^{-4}	4.14×10^{-4}	5.43×10^{-4}	5.32×10^{-4}
m equiv. transported	5.7×10^{-5}	2.0×10^{-5}	9.8×10^{-5}	4.2×10^{-5}
t-	0.10	0.06	0.18	0.08

Corrections for volume changes due to electrolysis were not attempted as these were judged to be within the limits of experimental error.

DISCUSSION

The conductivities of anhydrous cobaltous chloride and cobaltous bromide in acetonitrile (Table 1) do not exhibit the usual behavior which is found for inorganic electrolytes of either the 1:1 or the 2:1 type in water. Firstly, the conductances are very low; for a concentration of 10^{-2} eq. 1^{-1} at 25°C the equivalent conductances are 17.60 and 25.25 for $CoCl_2$ and $CoBr_2$ respectively. No value of this concentration has been reported for $CoCl_2$ in water , but the conductance of $CoBr_2$ is known[10] to

10. R.A. Robinson and R.H. Stokes; Electrolyte Solutions, Academic Press Publ., N.Y. (1959)

to be 116.3. Secondly, it is seen that there is a negative temperature dependence for conductance of the cobaltous salts in acetonitrile. The observed " anomalous " behavior of the cobaltous halides in acetonitrile must lie in a series of simultaneous processes, ionic and non-ionic, under Mass-Law control. Consideration of the optical properties of these solutions suggests the following as a model:

$$2CoCl_2 + 6CH_3CN \underset{K_1}{\rightleftharpoons} [CoCl_2 \cdot 3CH_3CN]_2 \underset{K_2}{\rightleftharpoons} Co(CH_3CN)_6^{+2} + CoCl_4^{-2} \qquad (3)$$

Taking C_1, C_2, C_3 and C_3', as the equilibrium concentrations of $CoCl_2$, $(CoCl_2 \cdot 3CH_3CN)_2$, $Co(CH_3CN)_6^+$ and $CoCl_4^{-2}$, respectively, with the restriction that $C_1 + C_2 + 2C_3 = C_0$, the initial stoichiometric concentration of $CoCl_2$, it follows that:

$$C_1 = C_0/[1+2(K_1K_2)^{\frac{1}{2}}]; \quad C_2 = K_1C_0^2/[1 + 2(K_1K_2)^{\frac{1}{2}}]^2 \qquad \text{and}$$

$$C_3 = (K_1K_2)^{\frac{1}{2}}/[1 + 2(K_1K_2)^{\frac{1}{2}}]$$

The expression for the extinction coefficient, ε, that derives from this is:

$$\varepsilon_0 = \left[(\varepsilon_3 + \varepsilon_3') \left(\frac{(K_1K_2)^{\frac{1}{2}}}{1+2(K_1K_2)^{\frac{1}{2}}} \right) - \varepsilon_1 \left(\frac{2(K_1K_2)^{\frac{1}{2}}}{1+2(K_1K_2)^{\frac{1}{2}}} \right) \right] + \left[(\varepsilon_2 - \varepsilon_1) \left(\frac{K_1}{1+2(K_1K_2)^{\frac{1}{2}}} \right) \right] C_0$$

where ε_1, ε_2, ε_3, and ε_3' are the extinction coefficients for the species designated in (3). This is the equation of a series of straight lines. The intercept will be positive since $\varepsilon_1 \left(\frac{2(K_1K_2)^{\frac{1}{2}}}{1+2(K_1K_2)^{\frac{1}{2}}} \right)$ will be much less than the term preceding it; the slope may be either positive or negative, depending on the relative magnitudes of ε_1 and ε_2. The model is thus adequate for the description of the spectrophotometric properties (cf. equations 1, and 2).

Comparison of the spectrophotometric spectra (Figure 1) with that reported by Libus[3] shows that the optical properties are in very close, if not exact, accord. While the species $CoCl_2Li_2$, $(CoCl_3L)^{-1}$ and $(CoL_6)^{+2}$ were suggested suggested by Libus[7], it is apparent from the present analyses that the dimeric species $(CoCl_2L_3)_2$, and $(CoCl_4)^{-2}$ will contribute importantly to the properties of the solutions.

