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Solvation of Cobalt(II) and Nickel(II) Ions in Acetone–Water and Ethanol–Water Solutions[1]

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Visible absorption spectra were measured for cobalt(II) perchlorate and nickel(II) perchlorate in the widest accessible range of acetone–water and ethanol–water solutions. The spectra were interpreted as showing the stepwise replacement of two H_2O molecules of the solvation sphere. For the first replacement, in the case of Co(II), the equilibrium quotient is 3.6 for acetone and 2.9 for ethanol. The corresponding values in the case of Ni(II) are 6.2 for acetone and 0.57 for ethanol. For the second replacement, in the case of Co(II), the equilibrium quotient is 1.5×10^{-2} for acetone and 6.0×10^{-3} for ethanol. The corresponding values in the case of Ni(II) are 2.1×10^{-2} for acetone and 4.9×10^{-3} for ethanol. The magnitude of these values, and in particular the small values for the second step, are discussed in relation to previously determined values for other metal ions, especially Cu^{2+}. The low values may arise from both a thermodynamic *trans* effect and a general solvent effect.

In an earlier study it was shown that for copper(II) perchlorate in the mixed solvents acetone–water and ethanol–water, the absorption spectra of the solutions indicated a minimum of association between the copper(II) cations and the anion perchlorate.[2] The spectral changes were interpreted as showing that the primary hydration sphere of the ion was changing in response to the changes of composition of the bulk solvent. A significant feature of the results was the large difference between the equilibrium constants for the exchange of one H_2O molecule for either acetone or ethanol and that for exchange of a second molecule. For acetone the two stepwise equilibrium quotients differed from each other by three orders of magnitude and for ethanol by nearly two orders of magnitude. The over-all results were consistent with polarographic studies by Nelson and Iwamoto under more anhydrous conditions which indicate an orderly decrease in tendency for subsequent dehydration steps.[3]

It is not clear whether the large difference between the first H_2O replacement and that of subsequent ones is a specific property of Cu(II) and might result from its distorted hydration structure. For a system composed of Cr(III) and H_2O–CH_3OH, Jayne and King[4] found a considerably more gradual decrease in affinity for successive steps of substitution by CH_3OH in the truly octahedral hydration shell of $Cr(H_2O)_6{}^{3+}$.

The present study was undertaken using the ions Ni(II) and Co(II) in order to see whether the disparity between the first and second equilibrium constants was unique to Cu(II) and to assess the relative importance of deviation from octahedral symmetry and of ligand field stabilization energy on the solvation equilibria. To avoid complications noted earlier for nitrate solutions,[2] the previously adopted procedure of using perchlorate as the only anion was followed throughout the present work.

Experimental

A Cary Model 14 recording spectrophotometer was used to take complete spectra of $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ dissolved in water, in pure acetone, and in pure ethanol. From these experiments it was decided to examine cobalt complexes at 5150 Å. and nickel complexes at 3800, 4000, and 4200 Å. A Beckman Model DU quartz prism spectrophotometer was used to determine absorption of light of the above wave lengths by the various solutions. In all cases, the tungsten lamp was used and a filter was incorporated for the 3800 Å. measurements. The cells used were matched 10-cm. cylindrical corex. The compartment for 10-cm. cells was kept at 25 ± 1° by use of Beckman thermospacers and added insulation of the cell compartment and cover. Water was pumped through the thermospacers from a bath with the temperature controlled to ±0.1°. The spectra were run *vs.* a solvent blank which was identical with the solution studied except that the salt was omitted. To minimize changes of solution composition due to exposure to the atmosphere, absorption cells were fitted with ground-glass stoppers, and solutions were prepared and stored in flasks of minimum volume. The water content of solutions was determined either by the Karl Fischer method or spectrophotometrically.[5] An automatic micropipet was used to prepare solutions. This instrument has an accuracy of 1% for 0.1-ml. deliveries.

Cobalt nitrate and nickel chloride were Mallinckrodt Chemical Works analytical grade. Cobalt perchlorate and nickel perchlorate were prepared by the action of excess perchloric acid on the respective carbonates. The solutions were heated to 80° for 2 hr., then cooled slowly, and the mixture was poured into a porcelain suction filter and washed with cold water. The salts were then dried in a vacuum desiccator over $Mg(ClO_4)_2$. The acetone used was Mallinckrodt A.R. acetone. The ethanol used was C.P. absolute ethanol.

