Conductance of Some Bivalent Metal Complexes of Ethylenediamine nitrate and perchlorate in Water-Methanol Media

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Equivalent conductance of tris(ethylenediamine)-cobalt(II), tris(ethylenediamine)-nickel(II) and bis(ethylenediamine)-copper(II) nitrate and perchlorate complex solutions in water, methanol and in their mixtures are measured at 25°C. The limiting equivalent conductance Λ_o and the first association constant K_{A1} were calculated using Fuoss-Edelson's method. The influence of the size of cation as well as the nature of the solvent medium are discussed. The Walden product ($\Lambda_o\eta_o$) for the salts in different solvent compositions shows a maximum value in water rich region; the height of the maximum is in the order $[Co(en)_3](NO_3)_2 > [Ni(en)_3](NO_3)_2 > [Cu(en)_2](NO_3)_2$ and $[Ni(en)_3](ClO_4)_2 > [Cu(en)_2](ClO_4)_2$. Finally, the limiting anionic conductances ($\lambda_o^{Nitrate}$ and $\lambda_o^{Perchlorate}$) are calculated in all proportions of the mixture.

Complexes of ethylenediamine with cobalt(II), nickel(II) and copper(II) salts as halides, nitrates and perchlorates were first prepared by Werner [1]. Pauling [2] enumerated a series of nickel complexes of the form $[Ni(en)_3]^{2+}$ with octahedral geometry. Sone and Kato [3] reported the square planar complexes of ethylenediamine with copper(II).

The solvent effect on ethylenediamine metal halide complexes was previously discussed using conductance data in water [4a], water-dioxane [4a], methanol [4b] and water-methanol mixtures [5]. This study is extended to the conductance behaviour of the corresponding nitrate and perchlorate complexes in the amphiprotic solvents - water and methanol and their mixtures - at 25°C. $[Co(en)_3](ClO_4)_2$ has been omited in these studies because of its explosive behaviour on drying.

Methanol was chosen for mixing with water on the following considerations:

(i) The methanol-water represents a good example of a strongly hydrogen-bonded system.

(ii) Methanol is completely miscible in all proportions with water; therefore, a wide range of dielectric constant values can be obtained.

(iii) The data for the limiting cationic conductance of these complex cations λ^+_o's at 25°C are available [5] for different aqueous methanol mixtures. So anionic equivalent conductance $\lambda_o^{Nitrate}$ and $\lambda_o^{Perchlorate}$ can be determined.

EXPERIMENTAL

Tris(ethylenediamine)-nickel(II) and bis(ethylenediamine)-copper(II) nitrates and perchlorates were prepared using Werner's

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method [1] - by treating the appropriate metal(II) nitrate or perchlorate (Prolabo grade) in the least amount of water and an equimolar quantity of ethylenediamine (BDH grade) followed by precipitating the complex with ethanol. Tris(ethylenediamine)-cobalt(II) nitrate was prepared using Tanaka and Harada's method [6] for the preparation of tris(ethylenediamine) cobalt(II) complexes - by treating an aqueous saturated solution of tris(ethylenediamine)-Co(II) chloride with an equimolar amount of nitric acid. Nitric acid treatment was repeated twice to ensure complete substitution. The complex was separated by adding methanol.

All complexes, except $[Co(en)_3](NO_3)_2$ were recrystallized three times from analytically pure methanol. $[Co(en)_3](NO_3)_2$ was recrystallized from methanol and conductivity water. Perchlorate complexes were dried at 40° and nitrate complexes at 80°C both in vacuum using Abderhalden apparatus [8]. The solvents (conductivity water and methanol BDH grade) were purified as described earlier [4a,8].

The values of 0.99704 ($g.ml^{-1}$) and 0.8903 cP [10] had been taken for density (d) and viscosity (η) respectively for water. Those of pure methanol were freshly measured as described before [8]. The measured values were found to be 0.78657 ± 10^{-5} ($g.ml^{-1}$) and 0.5439 ± 10^{-4} cP respectively - agreeing with the data obtained previously [8]. Therefore, the previously published δ and λ data for aqueous methanol mixtures [8] were used and the value in solvent mixture of the desired proportion was obtained by interpolation.

Dielectric constant (ε) were taken by interpolation using Bates and Robinson's data [11].

