

## Partial Molar Volumes and Partial Molar Adiabatic Compressibilities of Potassium Trioxalato Complexes of Al(III), Fe(III), Co(III), and Cr(III) Between 15° and 35°C

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The apparent and limiting apparent molal volumes of dilute aqueous solutions of  $K_3[Al(ox)_3] \cdot 3H_2O$ ,  $K_3[Fe(ox)_3] \cdot 3H_2O$ ,  $K_3[Co(ox)_3] \cdot 3H_2O$ , and  $K_3[Cr(ox)_3] \cdot 3H_2O$  complexes were determined from density data measured at 15°, 25°, and 35°C. The apparent and limiting apparent molal adiabatic compressibilities of these complexes were determined from measured ultrasonic sound velocities at 15°, 25°, and 35° in dilute aqueous solutions. The volume change associated with complex formation is discussed in terms of the nature of the coordinate bond and the overall hydration behavior of these complexes.

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**KEY WORDS:** Partial molar volumes; partial molar adiabatic compressibilities; ultrasonic velocity; complex ions; trioxalato complexes.

### 1. INTRODUCTION

The determination of partial molal volume  $V_2^0$  and partial molal adiabatic compressibility  $K_s^0$  are very powerful means for studying solute-solvent interactions in dilute solutions. Of the various classes of compounds so far used for studying these interactions, the complex compounds are especially useful since they provide series of compounds which may differ in size, or electrical charge density through substitution.<sup>(1-3)</sup> With the change of the central metal atom the nature of the coordination bonding undergoes appreciable change which is likely to affect the solute-solvent interactions. Therefore, we decided to examine the behavior of a series of mixed complexes with the same ligand

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and identical crystal structure but with different central metal atoms. The present paper reports the partial molal volumes and partial molal adiabatic compressibilities of the potassium trioxalato complexes of Al(III), Fe(III), Co(III), and Cr(III) in aqueous solution between 15 and 35°C. To our knowledge, a systematic study involving the above series has not so far been reported.

## 2. EXPERIMENTAL

### 2.1. Materials

The complexes studied in this work are  $K_3[Al(ox)_3] \cdot 3H_2O$ ,  $K_3[Fe(ox)_3] \cdot 3H_2O$ ,  $K_3[Co(ox)_3] \cdot 3H_2O$  and  $K_3[Cr(ox)_3] \cdot 3H_2O$ . These were prepared in our laboratory by standard methods<sup>(4)</sup> and were purified by repeated recrystallization. The complexes were dried initially in an electric oven at 80°C for 3–4 hrs and finally in a vacuum desiccator overnight. The stoichiometries of the complexes were established by chemical analysis and the purities were found to be better than 99.5% in all cases. There was no handling problem associated with the potassium trioxalato aluminate since it was found to be very stable and could be stored under ordinary laboratory condition. Potassium trioxalato ferrate and potassium trioxalato chromate are both heat and light sensitive and therefore, these compounds were stored in darkness below room temperature. Potassium trioxalato cobaltate was found to be unsuitable for storage and therefore, this compound was prepared and purified in small batches before each set of experiments.

### 2.2. Apparatus and Measurements

Solutions were prepared using freshly collected, doubly distilled water. All the solutions were prepared by weight and the weighings were vacuum corrected.

Densities were measured using an Anton Paar digital density meter DMA 60, with cell 602, coupled with a Heto thermostat. The temperature of the measuring cell was maintained to better than  $\pm 0.02^\circ C$ . The cell constant was evaluated using air and deionized water. For each measurement the cell was rinsed with distilled water followed by acetone and finally dried prior to injection of the solution. Duplicate readings were taken for each solution. The average uncertainty in the density measurement was within  $\pm 1 \times 10^{-5} \text{ g-cm}^{-3}$ .

Ultrasonic sound velocities in the solutions were determined using an ultrasonic interferometer (model M 82, Mittal) operating at 2MHz. The cell frequency was calibrated by using deionized water. The temperature of the cell was maintained using a Julabo F30 VC constant-temperature circulator

to better than  $\pm 0.02^\circ\text{C}$ . For each solution, readings were taken covering several resonance points. The measurements were repeated at least three times, and the average value was used for calculation of wavelength. The average uncertainty in the sound velocity determination was within  $\pm 0.2 \text{ m}\cdot\text{s}^{-1}$ .