The nature of the crystalline substrates $(CoX_3 \cdot 3CH_3CN)_x$, provides additional information on the type of the ion-solvent interactions in the CoX_2-CH_3CN systems. Cotton and Francis[11] have isolated crystalline coor-dination salts of the empirical formula $(CoCl_2 \cdot L_3)_2$ using dimethylsulfoxide as ligand. The observed magnetic moment (4.83 B.M.) and the UV reflectance

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11. F.A. Cotton and R. Francis, J. Amer. Chem. Soc. 82, 2986 (1960)

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spectrum leave little doubt that this compound may be correctly formulated as $[CoL_4]^{+2} [CoX_4]^{-2}$. In the present work, taking x = 2 (cf. ionization equilibria (3) and Cotton and Francis[11]), the values of the observed magnetic susceptibilities give values of 5.2 and 5.0 B.M. per formula weight respectively for the crystalline chloride and bromide from " solvated" substrates. From the magnetic properties it may be concluded that the structures are similar to those advanced by Cotton and Francis[11] for the stoichiometrically similar dimethylsulfoxide complexes, namely $Co(CH_3CN)_6^{+2}$ in octahedral configuration and CoX_4^{-2} in tetrahedral symmetry, with the bonding in both being the spin-free type for divalent cobalt[12]. The ionic nature of the " dimeric" substrate thus is additional support for the

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12. R.J. Gillespie and R.S. Nyholm; Quar. Rev. 11, 360 (1957)

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viewpoint that the predominant species in the CoX_2-CH_3CN solutions are CoX_2, $Co(CH_3CN)_6^{+2}$, CoX_4^{-2}, and $[Co(CH_3CN)_6^{+2}CoX_4^{-2}]^°$ (although additional species such as $CoX_3CH_3CN^{-1}$, $CoCl(CH_3CN)_5^{+1}$ are not ruled out).

It is apparent that a quantitative account of the electrical conductances for the cobaltous halides in CH_3CN in light of the theories of ionic interactions for electrolytes is not possible at present. Qualitatively it is of interest to note that the near invariancy of equivalent conductance phoreograms for $CoCl_2$ and $CoBr_2$ in this anhydrous solvent (Table 1), the negative temperature coefficient of conductance in the ambient temperature range (Table 2), the effect of water in trace amounts (Table 3), and the halide common-ion effect (Table 4) are graphic illustrations of the displacements of the several equilibria simultaneously present in these non-aqueous electrolyte solutions.

The rather abnormal values found for the transference numbers (t_+ 0.9; t_- 0.1) are also understood, in large part, as due to the presence of complex cationic and anionic species.

The transport data reported by Wormser[13] for $CoCl_2$ in acetone and propyl alcohol (where the cobaltous salt is similarly complexed) give the

13. Y. Wormser; Bull Soc. Chim. 395, 38 (1948)

value* for t_+ as 0.9_2. These values are not unlike those noted elsewhere[14]

14. D.A. MacInnes; Principles of Electrochemistry, Dover Publ. Co. N.Y. (1960)

for CdI_2 solutions in which complexes and intermediate ions influence the expected concentration changes around the electrodes of the transport cell.

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* The value reported by Wormser of 0.575 for t_+ is in error due to an incorrect analysis of the migration processes and electrode reaction in the cell.

The importance of interactions such as ion-solvent (dipole) and solute-solvent (dipole, crystal-field) as well as the coulombic ion-ion interactions relative to the properties of such structurally complex solutes in non-aqueous solutions is clearly apparent from the preceding results. The polar nature of acetonitrile (dipole moment, 3.37 (25°C); dielectric constant, 35.99 (25°C)) would enhance such interactions and undoubtedly contributes importantly to the finite solubilities of a wide range of higher valence type electrolytes in this anhydrous solvent.

List of Tables and Figures

Table 1

Equivalent Conductances for $CoCl_2$ and $CoBr_2$ in CH_3CN

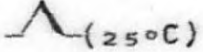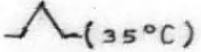| $c^{\frac{1}{2}}$	0°C		25°C		35°C	
	$CoCl_2$	$CoBr_2$	$CoCl_2$	$CoBr_2$	$CoCl_2$	$CoBr_2$
0.01	21.40	31.00	18.87	31.65	17.70	31.05
0.02	20.27	29.65	18.18	29.90	16.75	28.85
0.03	20.02	28.50	17.85	28.67	16.40	27.68
0.04	19.87	27.55	17.73	27.78	16.37	26.80
0.05	19.74	26.75	17.68	27.10	16.35	26.19
0.06	19.60	26.05	17.64	26.58	16.34	25.73
0.07	19.46	25.45	17.61	26.15	16.34	25.35
0.08	19.32	24.94	17.60	25.78	16.34	25.09
0.09	19.18	24.48	17.60	25.49	16.34	24.82
0.10	19.05	24.09	17.60	25.25	16.36	24.61
0.12	18.76	23.44	17.55	24.85	16.40	24.32
0.14	18.49	22.90	17.50	24.56	16.45	24.26
0.16	18.21	22.50	17.44	24.40	16.45	24.25
0.18	17.94	22.19	17.36	24.33	16.41	24.25
0.20	17.66	21.98	17.25	24.25	16.36	24.25
0.24	17.12		17.00		16.24	
0.28	16.58		16.77		16.11	
0.35	15.64		16.38		15.95	