An ac Beckman conductivity bridge Model RC No. 18A was used to measure the resistance (R) of the solutions at 3 kHz. The accuracy of measurement was ± 0.1 ohm for R<1000 and ± 0.3 ohm for R>1000. The temperature was adjusted at 25 ± 0.02°C using an ultrathermostat model MLW type U 10. An Erlenmeyer conductance cell with bright platinum electrodes (cell constant 0.03565 cm^{-1} ± 0.45 at 25°C) was used for dilution and measurement. The conductance measurements were described earlier [4,5]. The specific conductances κ_o of the used conductivity water and methanol are $(2\text{-}5) \times 10^{-7}$ and $(1\text{-}3) \times 10^{-7}$ S cm^{-1} respectively.

RESULTS AND DISCUSSION

Equivalent conductance of the salts at infinite dilution (Λ_o)

Experimentally determined equivalent conductance (Λ in $S.cm^2.eq^{-1}$) at different concentrations ($eq.dm^{-3}$) for the five unsymmetrical (2:1) complexes $[Co(en)_3](NO_3)_2$, $[Ni(en)_3](NO_3)_2$, $[Ni(en)_3](ClO_4)_2$, $[Cu(en)_2](NO_3)_2$ and $[Cu(en)_2](ClO_4)_2$ in both pure and mixed solvents are listed in Table 1.

A preliminary value for Λ_o for each solution was obtained by free hand extrapolation of Λ *vs* $C^{1/2}$ plot to zero concentration. In order to obtain a more accurate Λ_o value simultaneously with the corresponding first dissociation constant K_{D1}, Fuoss - Edelson (F-E) method [9] was applied for the above unsymmetrical (2:1) electrolytes using:

$$\Lambda' = \Lambda_o - \frac{X}{K_{D1}\,\Lambda_o} \qquad \ldots\ (1)$$

Table 1

Conductance dependence on concentration at 25°C

Concentration (C) in eq.dm $^{-3}$; Measured Conductance Λ in S.cm^2.eq^{-1}

$[CO(en)_3](NO_3)_2$

purewater		19.87%MeOH		40.15%MeOH		56.93%MeOH		75.89% MeOH	
C	Λ	C	Λ	C	Λ	C	Λ	C	Λ
12.225	166.94	20.033	106.78	20.032	86.781	21.038	78.064	14.413	78.235
9.1156	169.56	16.420	108.89	16.452	88.634	17.124	83.525	11.880	81.019
6.9371	171.71	12.313	111.00	12.824	90.596	12.856	86.257	9.0758	82.825
5.4708	173.35	9.0115	112.87	9.7270	92.607	9.5156	88.442	6.8334	88.430
4.3162	174.82	6.7527	114.58	7.5831	94.119	7.3135	90.223	5.1632	91.149
3.3641	176.00	5.2322	115.80	5.9698	95.581	5.7862	91.742	4.0099	95.100
		4.1168	116.83	4.7787	96.752	4.6840	92.915	3.3631	97.369
		3.2808	117.57	3.9460	97.651				

$[Ni(en)_3](NO_3)_2$

purewater		15.63%MeOH		29.35%MeOH		48.29%MeOH		71.25% MeOH	
C	Λ	C	Λ	C	Λ	C	Λ	C	Λ
25.343	104.40	18.543	85.073	17.467	74.323	11.732	69.906	16.343	71.829
20.727	106.54	15.761	87.120	14.207	75.780	8.5577	71.971	13.894	73.830
15.352	109.80	12.158	89.957	10.686	78.223	6.4954	74.089	10.199	77.353
11.287	113.41	9.0361	92.519	7.8993	80.688	5.1228	75.482	7.6309	79.584
8.3655	117.14	6.6821	95.240	6.0340	83.079	4.1398	76.740	5.8018	82.252
6.4020	120.35	4.9639	97.875	4.7129	84.755	3.3241	78.259	4.6686	83.794
		3.8494	99.444	3.8264	86.400			3.8317	85.766

