

Electrical Conductance and Ionpair Formation of Cobalt (II) Complexes of Acetophenonethiosemicarbazone Halides in Methanol-water Mixture at 25°C

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Summary: Conductance of Co(II) complexes of acetophenonethiosemicarbazone halides is measured at 25°C in methanol-water mixture (32.63 < D < 73.42). The conductance parameters derived from the Fuoss-Onsager conductance theory indicate that the solvation of halides decreases with the decrease of the dielectric constants until a certain minimum and then increases again. The plot of $\log K_A$ vs. $1/D$ is found to be non-linear indicating that the equation of association cannot be applied. The association constant is analysed using the solvent separated-ion pair model.

Introduction

Ion-pair formation of cobalt(II) complexes of acetophenonethiosemicarbazone halides in methanol solution was studied [1]. The conductometric measurements of these complexes in methanol-water mixtures at 25°C are recorded, and then analyzed in an attempt to illustrate the electrolyte-solvent interactions, using the Fuoss-Onsager equation [2]. The relation between K_A and size of anions in the above mentioned medium is discussed.

Results and Discussion

Conductance data for cobalt(II) acetophenonethiosemicarbazone halides in methanol-water mixtures at 25°C are obtained and represented in Fig. (1), where the equivalent conductance π ($\text{Ohm}^{-1} \text{equiv}^{-1} \text{cm}^2$) is given at several concentrations C in equiv./liter.

The data were analysed on an IBM-PC computer using the Fuoss-Onsager equation.

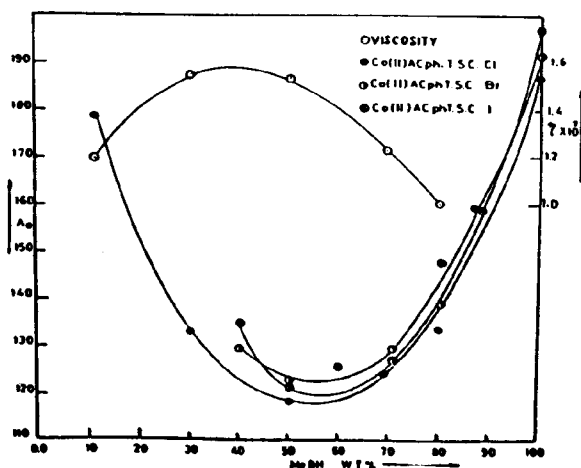


Fig.1: Variation of viscosity of solvent and π_0 with composition of solvent mixtures.

In all computations the accuracies required for the absolute values deviations are: ± 0.02 for π_0 ; ± 5 for $J < 200$; ± 5 for $J = 200 \rightarrow 1000$, and ± 10 for $J < 1000$. The results are depicted in Table 1.

It can be readily seen from Table 1 and Figure (1) that π_0 for cobalt(II) complexes of acetophenonethiosemicarbazone halides exhibit minima at 55 wt% methanol. One can observe that the composition at which the minima occur do not coincide with the maximum in the viscosity-methanol wt% (maximum at 40 wt % methanol).

The occurrence of a minimum in the value of π_0 , is an unexpected behaviour. Since on decreasing the dielectric constant, the ionic mobilities are hindered and the chance for ion-pair formation is more prevailing; so π_0 should decrease with decrease of the dielectric constant.

On the other hand Figures (2-4) show that a^0 , J and K_A pass through minimum values at certain dielectric constants.

The initial decreases in a^0 for Co(II) acetophenonethiosemicarbazone halides can be explained on the basis that the strength of hydrogen bonds between ions and water are so high to be affected by adding small amounts of methanol. On increasing methanol content depolymerisation occurs and an increase of a^0 values is observed.