### 3. RESULTS

#### 3.1. Density and Apparent Molal Volumes

The density data obtained are given in Table I. These values were converted to the apparent molal volume  $V_\phi$  ( $\text{cm}^3\cdot\text{mol}^{-1}$ ) of solute by using the equation

$$V_\phi = \frac{1000}{m d d_1} (d_1 - d) + M_2/d \quad (1)$$

where  $m$  is the molality of the solute ( $\text{mol}\cdot\text{kg}^{-1}$ );  $d$  and  $d_1$  are densities ( $\text{g}\cdot\text{cm}^{-3}$ ) of solution and solvent, respectively; and  $M_2$  is the molar mass of the solute ( $\text{g}\cdot\text{mol}^{-1}$ ).<sup>(5)</sup> Values of  $V_\phi$  are given in Table I.

The Redlich-Meyer<sup>(6)</sup> equation in the form

$$V_\phi = V_2^\circ + S_v m^{1/2} + B_v m \quad (2)$$

was fitted to the data at each temperature. Here,  $V_2^\circ$  is the limiting apparent molar volume of solute,  $S_v$  is the Debye-Hückel limiting slope, and  $B_v$  is an empirical parameter. The values used for  $S_v$  at 15, 25, and  $35^\circ\text{C}$  for 1:3 electrolytes were 22.07, 27.45, and 30.07, respectively. These values were taken from a compilation of Millero<sup>(7)</sup> using the proper valence factors given for higher-valence electrolytes.<sup>(1)</sup>

#### 3.2. Ultrasonic Velocities and Adiabatic Compressibilities

The measured ultrasonic velocities  $u$  ( $\text{m}\cdot\text{s}^{-1}$ ) and apparent molal adiabatic compressibilities  $K_{s\phi}$  at different temperatures are given in Table II. The adiabatic compressibilities  $\beta_s$  ( $\text{bar}^{-1}$ ) were evaluated using the Laplace equation

$$\beta_s = 100/u^2 d \quad (3)$$

The apparent molal adiabatic compressibilities  $K_{s\phi}$  of the solutes were calculated from

$$K_{s\phi} = \frac{1000(\beta_s - \beta_{s,1})}{m d_1} + \beta_s V_\phi \quad (4)$$

Table I. Densities and Apparent Molal Volumes<sup>a</sup>

<i>m</i>	<i>d</i>	<i>V</i> <sub>φ</sub>	<i>m</i>	<i>d</i>	<i>V</i> <sub>φ</sub>
K <sub>3</sub> [Al(ox) <sub>3</sub> ]·3H <sub>2</sub> O			K <sub>3</sub> [Fe(ox) <sub>3</sub> ]·3H <sub>2</sub> O		
15°C					
0.01065	1.00226	167.80	0.02065	1.00554	179.40
0.01594	1.00378	169.42	0.03171	1.00891	180.92
0.02406	1.00610	170.93	0.04321	1.01241	181.43
0.03204	1.00836	172.09	0.05337	1.01544	182.61
0.04032	1.01072	172.31	0.06476	1.01884	183.17
0.04692	1.01257	173.07	0.07286	1.02117	184.57
0.05459	1.01474	173.23	0.08450	1.02459	185.13
0.06173	1.01671	174.11			
25°C					
0.01062	1.00017	170.60	0.01104	1.00048	181.45
0.01590	1.00169	171.24	0.02062	1.00341	182.61
0.02401	1.00400	172.80	0.03167	1.00673	184.37
0.03298	1.00626	173.55	0.04317	1.01018	185.21
0.04027	1.00860	174.06	0.05331	1.01315	186.62
0.04687	1.01040	175.66	0.06471	1.01651	187.08
0.05452	1.01256	175.65	0.07279	1.01880	188.60
0.06163	1.01448	176.95	0.08440	1.02217	189.20
35°C					
0.01061	0.99711	174.08	0.01103	0.99742	185.74
0.01587	0.99861	175.32	0.02060	1.00030	187.41
0.02396	1.00086	177.49	0.03164	1.00359	188.26
0.03294	1.00307	178.68	0.04315	1.00697	189.52
0.04022	1.00535	179.40	0.05329	1.01988	191.22
0.04682	1.00716	179.94	0.06467	1.01316	192.07
0.05449	1.00925	180.38	0.07274	1.01547	192.59
0.06153	1.01119	180.75	0.08436	1.01876	193.55
K <sub>3</sub> [Co(ox) <sub>3</sub> ]·3H <sub>2</sub> O			K <sub>3</sub> [Cr(ox) <sub>3</sub> ]·3H <sub>2</sub> O		
15°C					
0.01307	1.00305	193.50	0.01056	1.00229	194.30
0.02054	1.00527	194.05	0.02132	1.00533	195.18
0.02776	1.00738	195.40	0.03125	1.00816	196.72
0.03897	1.01065	196.49	0.04161	1.01111	197.01
0.04784	1.01325	196.43	0.05151	1.01387	198.34
0.05592	1.01555	197.47	0.06541	1.01776	198.73
0.06476	1.01804	198.52	0.07876	1.02138	200.32
0.07345	1.02053	198.75	0.09042	1.02459	200.67
0.08593	1.02406	199.20			
25°C					
0.01306	1.00093	197.71	0.01055	1.00012	197.32
0.02052	1.00311	198.99	0.02131	1.00320	198.33
0.02774	1.00526	199.33	0.03124	1.00598	200.15