$[Ni(en)_3](ClO_4)_2$

purewater		21.86%MeOH		40.06%MeOH		61.18%MeOH		82.03% MeOH		Pure MeOH	
40.964	100.19	21.450	80.527	20.805	71.521	21.954	73.842	19.059	79.763	17.720	86.450
25.052	105.54	16.976	83.276	16.259	74.562	17.157	75.964	15.889	82.170	14.908	90.213
20.142	108.70	12.865	84.827	13.110	76.514	13.834	79.512	12.526	85.335	11.297	95.778
15.046	112.38	9.3262	88.503	9.9649	77.898	10.515	82.112	9.5190	88.406	8.4890	101.17
11.016	116.64	7.0203	91.382	7.4084	80.486	7.8176	84.468	7.1990	91.860	6.1381	107.54
				5.6753	82.477	5.9887	86.916	5.4656	94.861	4.7296	112.47
				4.3415	84.854	4.5844	89.008	4.3495	97.004	3.5327	117.49

$[Cu(en)_2](NO_3)_2$

purewater		19.93%MeOH		39.86%MeOH		53.09%MeOH		63.14% MeOH		78.87% MeOH	
23.389	116.08	20.867	84.612	21.082	64.634	19.200	67.418	21.906	68.515	21.912	71.687
19.103	117.48	17.317	85.425	15.986	65.957	9.1705	70.702	17.864	69.710	17.316	73.718
14.814	118.98	12.690	86.501	9.007	67.825	7.0095	71.487	13.043	71.533	13.317	75.942
11.600	120.22	9.0927	87.654	5.2426	69.004	5.3678	72.305	9.3950	72.971	9.8099	78.185
8.7742	121.54	6.8520	88.625	3.2246	69.984	3.1877	73.447	6.9486	74.223	7.4417	79.882
6.8644	122.75	4.3019	89.693					5.3407	75.038	5.9408	81.292
		3.5484	90.057					3.3960	76.336	4.8509	82.372
										3.7337	83.526

$[Cu(en)_2](ClO_4)_2$

purewater		19.21%MeOH		39.03%MeOH		58.08%MeOH		79.61% MeOH		Pure MeOH	
24.392	111.71	22.128	85.136	21.271	72.658	15.577	71.862	18.910	77.985	13.370	81.227
22.258	112.85	18.442	86.184	17.879	73.399	13.090	72.672	15.872	79.996	11.737	83.170
18.992	113.76	14.120	87.273	13.684	74.344	9.8258	73.853	12.109	82.253	9.6707	87.573
15.925	114.73	10.413	88.310	10.268	75.328	7.1594	75.103	8.8892	84.949	7.9055	91.357
13.102	115.88	7.8158	89.593	7.6477	76.182	5.2455	75.997	6.6182	86.863	6.3963	95.469
10.890	117.27	6.0459	90.489	5.8329	77.053	3.2442	76.814	5.0111	88.623	5.1605	99.624
		4.6389	91.563	4.5652	77.913	3.0206	77.478	3.8488	89.976	4.0372	104.06

* $[Co(en)_3](NO_3)_2$ is insoluble in pure methanol and hence date not available
* $[Ni(en)_3(NO_3)_2$ and $[Cu(en)_3](NO_3)_2$ data in pure methanol were published previously.

where $\Lambda' = \Lambda_{expt.}F$: (F a function of C and Λ_o) is used to correct the conductance ratio Λ / Λ_o for the effect of interionic forces on the mobility:

$$X = C'\Lambda'(\Lambda' - 1/2\Lambda_o)$$

with $C' = Cf_\beta$ where f_β is the cationic activity coefficient - calculated from Debye-Huckel law in the form

$$-\log f_\beta = \frac{250.3\ Z^2_\beta\ 3^{1/2}\ C}{\varepsilon^{3/2}} \quad \ldots\ (2)$$

Figures (1 and 2) are typical plots for Λ' - X of nitrate and perchlorate complexes under investigation in different aqueous-methanol media at 25°C.