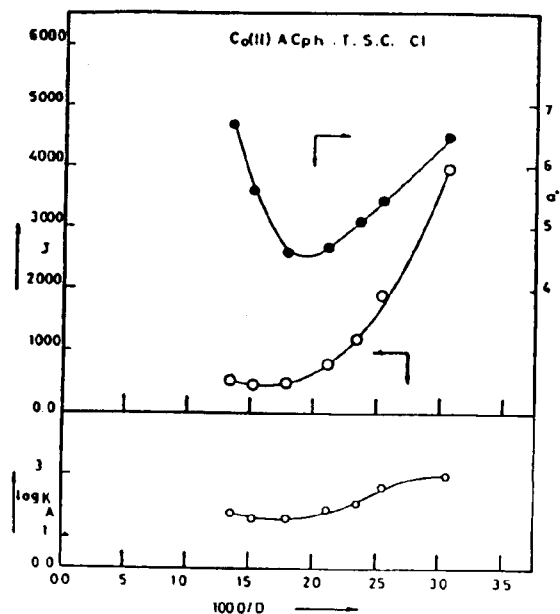


Fig. 2: Variation of a ; J and $\log K_A$ with dielectric constant.

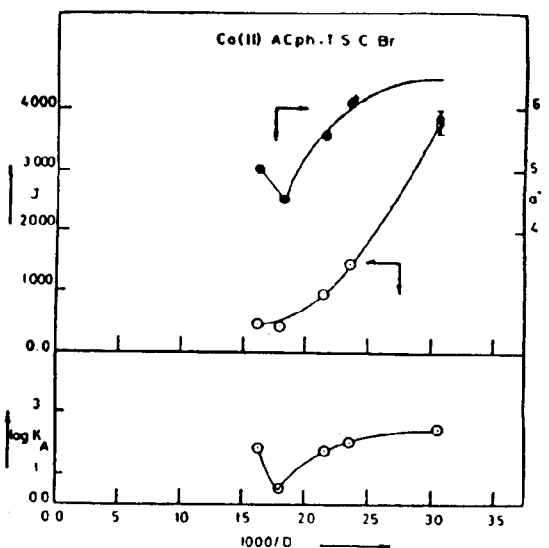


Fig.3: Variation of a ; J and $\log K_A$ with dielectric constant.

The minimum in $\log K_A$ vs. $1/D$ plot may be explained on the basis that: water is a highly associated solvent due to hydrogen bonds forming polymeric aggregates [6]. It is possible that pure water can stabilize the ion-pairs formed as a result of the molecular chains created by hydrogen bonding. On addition of methanol depolymerization oc-

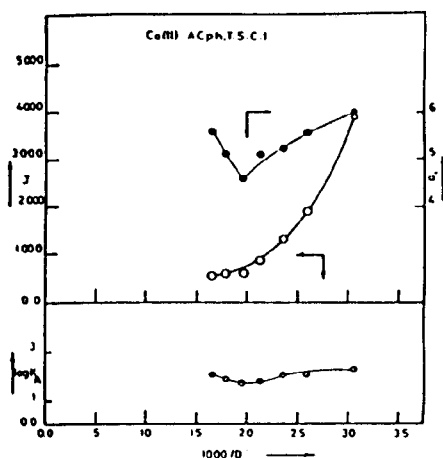


Fig.4: Variation of a ; J and $\log K_A$ with dielectric constant.

curs and less associated forms are produced, since it was seen from density and viscosity studies [7] that methanol-water is a strong hydrogen bonded system. On further increasing the methanol content the K_A values tend to increase regularly. In this region, it is assumed that over a certain methanol concentration, the water structure which could affect the association process of the ions would undergo less marked variation. Also the trend to a^0 shows that, on addition of methanol of water π_0 decreases (solvation decreases) till a minimum value and then increases for methanol-rich solution as discussed before.

