Conductometric Study of $NiCl_2$ and $CoCl_2$ in Water, Ethylene glycol-water and Glycerol-water Mixtures at various Temperatures

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Measurements of electrical conductance of $NiCl_2$ and $CoCl_2$ in aqueous and in mixtures containing 10%, 20% and 30% of ethylene glycol or glycerol in the temperature range 25°-40°C are presented. The constants K_{A1} for the ion pair (M^{2+}-Cl) formation have been calculated. The thermodynamic functions ΔH°_{A1}, ΔG°_{A1} and ΔS°_{A1} for the formation of that ion-pair have also been obtained.

Transport properties like electrical conductance of 2:1 type electrolytes have been treated largely as functions of the dielectric constant. Many investigations of electrical conductance in mixed solvents [1-4] showed that the conductance of electrolytes decreased with solvent viscosity and the degree of solvation increased; conductance also increased with the dielectric constant of the medium and temperature. The last is used in obtaining thermodynamic functions for the ion association phenomena.

In the association process, according to Eigen [5], the ions approach through a diffusion-controlled path, followed by de-solvation of the ions. The purpose of the present investigation is to determine the thermodynamic association constant, K_{A1} and to study the effect of composition, viscosity & dielectric constant of the solvents, the temperature and also the effect of cation size on the association of chlorides of 2:1 type.

EXPERIMENTAL

Cobalt(II) chloride hexahydrate (Merck), nickel(II) chloride hexahydrate (M&B) laboratory reagents were dissolved in deionized bidistilled water of conductance < 2×10^{-6} ohm^{-1} cm^{-1} (at room temperature).

Ethylene glycol and glycerol (both analytical reagents) are purified by heating carefully in a porcelain dish with stirring until the temperature reached 180°C, then cooled to nearly 100°C poured into a beaker and preserved in a desiccator (Glycerol is a very hygroscopic substance). Required solvent mixtures by weight percentages are prepared using these solvents and deionized distilled water. Mixing and dilution are done just before conducting the measurements.

The densities [6], viscosities [7] and the dielectric constants [8] of the various mixtures are summarized in Table 1

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Table 1

Density, Viscosity and Dielectric Constants - Different Solvent Mixtures & Temperatures

Solvent Mixture	% solvent w/w	Density (gm.cm^{-3}) 25°	30°	35°	40°	Viscosity (poise) 25°	30°	35°	40°	Dielectric Constant 25°	30°	35°	40°
Water	-	0.99707	0.99567	0.99406	0.99224	0.8937	0.8007	0.7225	0.656	78.55	76.73	74.91	73.120
Glycol/water	10	1.0108	0.99778	0.98490	0.97215	1.0063	0.870	0.754	1.591	75.60	73.88	72.03	70.29
	20	1.0241	1.0091	0.9786	0.9494	1.0494	1.300	1.185	1.020	72.80	71.04	69.34	67.52
	30	1.0377	1.0434	1.0111	0.9802	1.9925	1.701	1.497	1.292	69.80	68.08	66.31	64.51
Glycerol/water	10	1.0070	1.0405	1.0763	1.0118	1.1153	1.024	0.911	0.794	75.70	73.88	72.19	70.41
	20	1.0525	1.0350	1.0194	1.0534	1.542	1.360	1.192	1.025	72.90	71.12	69.42	67.70
	30	1.0070	1.0855	1.0709	1.0032	2.157	1.876	1.637	1.385	70.00	68.23	66.53	64.87

A closed conductivity cell model LTA 100 (cell constant = 1.00 cm) is thermostated at specified temperature to an accuracy of ± 0.1°C by a thermoelectric circulating system. The conductance measurments are carried out using LBR Model. conductivity meter at a frequency of 50 c/s and 3 Kc/s ±3%. The metal ion concentrations are in the range 6×10^{-4} to 4×10^{-3}M.