Table 2 reports the conductance parameters Λ_o and K_{A1} $(=1/K_{D1})$ derived from (F-E) equation. Density (d) and the viscosity (η) of pure methanol and water were used and the values in required solvent mixture were determined by interpolation. The interpolated values and ε (dielectric

constant) values [11] are also included in the Table 2. The accuracy required in these computations are ±0.02 for Λ_o and ±0.05 for K_{A1}

Inspection of Table 2 indicates that Λ_o in pure water for complexes with common cation, $\Lambda_o^{\text{Perchlorate salts}} < \Lambda_o^{\text{Nitrate salts}}$ while the reverse behaviour is obtained in methanol. If one takes the halide complexes of the cations under investigation [4a]. The order of Λ^o in water is: perchlorate < nitrate < chloride < iodide < bromide. Though this order does not go exactly parallel to solvation in protic solvents, it agrees with the data obtained for hexamine Co(III) complexes in water at 25°C [12]. However, the order in methanol (chloride < bromide < nitrate < iodide < perchlorate) is quite in agreement with anionic solvation in protic solvents [13].

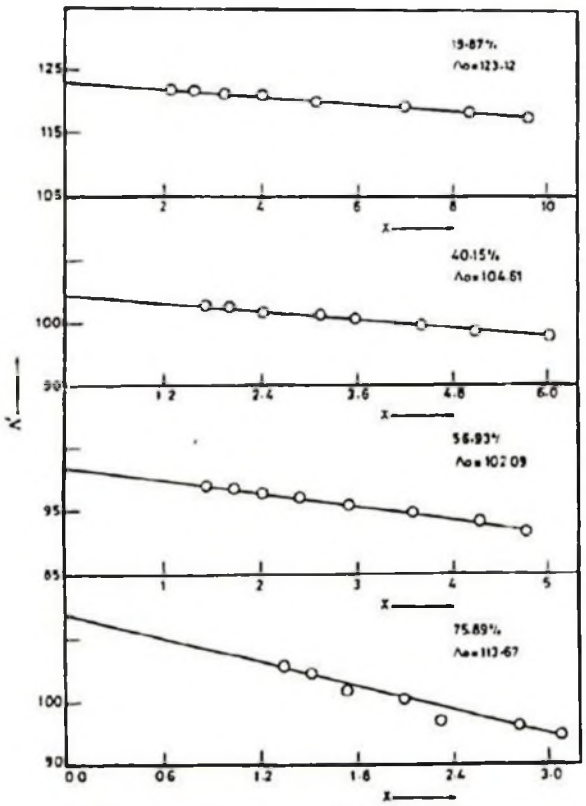


FIG 1 FUOSS AND EDELSON PLOTS FOR $[Co(en)_3](NO_3)_2$ IN METHANOL-WATER MIXTURES AT 25°C

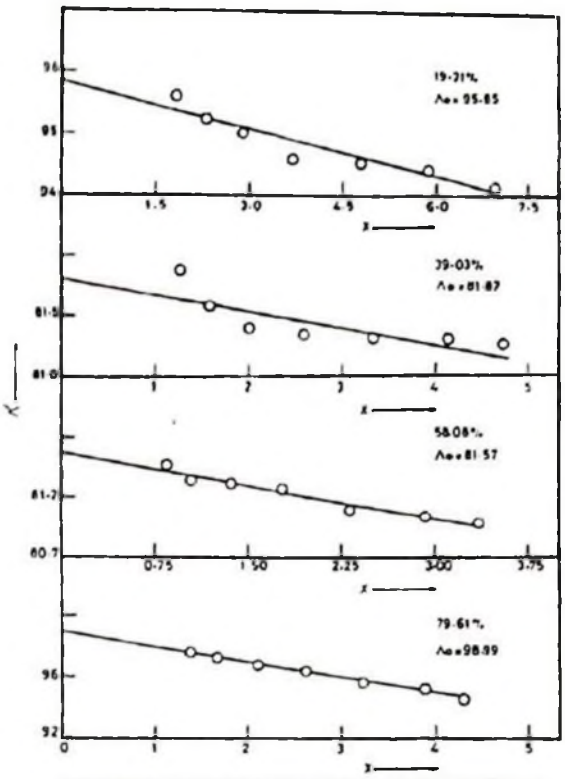


FIG 2 -FUOSS AND EDELSON PLOTS FOR $[Co(en)_3](ClO_4)_2$ IN METHANOL-WATER MIXTURES AT 25°C.

Solvent Effect

For a given complex in different aqueous methanol mixtures, Λ_o values show a minimum in the range around the maximum viscosity of the mixture [8,14]. The results can be explained assuming that at this range, the structure of the solvent around the ion changes remarkably on adding methanol to water.