Table 2

Temperature-Equivalent Conductance for a $CoCl_2-CH_3CN$
Solution of Constant Concentration ($C_{25\circ} = 2.483 \times 10^{-3}$ (eq/1))

T °C	$c^{\dagger}$(eq/1)$\times 10^3$	Λ
-44	2.71	15.3
-38	2.69	17.2
-27	2.66	19.1
-15	2.62	21.1
-3	2.58	21.8
+5	2.55	21.6
+11	2.53	21.4
+20	2.50	20.5
+22.5	2.49	20.0
+24	2.49	20.0
+31	2.46	18.9
+35.5	2.45	17.9
+40	2.43	17.2
+45	2.42	16.2
+50.5	2.40	15.4
+54	2.38	14.8
+60	2.36	13.8
+65	2.35	13.0
+68	2.34	12.5
+73	2.32	12.1

$\dagger$calculated from $C_{25\circ}$ and density variation corrections

Table 3

Equivalent Conductance of $CoCl_2-CH_3CN$ at 25° and 35°C with Successive
Additions of Water to an Original Solution of 50.985 Grams
at a Molality of 1.7602×10^{-2}, where $1000 \cdot \lambda = 1$ ml

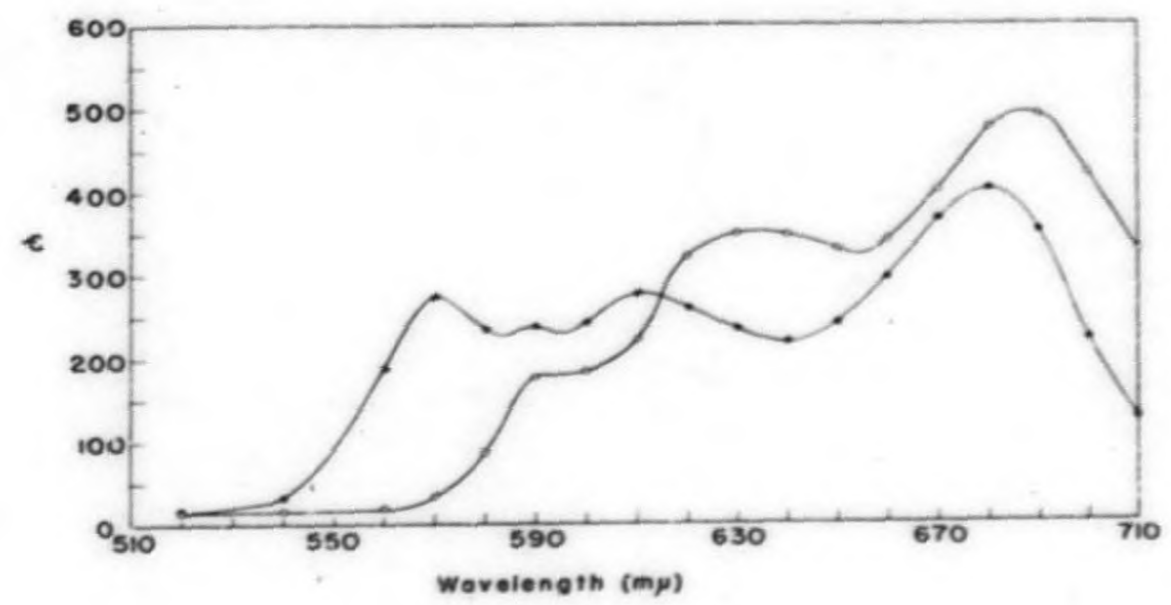| $\lambda^{\dagger}_{H_2O}$	Λ (25°C)	Λ (35°C)
0	17.43	16.43
25	18.25	17.19
50	19.00	17.94
100	20.67	19.22
150	21.52	20.55
200	22.37	21.49
250	23.18	22.44
300	23.77	23.19
400	24.74	24.44
500	25.55	25.55
600	26.14	26.36
750	26.78	27.35
1000	27.14	28.21

$\dagger$

λ = 96 corresponds to a solute-to-water ratio of 1:6

λ = 320 corresponds to a solute-water ratio of 1:20

Table 4

Equivalent Conductance versus Concentration of $CoCl_2$ at 25°C in the
Presence of a Constant Concentration of $(Et)_4NCl$ $(7.617 \times 10^{-4}$ eq/l)

$c(eq/l) \times 10^3$	$c^{\frac{1}{2}}$	Λ uncorrected for added Cl^-	Λ corrected for added Cl^-
34.43	0.186	18.1	14.7
14.95	0.123	20.4	12.3
9.92	0.099	21.6	9.4
5.82	0.077	26.0	5.2
4.16	0.065	30.4	1.3

Wavelength (mμ)

END