From the above picture of variation of both a^0 and K_A with dielectric constant, one can conclude that the sphere in continuum model cannot be applied to these systems. Further evidence in support of this conclusion can be obtained by using the expression [8].

$$\ln K_A = \ln(4\pi Na^3/3000) + e^2/a^0 DkT + U$$

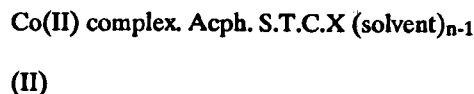
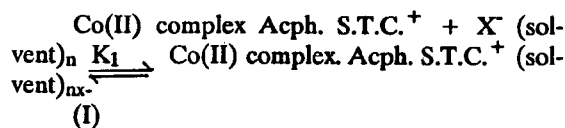
where

$$U = \Delta s/K - Es/kT$$

The factor Es/kT was introduced by Gilkeron [9] to account for the energy of ion-dipole interaction, which should be different from that when ion-pairs are considered. The entropy term Ds/K was included [8] to account for the change of entropy due to different arrangements of solvent molecules around free ions and ion-pairs.

The last column in Table 1 shows that U term decreased slightly as methanol wt % increases at the preliminary stages. This may be due to the fact that the entropy/Boltzman ratio $\Delta s/K$ decreases as the dielectric constant of medium decreases. This means that the ion-dipole interaction term increases as a result of modification of structure of the mixed solvent and interaction between solute and solvent. On further additions of methanol, the U term increases as the dielectric constant of medium decreases. This indicates that the entropy change due to solvent molecules arrangement around ions and ion pairs becomes greater than the ion-dipole interaction term, which may be attributed to the disturbance due to the fact that orientation of solvent molecules around the ions increases as the dielectric constant decreases.

Finally, the solvent separated-ion pairs model [10] is applied as follows:



The association constant is given by:

$$K_A = K \sum = \frac{[C_{(\text{ion-pairs})}][C_{(\text{CO(II) complex. Acph. S.T.C.}^+)}]}{[C_{X^-}(\text{solvent})_n]} \\ = K_1(1 - K_2)$$

where, $K \sum = K_A$ is obtained from conductance measurements.

$$K_1 = 4\pi Na^3/3000 e^b$$

From Table 2 it is evident that K_2 decreases primarily till a certain minimum then increases again as the wt % of MeOH increases. This behaviour may be explained on the basis that at first additions of MeOH, the formed ion-pair prefers the more solvated form (case I) to the desolvated form (case II). The subsequent increase in the value of K_2 on further additions of MeOH indicates a change in preference, where the ion-pair prefers

Table 1: The characteristic parameters for cobalt(II) complexes at acetophenonethiosemicarbazone halides in methanol- water mixtures at 25°C. Derived from Fuoss-Onsager equation.

MeOH wt %	D	1000/D	π_0	J	a^0	K_A	log K_A	U
Cobalt(II) complex of acetophenonethiosemicarbazone chloride								
11.76	73.42	13.620	178.83	562.36	6.66	57.373	1.75871	3.198
30.44	65.32	15.309	133.06	440.18	5.59	43.203	1.63551	3.051
50.42	56.06	17.838	118.32	475.63	4.58	45.656	1.65950	3.057
69.53	47.30	21.142	123.85	774.54	4.66	83.261	1.92044	3.246
80.38	42.36	23.607	133.15	1199.50	5.09	103.56	2.01519	3.143
87.11	39.26	25.471	159.45	1880.00	5.46	429.07	2.63253	4.339
100	32.63	30.647	186.85	3953.00	6.44	928.180	2.98145	4.563
Cobalt(II) complex of acetophenonethiosemicarbazone bromide								
40.50	60.70	16.474	129.29	461.31	5.01	66.63	1.82367	3.505
50.47	56.02	17.851	122.90	434.38	4.51	3.03	0.48096	0.354
70.95	46.66	21.432	129.47	965.51	5.55	55.27	1.74249	2.690
80.73	42.24	23.674	138.48	1454.90	6.10	177.42	2.06974	3.149
100	32.63	30.647	191.30	3731.00	5.78	274.84	2.43908	3.366
Cobalt(II) complex of acetophenonethiosemicarbazone iodide								
40.50	60.70	16.474	134.75	525.12	5.56	111.31	2.04653	3.888
50.47	56.02	17.851	121.17	536.71	5.15	79.30	1.89928	3.497
60.30	51.54	19.402	125.40	614.96	4.60	50.89	1.70660	2.971
70.95	46.66	21.432	126.97	8755.27	5.08	59.66	1.77568	2.832
80.73	42.24	23.674	147.70	1329.40	5.20	118.55	2.07390	3.262
88.57	38.56	25.934	158.35	1941.90	5.55	116.43	2.06606	2.981
100	32.63	30.647	197.35	3874.00	5.85	168.76	2.22727	2.877