On comparing Λ_o values for the five complexes under investigation in both water and methanol, it can be seen that their cations behave as solvophobic structure makers.

Generally, K_{A1} for complexes in MeOH have greater values than in water [4a] at same

Table 2

Pure and mixed solvents properties and conductance parameters for the complexes at 25°C

MeOH Wt %	d g.ml^{-1}	η centipoise	ε [12]	Λ_o S.cm^2.eq^{-1}	K_{Ass} l.mol^{-1}
$[CO(en)_3](NO_3)_2$					
0.00	0.9970	0.8903	78.30	184.61	73.747
19.87	0.94750	1.3970	69.80	123.12	70.522
40.15	0.90250	1.590	60.80	104.61	117.27
56.93	0.86725	1.429	53.00	102.09	219.02
75.89	0.82975	1.069	44.2	113.67	719.44
$[Ni(en)_3](NO_3)_2$					
0.000	0.99704	0.8903	78.30	132.42	164.35
15.36	0.95750	1.280	71.80	108.79	250.27
29.35	0.92650	1.546	65.60	94.45	259.44
48.29	0.88550	1.544	57.0	85.69	258.15
71.25	0.83900	1.159	46.45	96.82	339.94
100.0	0.78657	0.5445	32.70	140.35	522.39
$[Ni(en)_2](ClO_4)_2$					
0.00	0.99704	0.8903	78.30	129.83	106.73
21.86	0.7430	1.442	68.90	102.19	201.84
40.06	0.9030	1.592	60.85	92.48	225.93
61.18	0.85900	1.348	51.1	100.51	290.00
82.03	0.8185	0.9450	41.30	112.36	362.36
100.0	0.78657	0.5445	32.7	148.86	1113.7
$[Cu(en)_2](NO_3)_2$					
0.00	0.99704	0.8903	78.30	129.54	15.896
19.93	0.94750	1.397	69.75	93.68	9.7362
39.86	0.90300	1.592	60.95	73.36	10.519
53.00	0.87525	1.494	54.85	77.51	18.492
63.14	0.8550	1.310	50.15	82.13	20.014
78.87	0.8240	1.114	42.80	91.29	94.987
100.0	0.78657	0.5445	32.70	126.63	763.721
$[Cu(en)_2](ClO_4)_2$					
0.00	0.99704	0.8903	78.30	126.02	23.016
19.21	0.9490	1.380	70.05	95.85	24.753
39.03	0.90350	1.590	61.30	81.82	11.219
58.08	0.8650	1.407	52.50	81.57	15.151
79.61	0.82275	0.9980	42.45	98.99	100.39
100.0	0.78657	0.5445	32.70	138.79	885.2

* d and η values are by interpolation from the data in ref. [8]

conditions: the ion-pairs formed are more associated in methanol than in water, which agree with the dielectric constant expectations.

Bjerrum relationship [15] relates K_A with dielectric constant of the medium assuming the solvent as a structureless continuem (eq. 3)

$$\ln K_A = \ln \left[\frac{4\pi N_A a_o^3}{3000}\right] + \left[\frac{(Z_1Z_2)e^2}{a_o \varepsilon KT}\right] \quad .. (3)$$

where k, N_A and a_o are the Boltzmann's constant, Avogadro's number and the closest distance of approach of the two opposite ions with Z_1 and Z_2 are charges of the two ions. This indicates a linear relationship between log K_A *vs* $1/\varepsilon$. Fig. 3 shows that this is not obeyed. The curvature confirms the importance of the $U = \Delta S/k - E_s/kT$ term [16] which indicates a difference in the structure of the solvent around the ion in different media. The term $(-E_s/kT)$ accounts for the energy of ion-dipole interaction and $(\Delta S/k)$ measures entropy change responsible for the rearrangement of solvent molecules around free ions and around pairs. Addition of methanol to water causes variation in both terms.

