E.M.F. AND KINETIC STUDIES OF THE ION-PAIRING EFFECTS ON THE RATE OF AQUATION OF CHLOROPENTAMMINE CHROMIUM (III) PERCHLORATE IN DIFFERENT DICARBOXYLATE MEDIA

M.F. Amira*, SH. El-Shazly, M.M. Khalil and F.M. Abdel-Halim

Chemistry Department, Faculty of Science, Alexandria University, Egypt

The dissociation constants of ion-pairs of chloropentamine chromium with di-carboxylate have been obtained from e.m.f. of a cell comprising of glass and calomel electrodes. Rate Coefficients (k) for aquation of $[Cr(NH_3)_5Cl]^{2+}$ in 10% ethanol solutions of some dicarboxylates have been determined using potentiometric titration methods. A wide range values of k (ion), k (ion-pair), and dissociation constant have been obtained and in general there is a new correlation between k (ion-pair) and association constants among the studied dicarboxylate series.

Several studies [1-10] have been concerned with the kinetics of aquation of halogenopentammine chromium (III) in different media. Walker and Monk [6] found that the rate of aquation of chloropentammine chromium (III) ion is accelerated by nitrate, sulphate, malonate, phthalate and tartrate solutions. These effects were ascribed to the more reactive ion-pairs and their rate constants were calculated by applying the Waytte-Davies treatment [11]. These rate constants were approximately related to the ion-pair dissociation constants. The present work is an extension in six different dicarboxylate solutions. Solvent used is 10% (v/v) ethanol because greater ion association occurs in this solvent. So any relation between ion-pair rate coefficient and the corresponding association constant of the dicarboxylate ions can be clearly observed.

EXPERIMETNAL

Chloropentamminechromium (III) chloride, was prepared according to the published method [12,13], was purified and then the corresponding perchlorate was precipitated by adding warm acidified solution of concentrated lithium perchlorate and by cooling in ice-water. The complex salt was washed free of acid with alcohol and diethyl ether and then dried at 110°C. Analar chemicals were used for making stock solutions of the ion-pairing ligands.

The rate of aquation was followed by the potentiometric titration of the released chloride as described earlier [14], using timed samples cooled by ice-water.

The ion-pair dissociation constants were determined form e.m.f.s. of the cell;

$H_2L(m_1)$, $Na_2CO_3(m_2)$, complex perchlorate(m_3)/SCE

Readings were taken in absence of complex salt to calculate E° of the cell and then followed by five different additions of the complex salt. EMFS were read to 0.1 mv using Beckman 4500 digital pH meter.

RESULTS AND DISCUSSION

Ion-Pair Dissociation Constant (K_{diss})

The thermodynamic dissociation constants of ion-pair formed between complex ion (CPX^{2+}) and dicarboxylate ions (L^{2-}) [succinate, malate, tartrate, malonate, maleate or phthalate] have been determined from EMF measurements. The method of calculation was based on the following equations,

$$K_1 = [H^+][HL^-]\, f_1^2 / [H_2L] \quad (1)$$

$$K_2 = [H^+][L^{2-}]\, f_2 / [HL^-] \quad (2)$$

$$E = E^\circ - k' \log [H^+]\, f_1 \quad (3)$$

$$-\log f_1 = 0.5\, Z_1^2 \,[I^{1/2}/(1+1\ \ 3I^{1/2}) - 0.3I] \quad (4)$$

$$[HL^-] = m_1 - m_2 - [H^+] - 2[H_2L] \quad (5)$$

$$[L^{2-}] = m_1 - [HL^-] - [H_2L] \quad (6)$$

$$[CPXL] = m_1 - [H_2L] - [HL^-] - [L^{2-}] \quad (7)$$

$$[CPX^{2+}] = m_3 - [CPXL] \quad (8)$$

$$I = 0.5\{[H^+] + [HL^-] + 4[L^{2-}] + 2m_2 + 2m_3 + 4[CPX^{2+}]\} \quad (9)$$

$$K_{diss} = [L^{2-}][CPX^{2+}]\, f_2^2 / [CPXL] \quad (10)$$

E° was computed from equation (3) by knowing f_1 from equation (4) with successive approximations method. The free hydrogen ion concentration can thus be estimated from equation (3). Equations (1) and (2) besides (5)-(10) are used for calculating K_{diss} with successive approximation method. A basic computer program was designed for this purpose. Most of K_{diss} values were taken from the average values of three independent runs. For each run five different additions of complex salt were performed producing five different values of K_{diss} which are more or less constant. The detailed results of a typical run is shown in Table (1).