Data treatment

In this investigation. the following ionic equilibria may be considered:

$$M^{2+} + Cl^- \underset{}{\overset{(K_{A1})}{\rightleftharpoons}} MCl^+ \qquad \ldots (1)$$

$$MCl^+ + Cl^- \underset{}{\overset{(K_{A2})}{\rightleftharpoons}} MCl_2 \qquad \ldots (2)$$

The true thermodynamic contants (K_{A1} for step 1 and K_{A2} for step 2) are given by

$$K_{A1} = \frac{\text{(Activity of } MCl^+\text{)}}{\text{(Activity of } M^{2+}\text{.)} \quad \text{(Activity of } Cl^-\text{)}}$$

$$K_{A2} = \frac{\text{(Activity of } MCl_2\text{)}}{\text{[Activity of } MCl^+\text{.]} \quad \text{[Activity of } Cl^-\text{]}}$$

Fuoss and Edelson [9] established a theory on the assumption that $K_{A1} >> K_{A2}$ and valid for cases where the first step is the most dominent one. They proposed the following equation:

$$\Lambda F = \Lambda_o - \frac{X K_{A1}}{\Lambda_o} \qquad \ldots (3)$$

where $X = c\gamma_{2,}\Lambda F(\Lambda F - \Lambda_o/2)$ and

$$F = (1-\delta c^{1/2})^{-1} + \frac{(\Lambda_o - \lambda_o)/2\Lambda}{1 + (\Lambda_o - \lambda_o)/2\Lambda}$$

Where Λ and Λ_o are the equivalent and the limiting equivalent conductances

respectively, λ_o is the limiting equivalent conductance of Cl. δ is Onsager's slope divided by Λ_o and c is the molar concentration of Cl^-. The ion activity coefficient γ^{2+} of M^{2+}, was evaluated by the Debye-Huckel second approximation (equation 4).

$$\log \gamma = \frac{-A |Z_i|^2 I^{1/2}}{1 + Ba I^{1/2}} \quad .... (4)$$

For the ionic size parameter (a) of M^{2+}, we have assumed the value of 6A° for the Ni^{2+} and Co^{2+} metal ions which are often assigned for them in aqueous medium [10].

The value of λ_o is 76.36 $cm^2.mol^{-1}$ in water medium at 25.0°C [11]. On the basis of this value, we have calculated the λ_o's in glycol-water and glycerol-water mixtures at various temperatures upto 40°C. The value of Λ_o at a given temperature is calculated with an arbitrary estimate of λ_o. Equation 3 is solved for the two unknown parameters K_{A1} and Λ_o by an iterative procedure. The Λ_o's of $CoCl_2$ and $NiCl_2$ are estimated at the temperature in all solvent mixtures under investigation. The above procedure is then iterated until λ_o becomes a constant value where, the second estimate of λ_o is calculated by multiplying the ratio of the

Table 2

Limiting Equivalent Conductance (ohm $^{-1}$.cm^2.mol^{-1}) of $CoCl_2$, $NiCl_2$ and Cl in Different media and Temperatures

Solvent Mixture	% solvent w/w	Λ_o of $CoCl_2$				Λ_o of $NiCl_2$				λ_o of Cl			
		25°	30°	35°	40°	25°	30°	35°	40°	25°	30°	35°	40°
Water	-	130.300	143.843	157.389	171.673	129.200	142.000	156.101	170.254	76.369	84.275	92.200	100.550
Glycol/water	10	109.342	121.000	132.045	144.000	97.740	107.876	118.026	128.728	57.562	63.533	69.508	75.814
	20	98.064	108.245	118.404	129.140	77.233	85.250	93.273	101.739	45.524	50.250	54.979	59.458
	30	85.400	94.308	103.170	112.525	63.700	70.300	77.000	83.900	37.587	41.490	45.385	49.498
Glycerol/water	10	101.312	111.832	122.364	133.443	85.510	94.402	103.300	112.639	50.670	55.88	61.139	66.681
	20	83.039	91.691	100.325	109.440	67.240	74.237	81.237	88.604	40.046	44.203	48.363	52.73
	30	71.483	78.908	86.339	94.174	58.700	64.000	71.000	77.000	34.900	38.586	42.315	46.04

Table 3

Ionic Association Constants K_{A1} of $CoCl_2$ & $NiCl_2$ in different Media and Temperatures.

Solvent Mixture 25°	% solvent w/w	$CoCl_2$				$NiCl_2$			
		25°	30°	35°	40°	25°	30°	35°	40°
Water	-	5.993	6.089	6.295	6.371	5.513	5.608	5.804	5.880
Glycol/water	10	11.041	11.170	11.221	11.4820	10.157	10.287	10.345	0.598
	20	14.404	14.455	14.800	14.918	13.251	13.313	13.645	3.769
	30	18.788	18.861	19.292	19.419	17.218	17.370	17.787	7.923
Glycerol/water	10	16.210	16.314	16.492	16.556	14.913	15.025	15.205	5.281
	20	20.033	20.309	20.370	20.654	18.430	18.704	18.781	9.063
	30	24.947	25.235	25.410	25.704	22.951	23.341	13.428	3.724

mean value of their Λ_o's at the required temperature to that at 25°C by 76.36. Since the determined K_{AI}'s include relatively large error and λ_o does not control the values of K_{AI} and Λ_o strongly, it is not important to evaluate the λ_o very accurately.