A glance at Table 2 indicates that K_{A1} values in water for complexes with common cation do not follow regular trend; K_{A1} of $[Ni(en)_3]^{2+}$ for nitrate salt > perchlorate salt, while for $[Cu(en)_2]^{2+}$ the order is perchlorate salt > nitrate salt. In case of nickel complexes, the data could be explained on a probability factor concerning the association reaction. When the cation complex and its anion are associated to form ion-pair, the distribution of charge density on the anion

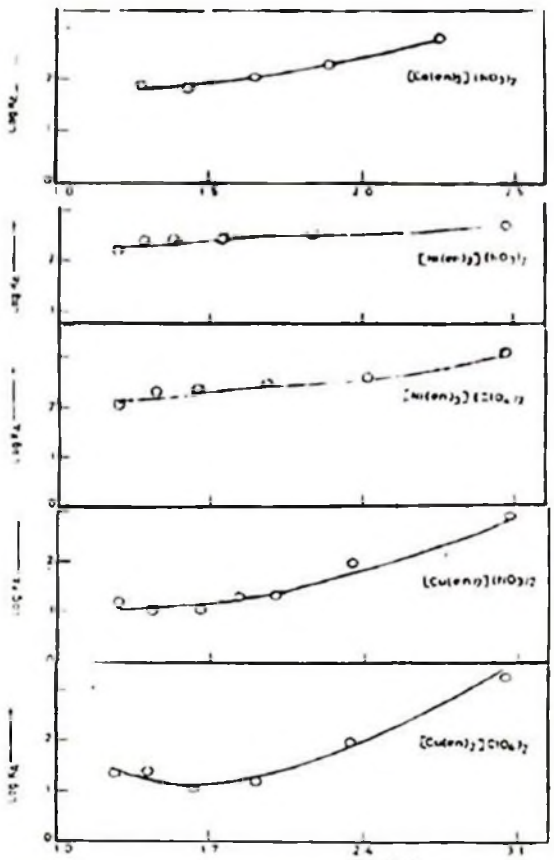


FIG. 3-Variation of Λ_o and log K_A with 100/ε for the complexes in methanol-water mixtures at 25°C.

becomes predominant by the main step in the association process. The charge density distribution on the regular tetrahedral perchlorate ion is completely different from that of the planar nitrate ion. The latter has a much higher affinity toward hydration. This may be confirmed from the calculations of the distance of closest approach (a_o) of the ion-pair $[Ni(en)_3X]^+ X^-$. The a_o is 4.27 A° for nitrate and 4.35 A° for perchlorate [10].

In case of copper complexes, either in pure or in mixed solvents, the variation of K_{A1} (perchlorate salt > nitrate salt) is attributed to the stronger intermolecular hydrogen-bond formation leading to a more stable quasi rigid structure in case of perchlorate

complex which compete strongly with the charge-charge interaction.

Inspection of K_{Al} in methanol for $[Ni(en_3)]X_2$ ($X = NO_3^-$ or ClO_4^-) shows that K_{Al} for perchlorate salt > nitrate salt. As in case of water, K_{Al} in MeOH also does not proceed parallel to solvation. Yokoyama and Kon [12] also found that K_{Al} values for $[Co(NH_3)_6]X_3$ ($X = Cl^-, Br^-, I^-, NO_3^-$ or ClO_4^-) in aqueous solution at 25°C were not in good agreement with the solvation process.

It can be concluded from the previous discussion that ion-pair formation can be detected for the complexes under investigation in the used solvents and can be illustrated by the following step [18].

$$M^{2+}(MeOH)_m\ X^-(MeOH)_n$$

$$\rightleftharpoons \quad (Me)$$

$$M^{2+}..O-H\ ...\ O-H...\ X^- \ + (m+n-2)\ MeOH$$

$$\rightleftharpoons \quad (Me)$$

Solvated Ions forming pair

$$M^{2+} - O - H\ ....X^- \ + (m+n-1)MeOH$$

$$\rightleftharpoons$$

Solvated cation with bare anion

$$M^{2+}\ ....X^- + (m+n)MeOH$$

bare ion forming pair

Walden Product

The Walden product $\Lambda_o\eta_o$ for the investigated complexes in methanol water mixtures at 25°C are represented graphically in figure 4. The plots are nonlinear and this is similar to that found in other aqueous binary mixtures for various electrolytes [4b, 19, 20].