The data obtained were interpreted in terms of two consecutive solvent-exchange equilibria

$$K_1 = \frac{[M(H_2O)_{x-1}(A)^{2+}][H_2O]}{[M(H_2O)_x{}^{2+}][A]}$$

$$K_2 = \frac{[M(H_2O)_{x-2}(A)_2{}^{2+}][H_2O]}{[M(H_2O)_{x-1}(A)^{2+}][A]}$$

where M indicates either Co or Ni, and A either acetone or ethanol. For a solution containing two absorbing species in equilibrium, the relationship between the apparent extinction coefficient ϵ (*i.e.*, optical density per formal concentration of metal ion) and those of the two individual species, ϵ_0 and ϵ_1, can be expressed as

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[1] The work was presented in part at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1962.

[2] N. J. Friedman and R. A. Plane, *Inorg. Chem.*, **2**, 11 (1963).

[3] I. V. Nelson and R. T. Iwamoto, *ibid.*, **3**, 661 (1964).

[4] J. C. Jayne and E. L. King, *J. Am. Chem. Soc.*, **86**, 3989 (1964).

[5] V. P. Vendt, *Dokl. Akad. Nauk SSSR*, **65**, 689 (1950).

$$\frac{1}{\epsilon - \epsilon_0} = \frac{1}{\epsilon_1 - \epsilon_0} + \frac{[H_2O]}{K_1(\epsilon_1 - \epsilon_0)[A]}$$

where $[H_2O]$ and [A] are the actual concentrations of free solvents. Thus, a plot was made of $1/(\epsilon - \epsilon_0)$ *vs.* $[H_2O]/[A]$ for points of moderate to low concentration of either ethanol or acetone. The resulting curve was a straight line with intercept of $1/(\epsilon_1 - \epsilon_0)$ and slope of $1/K_1(\epsilon_1 - \epsilon_0)$. Because the second equilibrium was ignored, these values represented only first approximations. Data obtained at low H_2O concentration were treated in an analogous way using the expression

$$\frac{1}{\epsilon_2 - \epsilon} = \frac{1}{\epsilon_2 - \epsilon_1} + \frac{K_2[A]}{(\epsilon_2 - \epsilon_1)[H_2O]}$$

thereby obtaining approximate values for K_2. These then were used to correct K_1 values and *vice versa* until consistent values were obtained.

The data were also used to evaluate extinction coefficients and equilibrium constants assuming that there are more than two consecutive solvent-exchange equilibria. As in the earlier study,[2] the best fit of the data was obtained for the two-equilibrium approach, which as noted above is consistent with the polarographic studies at lower H_2O concentration.[3]

Results and Discussion

Although large changes of extinction coefficient were observed, there were but slight peak shifts in the visible region when the solvent for nickel and cobalt perchlorates was changed from water to acetone to ethanol. Table I summarizes the effect.

TABLE I

ABSORPTION MAXIMA OF SOLVATED IONS, mμ

System	Peak	ϵ_{max}
$Ni(ClO_4)$ in water	395	5.05
$Ni(ClO_4)$ in acetone	397	7.85
$Ni(ClO_4)_2$ in ethanol	403	7.10
$Co(ClO_4)_2$ in water	513	4.90
$Co(ClO_4)_2$ in acetone	515	10.51
$Co(ClO_4)_2$ in ethanol	517	8.30

This peak shift is a measure of the ligand field stabilization energy provided by each ligand for a particular metal. Therefore, the shifts to longer wave length indicate that the order of stabilization by ligands is: H_2O > acetone > ethanol. The fact that the size of the shifts is small indicates that the ligand field strengths of these three oxygen bases are similar. Furthermore, the relatively small changes in the spectra indicate that no appreciable changes in symmetry take place during the complexation.

TABLE II

FORMAL EXTINCTION COEFFICIENTS FOR 2.41×10^{-3} *M* $Ni(ClO_4)_2$

Mole % Acetone	ε (3800Å)	ε (4000Å)	ε (4200Å)	Mole % Ethanol	ε (3800Å)	ε (4000Å)	ε (4200Å)
0	3.79	5.02	2.64	5.8	3.84	5.03	2.61
4.7	3.82	5.07	2.68	15.8	3.86	5.13	2.71
8.9	3.83	5.14	2.73	23.6	3.88	5.24	2.81
19.7	3.84	5.26	2.80	33.9	3.95	5.38	2.93
29.0	3.85	5.36	2.83	43.5	3.96	5.55	3.06
38.0	3.86	5.39	2.85	51.9	3.92	5.63	3.27
50.7	3.88	5.44	2.88	60.6	3.92	5.75	3.33
59.3	3.88	5.48	2.92	64.7	3.93	5.80	3.39
70.8	3.89	5.49	2.95	72.5	3.87	5.92	3.49
79.7	3.90	5.62	2.99	82.8	3.74	6.07	3.82
86.0	3.96	5.77	3.06	90.8	3.63	6.27	4.36
91.4	4.17	5.93	3.22	98.3	3.24	6.57	4.88
96.3	4.34	6.48	3.59	99.1	3.06	6.68	5.25
98.3	4.45	6.88	4.07	99.2	3.03	6.79	5.47
99.1	4.50	7.14	4.29	99.5	2.96	6.85	5.70
99.5	4.54	7.39	4.44				
99.9	4.91	7.78	5.14				