Table I. Continued.

$m$	$d$	$V_\phi$	$m$	$d$	$V_\phi$
0.03894	1.00826	200.89	0.04159	1.00889	200.79
0.04780	1.01094	201.50	0.05148	1.01163	201.54
0.05588	1.01320	202.46	0.06536	1.01540	203.25
0.06471	1.01571	202.51	0.07870	1.01906	203.44
0.07340	1.01808	203.84	0.09035	1.02213	204.86
0.08587	1.02157	204.10			
35°C					
0.01306	0.99785	202.72	0.02130	1.00004	205.32
0.02051	0.99999	203.61	0.03123	1.00278	206.07
0.02773	1.00210	204.70	0.04157	1.00557	207.93
0.03892	1.00507	205.10	0.05146	1.00827	208.10
0.04778	1.00766	206.92	0.06531	1.01193	210.05
0.05584	1.00992	207.10	0.07867	1.01551	210.19
0.06467	1.01237	207.35	0.09030	1.01846	211.98
0.07335	1.01469	208.68			
0.08583	1.01809	209.24			

<sup>a</sup>Units:  $m$ , mol·kg<sup>-1</sup>;  $d$ , g·cm<sup>3</sup>;  $V_\phi$ , cm<sup>3</sup>·mol<sup>-1</sup>.

where the subscript 1 designates the solvent. The adiabatic compressibilities of pure water, as derived from the Laplace equation, were 46.027, 44.767, and 43.593 at 15, 25, and 35°C, respectively.

An equation of the form

$$k_{s\phi} = K_s^0 + S_{ks}m^{1/2} + B_{ks}m \quad (5)$$

where  $K_s^0$  is the limiting apparent molal adiabatic compressibility of the solute,  $S_{ks}$  is the Debye-Hückel limiting slope, and  $B_{ks}$  is an empirical parameter, is normally recommended for evaluating the experimental data using reported Debye-Hückel limiting slope values for 1:3 electrolytes.<sup>(7,8)</sup> However, as has been pointed out by Kawaizumi *et al.*,<sup>(1)</sup> for all practical purposes, the concentration dependence of  $K_{s\phi}$  can be represented by the empirical equation

$$K_{s\phi} = K_s^0 + S'_{ks}m^{1/2} \quad (6)$$

Differences between  $S_{ks}$  and  $S'_{ks}$  were found by Kawaizumi *et al.*, particularly for large ions, such as those studied here.<sup>(9)</sup> These differences, however, cannot significantly change the limiting values of the adiabatic compressibilities. Precision determination of  $S'_{ks}$  is difficult, particularly for large complex molecules, and differ from the calculated value of  $S_{ks}$  for 1-3 type electrolytes (23.8, 32.8, and 41.2 for 15, 25, and 35°C, respectively). Fortunately, differences in  $K_s^0$  due to the different extrapolation procedures are not so great as