Fig. 4 shows that Walden product as a function of MeOH consentraion for all complexes passes through a maximum in water rich region at about 20-30 MeOH wt. % and height of the maximum follows the trend $[Co(en)_3](NO_3)_2 > [Ni(en)_3]X_2 > [Cu(en)_2]X_2$ where $X = NO_3^-$ or ClO_4^-. This difference of the height can be explained on the basis of hydrophobic dehydration [20b, 21 & 22] of cations due to the presence of co-solvent (MeOH) in the water rich region. Addition of small proportion of MeOH causes depolymerization of water and hence dehydration of solvated cations may occur. Further addition of MeOH permits replacement of water molecules by methanol

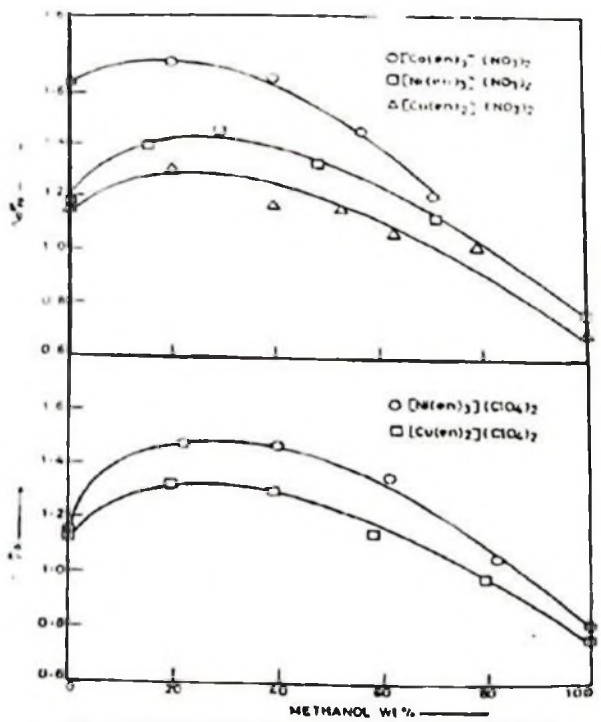


FIG. 4 -VARIATION OF WALDEN PRODUCT WITH METHANOL-WATER COMPOSITION FOR NITRATE AND PERCHLORATE COMPLEXES.

Table 3

Limiting ionic conductances (S.cm^2.eq^{-1} with error indicated) at different MeOH-water compositions at 25°C

MeOH wt. %	Cationic conductance [ref 5] of $[Co(en)_3]^{2+}$	$[Ni(en)_3]^{2+}$	$[Cu(en)_2]^{2+}$	Anionic conductane NO_3^-	ClO_4^-
0	114.06±0.32	61.68±0.22	57.93±0.42	71.60[12]	67.20[12]
10	76.9±0.30	59.3±0.21	53.0±0.38	58.1±0.16	57.4±0.19
20	70.9±0.31	57.1±0.19	47.3±0.25	46.4±0.17	47.7±0.19
30	68.2±0.18	54.8±0.20	42.8±0.17	39.2±0.17	42.2±0.20
40	66.2±0.26	53.0±0.18	40.0±0.19	34.8±0.15	39.5±0.13
50	64.8±0.28	52.0±0.13	39.4±0.21	33.6±0.13	39.3±0.17
60	64.3±0.25	52.2±0.18	40.1±0.13	36.2±0.18	42.1±0.16
70	64.5±0.12	53.0±0.19	42.2±0.15	41.4±0.14	46.5±0.18
80	-	57.1±0.21	46.4±0.18	47.9±0.14	53.1±0.16
90	-	64.3±0.18	52.3±0.15	54.5±0.16	62.1±0.15
100	-	78.41±0.18	66.72±0.11	61.24 [23]	70.94[24]

molecules. Accordingly ion-solvent interaction increases and $\Lambda_o\eta_o$ decreases.

Determination of Single Ionic Conductances

The derived cationic conductances of $[Co(en)_3]^{2+}$, $[Ni(en)_3]^{2+}$ and $[Cu(en)_2]^{2+}$ at all proportions of MeOH at 25°C, were previously obtained from their iodide complexes [5]. Subtration of cationic conductance from the conductances of nitrate and perchlorate complexes gives average values for $\lambda_o^{Nitrate}$ and $\lambda_o^{Perchlorate}$ in different solvent mixtures. The data are listed in Table 3.

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