Table 2: Estimation of K2 for cobalt(II) complexes of acetophenonethiosemicarbazone halides in methanol-water mixtures at 25°C

MeOH	K_A	K_1	K_2
Cobalt (II) complex of acetophenonethiosemicarbazone chloride			
11.76	57.373	2.344	23.477
30.44	43.203	2.044	20.137
50.42	45.656	2.147	20.265
69.53	83.261	3.241	24.690
80.38	103.50	4.469	22.173
87.11	429.070	5.601	75.606
100	928.180	9.685	94.837
Cobalt(II) complex of acetophenonethiosemicarbazone bromide			
40.50	66.63	2.001	32.298
50.47	3.07	2.124	0.425
70.95	55.27	3.751	13.735
80.73	117.42	5.035	22.321
100	274.84	9.493	27.952
Cobalt(II) complex of acetophenonethiosemicarbazone iodide			
40.50	111.310	2.280	47.820
50.47	79.302	2.402	32.015
60.30	50.886	2.607	18.519
70.95	59.660	3.513	15.983
80.73	118.550	4.53	25.095
88.57	116.430	5.907	18.711
100	168.760	9.498	16.768

the desolvated form to the more solvated form. The conclusions are in good agreement with those obtained from considering both the U term and K_A as previously discussed.

Figure 5 shows that the Walden product $\sigma\pi^0$, a function of solvent composition, for cobalt(II) complexes of acetophenonethiosemicarbazone halides in methanol-water mixtures at 25°C varies in the usual manner, i.e., it decreases with decreasing dielectric constant. This is in agreement with general findings on several small size (uni-univalent) [11,12] and (bi-bivalent) [13] systems and can be attributed to ion-solvent relaxation drag [14,15].

The electrostatic radii R^+ and R^- can be determined by using the Stokes' equation in the following form:

$$R_{\pm} = 0.8194 \times 10^{-8} / \lambda_0^{\pm} \eta_0$$

It is clear that application of Stoke's equation needs the determination of the true values of ionic conductance. According to the Fuoss assumption

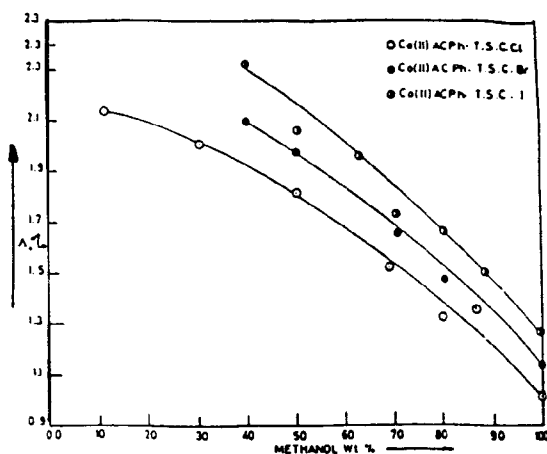


Fig.5: Variation of Walden product with composition of solvent mixture

[16] that the transport number is independent of the solvent composition, the ionic equivalent conductances for cations and anions in methanol-water mixtures are calculated and introduced in the Stokes equation. The results are contained in Table 3.

It can be readily seen from Table 3 that the values of R^+ and R^- increase on decreasing the dielectric constant. This can be explained on the basis that the addition of water to an alcoholic electrolyte solution diminishes the ionic radii [17].