Table II. Ultrasonic Velocities and Apparent Molal Adiabatic Compressibilities<sup>a</sup>

<i>m</i>	<i>u</i>	$10^4 K_{s\phi}$	<i>m</i>	<i>u</i>	$10^4 K_{s\phi}$
K <sub>3</sub> [Al(ox) <sub>3</sub> ]·3H <sub>2</sub> O			K <sub>3</sub> [Fe(ox) <sub>3</sub> ]·3H <sub>2</sub> O		
15°C					
0.01658	1476.51	-127.25	0.01846	1476.48	-124.36
0.02405	1477.42	-126.78	0.03257	1477.90	-122.46
0.03522	1478.69	-125.50	0.05027	1479.74	-121.54
0.05207	1480.65	-123.87	0.06479	1481.44	-120.62
0.06884	1482.70	-123.30	0.07693	1482.48	-120.00
25°C					
0.01654	1498.63	-120.74	0.01843	1498.56	-114.73
0.02400	1499.55	-120.12	0.03251	1500.06	-113.68
0.03514	1500.84	-119.52	0.05016	1501.84	-111.31
0.05195	1502.74	-117.06	0.06469	1503.28	-110.44
0.06869	1504.79	-116.52	0.07677	1504.66	-109.79
35°C					
0.01649	1520.78	-108.54	0.01836	1520.62	-103.10
0.02397	1521.65	-108.22	0.03240	1521.84	-102.46
0.03503	1522.78	-107.36	0.05000	1523.25	-100.47
0.05179	1524.57	-105.92	0.06458	1524.29	-98.21
0.06847	1526.10	-102.43	0.07659	1525.30	-98.06
K <sub>3</sub> [Co(ox) <sub>3</sub> ]·3H <sub>2</sub> O			K <sub>3</sub> [Cr(ox) <sub>3</sub> ]·3H <sub>2</sub> O		
15°C					
0.01306	1476.12	-120.55	0.02055	1477.04	-117.10
0.02087	1477.04	-119.98	0.04114	1479.46	-115.88
0.04044	1479.44	-119.32	0.06668	1482.41	-114.02
0.06227	1482.10	-117.88	0.07876	1484.18	-113.98
0.07984	1484.26	-116.86	0.08854	1485.08	-113.44
0.10053	1486.72	-115.85	0.10127	1486.53	-112.73
25°C					
0.01305	1498.21	-109.02	0.02050	1499.06	-108.08
0.02082	1499.14	-108.10	0.04105	1501.34	-105.78
0.04035	1501.31	-106.04	0.06653	1504.19	-104.26
0.06213	1503.72	-104.40	0.07866	1505.79	-103.00
0.07966	1505.66	-103.22	0.08835	1506.56	-102.62
0.10030	1507.79	-101.02	0.10105	1507.93	-102.00
35°C					
0.01304	1520.42	-98.33	0.02044	1521.26	-97.66
0.02079	1521.15	-96.50	0.04092	1523.28	-94.22
0.04023	1523.04	-94.60	0.06632	1525.76	-92.48
0.06194	1525.11	-92.68	0.07856	1527.32	-91.46
0.07942	1526.76	-91.77	0.08806	1527.90	-91.28
0.09999	1528.66	-89.87	0.10072	1528.93	-89.62

<sup>a</sup>Units: *u*, m·s<sup>-1</sup>; *K*<sub>sφ</sub>, cm<sup>3</sup>·mol<sup>-1</sup>·bar<sup>-1</sup>.

to significantly affect the general discussion of the present experimental results.