RESULTS

K_{AI} and Λ_o values for $CoCl_2$ and $NiCl_2$ in water, glycol-water and glycerol-water mixtures at different proportions in the various temperatures in the range 25°-40°C are summarized in Table 2 and 3. The values of λ_o are also given in Table 2.

The standard free energy changes ($\Delta G°_{AI}$) of the reaction (1) have been calculated using the relation $\Delta G°_{AI} = -RT(\ln K_{AI})$. The standard enthalpy changes ($\Delta H°$)are determined using the equation $d(\ln k)/d(T^{-1}) = -\Delta H°/R$ by fitting the data to log K_{AI} vs T^{-1} by the least-square method. In addition, the standard entropy change, $\Delta S°_{AI}$, is evaluated from the equation: $\Delta S°_{AI} = (\Delta H°_{AI} - \Delta G°_{AI})/T$, where T is the absolute temperature. These thermodynamic parameters are summarized in Table 4.

Table 4

Thermodynamic Functions for Ion pairs of $CoCl_2$ and $NiCl_2$ in Different media and Temperatures

Solvent	% solvent	$-\Delta H°_{AI}$ (kJ.mol^{-1})				$\Delta G°_{AI}$ (J.mol^{-1}.)				$\Delta S°_{AI}$ (J.mol^{-1}.K^{-1})
Mixture	w/w	25°	30°	35°	40°	25°	30°	35°	40°	25°
Thermodynamic Functions of $CoCl_2$										
Water	-	4.434	4.548	4.708	4.816	19.788	19.839	20.037	20.061	462.98
Glycol/water	10	5.947	6.075	6.188	6.356	22.606	22.635	22.652	22.803	789.60
	20	6.605	6.725	6.896	7.029	24.811	24.820	24.970	24.995	894.96
	30	7.253	7.395	7.575	7.715	27.120	27.142	27.251	27.263	818.56
Glycerol/water	10	6.898	7.030	7.173	7.300	24.825	24.851	24.915	24.921	500.27
	20	7.422	7.581	7.714	7.875	27.045	27.112	27.112	27.196	637.22
	30	7.965	8.128	8.280	8.444	28.914	28.973	28.995	29.057	650.90
Thermodynamic Functions of $NiCl_2$										
Water	-	4.227	4.341	4.501	4.608	19.333	19.390	19.593	19.622	1534.07
Glycol/water	10	5.740	5.869	5.980	6.140	22.264	22.318	22.318	22.473	894.26
	20	6.399	6.518	6.688	6.821	24.602	24.610	24.764	24.791	939.03
	30	7.047	7.188	7.367	7.506	26.902	26.922	27.067	27.080	969.74
Glycerol/water	10	6.691	6.820	6.965	7.091	24.378	24.400	24.476	24.488	573.32
	20	7.216	7.374	7.506	7.667	26.597	26.652	26.676	26.763	710.28
	30	7.759	7.921	8.072	8.236	28.589	28.651	28.677	28.742	760.73

DISCUSSION

Inspection of the data in Table 2, shows that Λ_o values of $CoCl_2$ are relatively higher than those of $NiCl_2$. The Λ_o for a given salt decreases as the proportion of either glycol or glycerol in the medium increases; This decrease is more in glycerol than in glycol mixture. This is probably due to the intramolecular hydrogen bonding [12]. (Hydrogen bonding is expected to be greater in glycerol-water as compared to glycol-water mixtures of similar dielctric constant.) This hydrogen bonding retards the mobility of the ions and consequently, results in a decrease of the conductance. Viscosity also could be contributing to it. It has also been found that Λ_o values increase with the temperature. The viscosity of these mixed solvents are smaller at higher temperatures; the conductance increases with increasing temperature - but with a slower rate at higher temperatures [13].

In the present investigation, the values of Walden product ($\Lambda_o\eta$) decrease with an increase in temperature. This observation is common to both $CoCl_2$ & $NiCl_2$ salt. This decrease is often found in the data for aqueous solutions and are also found to agree with some literature data [14]. It is explained partially as a thermal expansion of the solvent sheath. In other words, the solvated ion expands due to the activation of solvent molecules forming the sheath.