TABLE 1

RUN(II), TARTRATE BUFFER (10% ETHANOL), T=40°C
E° = -0.4318 VOLT m = 0.02978M
m = 0.01976M

10 m =	2.18	3.96	6.12	7.85	9.84
-E(volt) =	0.1792	0.1802	0.1813	0.1822	0.1832
10 K =	6.76	6.62	6.67	6.38	6.06

The average K_{diss} values for different ion-pairing dicarboxylate ligands are given in Table (2).

It is clear that the reactivity of the ion-pairing ligands toward the ion-pair formation followed the order; succinate > malate > tartrate > malonate > maleate > phthalate. In most buffers the value of ion-pair dissociation constant in 10% ethanol is lower than that in pure aqueous medium [9] since greater ion association occurs in this solvent. This will give more favourable conditions for highlighting any relation between ion-pair rate coefficient and association constant.

Ion-pair Rate Coefficient (k_{ip})

The ion-pair rate coefficient (k_{ip}) was calculated according to Wyatt and Davies [11] equation with its simplest form

$$k_{obs}\ C + k_1(C-[CPXL]) + k_{ip}\ [CPXL]$$

where k_{obs} is the observed pseudo first order rate coefficient, k_1 is the rate coefficient of the aquation of the free complex ion, C is the stoichiometric concentration of complex salt and [CPXL] is the initial concentration of ion-pair (CPXL). The later values were calculatd by an interactive procedure using the known dissociation constants (Table 2) of the ion-pairs. The principle of calculating [CPXL] based on relating equations 1,2,5,7,8 and 10 in one equation of the form

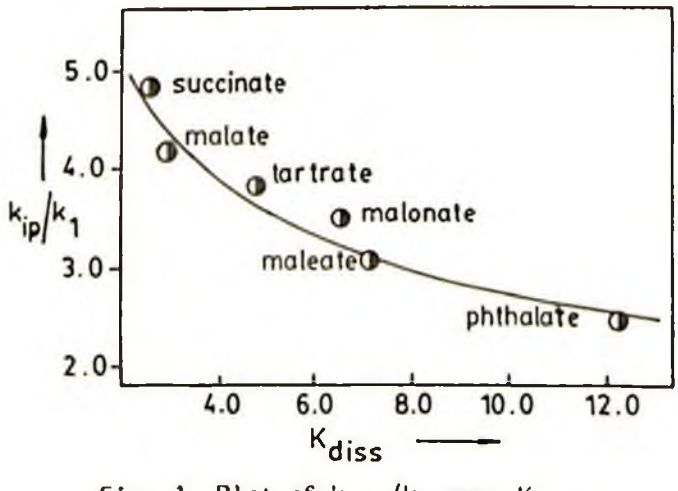


Fig. 1 Plot of k_{ip}/k_1 ver, K_{diss}

TABLE 2

AVERAGE K_{diss} VALUES AT 40°C

Buffer	10^3 K_{diss} in 10% ethanol				10 K_{diss} in water
	Run I	Run II	Run III	Average	
Succinate	12.1 ± 0.3	12.0 ± 0.4	12.3 ± 0.3	12.13 ± 0.15	12.10
Malate	7.2 ± 0.4	7.1 ± 0.3	-	7.15 ± 0.07	12.00
Tartrate	6.9 ± 0.2	6.5 ± 0.2	6.4 ± 0.4	6.60 ± 0.26	10.50
Malonate	4.7 ± 0.2	4.9 ± 0.2	-	4.80 ± 0.14	8.65
Maleate	3.2 ± 0.1	2.6 ± 0.1	-	3.00 ± 0.28	4.55
Phthalate	2.8 ± 0.1	2.7 ± 0.1	2.7 ± 0.4	2.73 ± 0.06	4.50

$$[CPXL]^2 = b[CPXL] + C = 0$$

where $b = -\left[(m_3 + m_1 - [HL^-] - [H_2L]) + K/f_2^2\right]$

and $C = m_3\left[m_1 - [HL^-] - [H_2L]\right]$

The different values of K_1, K_{obs}, K_{ip} and K_{ip}/K_1 in different dicarboxylate solutions containing 10% ethanol for the aquation of chloro-complex are summarized in Table(3).

The average values of K_{diss}, K_{ass}, K_{ip} and K_{ip}/K_1 are listed in Table (4).