Absorption data are tabulated in Table II for Ni(II) and in Table III for Co(II). The equilibrium constants for the stepwise substitution for H_2O molecules of the hydrated ions are given along with the evaluated extinction coefficients in Table IV. For any series of experiments at a fixed wave length, the constancy of *K* values would indicate precisions of the order of ±5%. Furthermore, experimental curves could be duplicated from the calculated *K* values to a precision comparable to that of the previous work.[2] However, as the values of Table IV show there is a random, mean deviation which averages 17%.

TABLE III

FORMAL EXTINCTION COEFFICIENTS FOR 1.53×10^{-3} *M* $Co(ClO_4)_2$

Mole % Acetone	ε (5150Å)	Mole % Acetone	ε (5150Å)	Mole % Ethanol	ε (5150Å)	Mole % Ethanol	ε (5150Å)
0	4.88	70.8	5.99	0	4.88	64.7	6.08
4.7	5.00	79.3	6.03	5.8	4.97	72.5	6.14
8.9	5.05	85.7	6.14	15.8	5.10	82.8	6.27
19.7	5.18	91.4	6.56	23.6	5.29	90.8	6.34
29.0	5.31	96.0	7.06	33.9	5.62	98.6	6.54
38.0	5.51	98.3	8.12	43.9	5.82	99.2	6.99
50.7	5.75	99.1	8.63	51.9	5.95	99.5	7.32
59.3	5.84	99.5	8.82	60.6	6.01	99.9	8.20
		99.9	10.38				

TABLE IV

EXTINCTION COEFFICIENTS AND EQUILIBRIUM CONSTANTS FOR SUCCESSIVE SUBSTITUTION IN HYDRATION SHELLS

System	Wave length, Å.	ϵ_0	ϵ_1	ϵ_2	K_1	K_2
Ni(II)–acetone	3800	3.79	3.85	4.93	7.5	2.2×10^{-2}
Ni(II)–acetone	4000	5.02	5.44	7.81	4.7	2.5×10^{-2}
Ni(II)–acetone	4200	2.62	2.90	5.27	6.5	1.4×10^{-2}
Ni(II)–ethanol	3800	3.79	4.14	2.94	0.54	6.8×10^{-2}
Ni(II)–ethanol	4000	5.02	6.39	6.87	9.55	3.6×10^{-2}
Ni(II)–ethanol	4200	2.62	3.84	5.72	0.62	4.3×10^{-2}
Co(II)–acetone	5150	4.88	5.72	10.51	3.6	1.5×10^{-2}
Co(II)–ethanol	5150	4.88	6.01	8.28	2.9	6.0×10^{-3}

For comparison with the earlier results for Cu(II) in the two-solvent mixtures, the average values of the equilibrium constants from Table IV are listed in Table V along with those of ref. 2. The present values are seen to show just as large a disparity between the values of K_1 and K_2 as do the previous results for Cu(II). Apparently, this disparity does not arise from the nonoctahedral structure of the solvated Cu(II) species. An examination of the K_1 values shows that they do not deviate greatly from the statistical value of 6. This fact also indicates that the three ligands, water, acetone, and ethanol, do indeed provide similar ligand field stabilization energies. However, for each

TABLE V

EQUILIBRIUM CONSTANTS FOR SUCCESSIVE SUBSTITUTION IN HYDRATION SHELLS

System	K_1	K_2
Co^{2+} in acetone	3.6	1.5×10^{-2}
Co^{2+} in ethanol	2.9	6.0×10^{-3}
Ni^{2+} in acetone	6.2	2.1×10^{-2}
Ni^{2+} in ethanol	0.57	4.9×10^{-3}
Cu^{2+} in acetone[2]	3.7	3.1×10^{-3}
Cu^{2+} in ethanol[2]	1.8	3.9×10^{-2}

metal, K_1 in acetone exceeds that in ethanol, in agreement with spectral evidence for slightly greater stabilization by acetone. Also, since, in general, the values of K_1 are less than 6, both ethanol and acetone are seen to provide slightly less ligand field stabilization than does water. This is also in agreement with the spectral shifts.