It was observed that the values of a^0 was found to be greater than that of Stoke's radii ($R^+ + R^-$) for Co(II) complexes of acetophenonethiosemicarbazone halides in mixed solvent. The behaviour can be explained on the basis of Nightingale's [18] conclusions. The summation ($R^+ + R^-$) increases with decreasing the dielectric constant of the medium which may be due to cosolvent structure [3].

Experimental

Preparation of cobalt(II) complexes of acetophenonethiosemicarbazone halides are reported [1].

Methanol (BDH) was purified as reported [1]. Its specific conductance γ_0 amounted to $(2.72-7.08 \times 10^{-7}) \text{ Ohm}^{-1} \text{ cm}^{-1}$.

Conductivity water was prepared as reported [3]. Its specific conductance γ_0 amounted to $(5-7 \times 10^{-7}) \text{ Ohm}^{-1} \text{ cm}^{-1}$.

Properties of solvent mixtures

Densities (d) of the mixtures were determined using a 20 ml pycnometer at $25 \pm 0.02^\circ\text{C}$.

Viscosities (η) were measured using a modified Ubeloehde suspended level viscometer

Table-3: Calculation of the radii of ions of cobalt (II) complex of acetophenonethiosemicarbazone halides in methanol-water mixture at 25°C .

Cobalt(II) complex of acetophenonethiosemicarbazone chloride							
MeOH	$\lambda_0\eta_0$	$\lambda_0-\eta_0$	R^-	$\lambda_0+\eta_0$	R^+	$R^+ + R^-$	a^0
11.76	2.13612	0.59880	1.37	1.53732	0.53	1.90	6.66
30.44	2.06576	0.57908	1.42	1.48667	0.55	1.97	5.59
50.42	1.81952	0.51009	1.61	1.30944	0.63	2.24	4.58
69.53	1.52340	0.42706	1.92	1.09630	0.75	2.67	4.66
80.38	1.33283	0.37367	2.19	0.95916	0.85	3.04	5.09
87.11	1.36250	0.38196	2.15	0.98054	0.84	2.99	5.46
100	1.01736	0.28520	2.87	0.73292	1.12	3.99	6.44
Cobalt(II) complex of acetophenonethiosemicarbazone bromide							
40.50	2.05313	0.60693	1.35	1.446195	0.57	1.92	5.01
50.47	1.88959	0.55857	1.47	1.33101	0.62	2.09	4.51
70.95	1.55558	0.45981	1.78	1.09577	0.75	2.53	5.55
80.73	1.37649	0.40694	2.01	0.96958	0.85	2.86	6.10
100	1.04159	0.30790	2.66	0.73292	1.12	3.78	5.78
Cobalt(II) complex of acetophenonethiosemicarbazone iodide							
40.50	2.13983	0.68046	1.20	1.45937	0.56	1.76	5.56
50.47	1.86299	0.59240	1.38	1.27059	0.64	1.02	1.15
60.30	1.75372	0.55758	1.47	1.19614	0.69	2.16	4.60
70.95	1.52554	0.48505	1.69	1.04050	0.79	2.84	5.08
80.73	1.46814	0.46678	1.76	1.00136	0.82	2.58	5.20
88.57	1.30243	0.41413	1.98	0.88830	0.92	2.90	5.55
100	1.07453	0.34166	2.46	0.73292	1.12	3.52	5.85

with flow time at 25°C of 172.4s for conductivity water.

Dielectric constant (D) were obtained by interpolation from a large scale plot of data [4]. In the same way viscosities and densities of experimental solvent mixtures used were interpolated from large-scale plots of their data.

An Erlenmeyer cell with the bright platinum electrodes was used. Its cell constant is $0.05443 \pm 0.45\%$ as calculated using the Lind, Zwolenik, and Fuoss [5] equation.

A "pye" conductance bridge, Model 11700, was used for measuring the resistance of the solutions.

Preparation of solutions

All solutions were prepared by weight reduced to vacuo. Salts were weight by difference on a microbalance which reads up to ± 0.1 mg. Dilution was carried out successively into the cell by siphoning the solvent by means of a dispenser.

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