The plot of k_{ip}/k_1 vs K_{diss} for six different ion-pairing dicarboxylate anions is shown in Figure(1). It is clear that a better non-linear correlation exists in 10% ethanol solvent than that in pure aqueous medium [9]. Moreover a new empirical correlation is realized between K_{ip} and K_{ass} from the linear log, log plot shown in Figure (2). This new correlation takes the form

$$K_{ip} = A\ K_{ass}^{B}$$

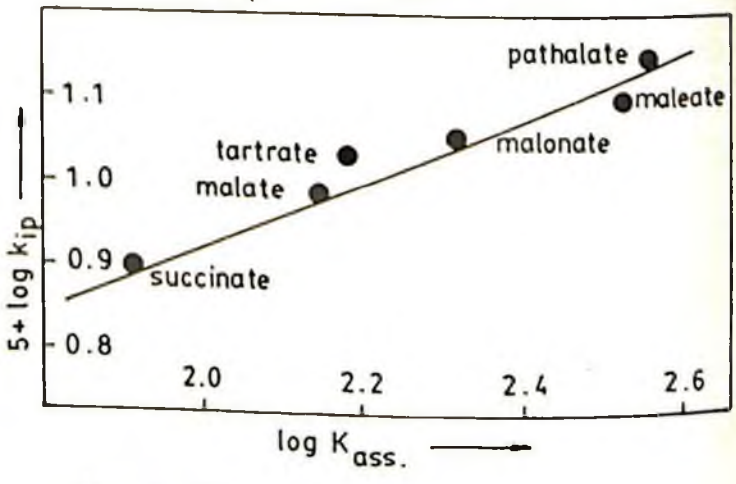


Fig. 2 Plot of log k_{ip} ver, K_{ass}

TABLE 3

VALUES OF RATE COEFFICIENTS k_1, k_{obs}, k_{ip} AND k_{ip}/K_i FOR DIFFERENT 10% ETHANOLIC DICARBOXYLATE MEDIA
T = 40°C
$10^5 K_i = 2.93 \pm 0.09$

Buffer	$10^3 m_1$	$10^3 m_2$	$10^3 m_3$	$10^5 k_{obs}$	10^4[CPXL]	$10^5 k_{ip}$	k_{ip}/k_i
	21.68	16.40	30.20	3.55±0.12	3.90	7.73	2.64
Succinate	24.10	18.22	31.80	3.52±0.09	5.10	6.61	2.26
	26.50	20.04	31.70	3.65±0.15	5.20	7.30	2.49
	28.91	21.86	32.00	3.65±0.10	5.40	7.16	2.44
	28.78	21.86	26.70	4.25±0.08	5.90	8.87	3.03
Malate	31.18	23.39	27.30	4.30±0.11	6.10	9.10	3.10
	35.98	26.99	26.90	3.95±0.17	6.30	8.72	2.98
	38.38	28.79	37.60	4.44±0.09	9.00	9.27	3.16
	26.35	19.79	26.10	4.59±0.04	6.10	10.04.	3.43
Tartrate	28.74	21.59	27.50	4.71±0.04	6.60	10.34	3.53
	21.59	16.19	26.80	5.20±0.05	7.10	11.54	3.94
Malonate	33.59	25.19	26.70	5.37±0.10	8.10	10.93	3.73
	31.20	23.40	27.10	6.59±0.08	10.90	12.04	4.11
Maleate	33.90	25.20	26.80	6.76±0.08	10.90	12.37	4.22
	30.96*	11.70	27.00	8.47±0.12	13.48	14.03	4.79
Phthalate	35.73	13.79	27.60	8.93±0.25	14.34	14.48	4.94

* m = Potassium hydrogen phthalate concentration.

TABLE 4

AVERAGE VALUES OF K_{diss}, K_{ass}, K_{ip} and K_{ip}/K_i for different bufferes at 40°C

Buffer	$10^3 \bar{K}_{diss}$	$\bar{K}_{ass}$	$10^5 \bar{k}_{ip}$	$\bar{k}_{ip}/\bar{K}_i$
Succinate	12.13±0.15	82.44	7.20±0.46	2.41±0.10
Malate	7.15±0.07	139.86	8.94±0.24	3.05±0.08
Tartrate	6.60±0.26	151.52	10.19±0.15	3.48±0.05
Malonate	4.80±0.14	208.33	11.24±0.31	3.84±0.10
Maleate	3.00±0.28	333.33	12.21±0.17	4.17±0.06
Phthalate	2.73±0.06	366.30	14.26±0.23	4.87±0.08

where A and B are empirical constants and have the values 0.988 and 0.45 respectively. This correlation can be considered as a linear free energy relationship (LFER) which seem more or less identical with the Bronsted linear free energy relationship [15] of the base catalyzed reaction where K_{ass} can be considered as the basisity strength of the ion-pairing dicarboxylate ligand. The constant B takes its normal value in parallel to that of Bronsted constant B (0.33-0.90). The basisity strength increse in the order, succinate-malate - tartrate - malonate - maleate - phthalate. The first four ligands are mainly affected by the gradual increase of the inductive effect, the gradual effect on the delocalization of the negative charge on the carboxylate anion while the latter two ligands are markedly affected by the mesomeric effect due to the highly conjugated structure.

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