The K_{A1} values (Table 3) are quite characteristic. There appears to be a close relationship between the K_{A1} values and the strength of solvation of Co^{2+} and Ni^{2+}. Stronger is the solvation of M^{2+}, lower is the association between M^{2+} and Cl^{-1}. Comparing the K_{A1} of the two salts, the values of $CoCl_2$ are greater than those of $NiCl_2$ (Table 3). Comparing the values in different media, thermodynamic association constants K_{A1} of $CoCl_2$ and $NiCl_2$ were found to proceed in the following order: glycerol-water > glycol-water > water. Regarding the solvation effect, glycerol-water mixture is expected to show more intramolecular hydrogen bonding than glycol-water mixture which in turn is expected to show more intramolecular hydrogen bonding than water.

The results of thermodynamic functions in Table 4, can throw more light on ionic associations. Basically, the ion-pair is formed by the action of the coulombic forces in a continuum medium; so both the values of ΔH° and ΔS° of the ion-pair formation is expected to be negative. But all the experimental values of ΔH°_{A1} and ΔS°_{A1} in Table 4 are postive. It has been found that, the solvation of ions is weakened when the ion-pair is formed. The positive nature of ΔS°_{A1} and ΔH° indicates that the association phenomena is not only coulombic but is very much affected by the solvation-de-solvation of the free ions as well as the ion-pairs.

As shown in Table 3, the variation of K_{A1} with temperature is within 10% only, which is relatively small to ensure a good trend in the evaluated thermodynamic parameters. Thus, the variation of ΔS° with temperaure can be considered practically invariant, although one might expect to see reverse relationship between ΔS° and temperature.

The association constants are related to the basic parameters through the Bjerrum equation [15,16]:

Table 5

Values of solvation free energies $-\Delta G^{\circ}_{s}$ (kJ.mol^{-1}) for $CoCl_2$ and $NiCl_2$ in different solvents at 25°C - 40°C.

Solvent Mixture	% solvent w/w	$CoCl_2$ 25°	30°	35°	40°	$NiCl_2$ 25°	30°	35°	40°
Glycol/water	10	1746.36	1745.80	1745.20	1744.60	1780.40	1779.87	1779.25	1778.60
	20	1745.48	1744.88	1744.27	1743.58	1779.50	1778.90	1778.27	1779.57
	30	1744.40	1743.80	1743.10	1742.36	1778.45	1777.79	1777.08	1776.30
Glycerol/water	10	1746.40	1745.80	1745.30	1744.70	1780.46	1779.87	1779.30	1778.67
	20	1745.50	1744.90	1744.30	1743.70	1779.50	1778.90	1778.30	1777.60
	30	1744.50	1743.80	1743.20	1742.50	1778.50	1777.85	1777.17	1776.48

$$K_A = \frac{4\pi Na^3}{3000} \exp \frac{Z_i Z_j e_o^2}{a \varepsilon kT} \quad \ldots (5)$$

where N is the Avogadro number, a is the collision distance, Z_i and Z_j are the valencies of the two ions, e_o is the electronic charge, ε is the dielectric constant, k is the Boltzmann constant and T is the absolute temperature. Examination of this equation shows that it is composed of two factors - i) the pre-exponential term $k_o = 4\pi Na^3/3000$ and ii) the exponential term exp (b) where b the Bjerrum ratio $= (Z_i Z_j e_o^2)/(a\varepsilon kT)$. It should be noted that k_o and the exp (b) are mathematically in competition in terms of the parameter a; k_o increases with increasing a but exp(b) decreases.

The plots of log K_{A1} vs $1/\varepsilon$ for $CoCl_2$ and $NiCl_2$ over a limited range of solvent compositions at various temperatures from 25°-40°C shows a good linerity (as the theory predicted) and the value of a can be calculated from the slope according to equation (5).

Solvation free energies ΔG°_{s} of Co^{++} and Ni^{++} for all solvents were calculated theoretically using the equation of Born [17], which has been modified by Latimer [18]; the values of ΔG°_{s} are computed and included in Table 5.

The Co^{++} and Ni^{++} solvation free energies steadily increase for all sovlents in the order: 10% < 20% < 30% (w/w) for each solvent and for all temperature. ΔG°_{s} increase with increasing temperature.

There is a good linear relationship between ΔG° (= -RT lnK_A) and ΔG°_{s}. Hence, it seems that the solvation energy of ions is a very important factor in controlling ionic association; when the solvation of ions is weak, the association is greater.

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