Statistically K_2 values should be either 2 or $^1/_2$, depending on whether the complex formed is the *cis* isomer or the *trans* isomer. Of the two possible forms, the latter might be expected to be favored because of steric hindrance at the *cis* sites. However, the K_2 values are small even as compared to the *trans* value of $^1/_2$. Two causes for the low values can be imagined. One would be a thermodynamic *trans* effect; that is induced dipoles tending to favor two different ligands at the *trans* positions. A second contributing cause could be a solvent effect. The second substitution occurs in solutions where the solvent is predominantly organic. Therefore, the reaction which requires separation from the charged ion of the H_2O molecule which is more polar than the entering solvent molecule will be inhibited by the low dielectric constant of the predominantly organic solvent. Whatever the detailed explanation, its nature must be such as not to depend markedly on the identity of the metal ion, since the values of K_2 in Table V are remarkably free from trends.

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Cobalt(II) Species in Fused Chloride Solvents[1]

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Absorption spectra in the range 4000–34,000 cm.$^{-1}$ of Co(II) in molten KCl–$AlCl_3$ mixtures have been studied as a function of melt composition. The Co(II) spectra in melts varying from 0 to 42 mole % KCl are interpreted as due to $Co(Al_2Cl_7)_2$ species with Co(II) in octahedral coordination. In the region 42–49.9 mole % KCl, the spectral data and mathematical analysis of the equilibrium indicate the formation of the mixed complex $Co(Al_2Cl_7)(AlCl_4)$ with Co(II) in a severely distorted octahedral environment of chlorides. The spectrum of this species is characterized by a splitting of the ^4P band into three components with an over-all separation of 3400 cm.$^{-1}$. At 300°, the equilibrium constant for the reaction $Co(Al_2Cl_7)_2 + AlCl_4^- = Co(Al_2Cl_7)(AlCl_4) + Al_2Cl_7^-$ is found to be $K = 3.5 \times 10^{-2}$. The solid phase in equilibrium with the mixed complex is $CoCl_2$. The solubility of $CoCl_2$ at 300° decreases to values less than 8×10^{-4} *M* as the KCl:$AlCl_3$ ratio approaches 1. In melts with KCl:$AlCl_3$ ratios larger than 1 as well as in molten alkali chlorides, $MgCl_2$, $CdCl_2$, and $PbCl_2$, the Co(II) spectra are characteristic of the $CoCl_4^{2-}$ species. The degree of distortion of the $CoCl_4^{2-}$ species and the oscillator strength of the ^4P band transitions are correlated with the ionic potential of the melt cations. The Co(II) spectrum in solid and liquid $MgCl_2$ is discussed with reference to the structure of molten $MgCl_2$.

Introduction

The dipositive 3d transition metal ions have been shown to occur as markedly different ionic species in the highly dissociated alkali chloride melts compared with the nondissociated aluminum chloride melt.[2,3] It is therefore of interest to study the equilibria between the various species in mixtures of the alkali chlorides with aluminum chloride.

The different ionic species are in all probability correlated with changes in the thermodynamic activity coefficients of the 3d ions. This expectation is made plausible by a consideration of ion polarizabilities. Thus, in alkali chloride melts, the dipositive 3d ions tend to polarize the chloride ions more strongly than do the solvent alkali cations, while in aluminum chloride melts the reverse situation occurs with the solvent Al(III) ions exerting the stronger polarizing force. On this basis, the activity coefficients of the 3d ions are expected to be smaller in alkali chloride than in aluminum chloride rich melts.

We have chosen to study the equilibria between Co(II) species in the KCl–$AlCl_3$ binary system in order to gain further insight into the forces governing the behavior and stability of such species as a function of the ionic nature of the melt. Clearly, such information is important to a basic understanding of the thermodynamics of a large class of metal ions in molten salt systems.

In the LiCl–KCl eutectic melt the absorption spectrum of Co(II) is that of the tetrahedral $CoCl_4^{2-}$ species.[2] The occurrence of the $CoCl_4^{2-}$ rather than the $CoCl_6^{4-}$ species in this highly ionic melt can be rationalized in terms of large (~30 kcal.) electrostatic repulsion energies favoring the four- over the six-coordinated form.[2] In the covalent $AlCl_3$ melt, however,

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] D. M. Gruen and R. L. McBeth, *Pure Appl. Chem.*, **6**, 23 (1963).

[3] H. A. Øye and D. M. Gruen, *Inorg. Chem.*, **3**, 836 (1964).