All the compounds studied in the present work are water soluble at normal temperature with  $K_3[Al(ox)_3]$  showing the lowest solubility. The highest concentration that was available for  $K_3[Al(ox)_3]$  at experimental temperatures was about  $0.06m$ . The apparent molal volumes and apparent molal adiabatic compressibilities presented in Tables I and II, respectively, show some scatter at lower concentrations within the limit of experimental errors. Meaningful extrapolated values for infinite dilutions, therefore, can be obtained by the least-squares method. The least-squares values of  $V_2^0$  and  $K_s^0$  with their standard deviations are listed in Table III. The experimental values of  $B_v$  and  $S'_{ks}$ , also listed in Table III, are positive for all the above complexes. In order to check the accuracy of our experimental data, we determined  $V_2^0$  for NaCl at 25°C and obtained a value of 16.85, as against 16.62 quoted by Millero.<sup>(7)</sup> Similarly we determined  $K_s^0$  for standard sodium chloride at 25°C as  $-51.5 \times 10^{-4} \text{ cm}^3\text{-mol}^{-1}\text{-bar}^{-1}$ , against the reported<sup>(10)</sup> value of  $-50.5 \times 10^{-4} \text{ cm}^3\text{-mol}^{-1}\text{-bar}^{-1}$ .

**Table III.** Limiting Apparent Molal Volumes and Limiting Apparent Molal Adiabatic Compressibilities of the Solutes<sup>a</sup>

Solute	15°C	25°C	35°C
		$V_2^0$	
$K_3[Al(ox)_3] \cdot 3H_2O$	$165.61 \pm 0.48$	$167.25 \pm 0.28$	$171.24 \pm 0.54$
$K_3[Fe(ox)_3] \cdot 3H_2O$	$175.46 \pm 0.26$	$178.06 \pm 0.26$	$182.21 \pm 0.24$
$K_3[Co(ox)_3] \cdot 3H_2O$	$190.68 \pm 0.32$	$194.50 \pm 0.69$	$199.03 \pm 0.31$
$K_3[Cr(ox)_3] \cdot 3H_2O$	$191.62 \pm 0.28$	$194.14 \pm 0.29$	$200.25 \pm 0.41$
		$B_v$	
$K_3[Al(ox)_3] \cdot 3H_2O$	41.4	43.2	40.7
$K_3[Fe(ox)_3] \cdot 3H_2O$	38.2	38.0	31.7
$K_3[Co(ox)_3] \cdot 3H_2O$	27.7	22.5	16.8
$K_3[Cr(ox)_3] \cdot 3H_2O$	27.8	25.7	26.4
		$10^4 K_s^0$	
$K_3[Al(ox)_3] \cdot 3H_2O$	$-131.49 \pm 0.23$	$-125.38 \pm 0.40$	$-114.83 \pm 0.86$
$K_3[Fe(ox)_3] \cdot 3H_2O$	$-128.18 \pm 0.21$	$-119.93 \pm 0.29$	$-108.94 \pm 0.56$
$K_3[Co(ox)_3] \cdot 3H_2O$	$-123.43 \pm 0.31$	$-113.57 \pm 0.25$	$-102.56 \pm 0.27$
$K_3[Cr(ox)_3] \cdot 3H_2O$	$-120.73 \pm 0.20$	$-113.00 \pm 0.19$	$-103.45 \pm 0.39$
		$S'_{ks}$	
$K_3[Al(ox)_3] \cdot 3H_2O$	31.9	34.2	43.4
$K_3[Fe(ox)_3] \cdot 3H_2O$	29.8	37.1	39.7
$K_3[Co(ox)_3] \cdot 3H_2O$	23.0	37.9	39.5
$K_3[Cr(ox)_3] \cdot 3H_2O$	24.8	34.8	42.7

<sup>a</sup>See Tables I and II for units.

#### 4. DISCUSSION

It is seen from Table III that  $V_2^0$ , which is positive and large for all the complexes, increase with increasing temperature. On the other hand,  $K_s^0$ , which is negative for all the complexes, becomes less negative with increasing temperature. For each temperature,  $V_2^0$  values follow the sequence  $V_2^0(\text{K}_3[\text{Al}(\text{ox})_3]) < V_2^0(\text{K}_3[\text{Fe}(\text{ox})_3]) < V_2^0(\text{K}_3[\text{Co}(\text{ox})_3]) < V_2^0(\text{K}_3[\text{Cr}(\text{ox})_3])$ . The derivative  $dV_2^0/dT$  is different for all the complexes and seem to depend on  $V_2^0$  *i.e.*, complexes with higher  $V_2^0$  showing higher  $dV_2^0/dT$ .

In order to understand the interactions of the complex anions with the solvent, it is necessary to calculate ionic  $V_2^0$  values. This was done by deducting for  $\text{K}^+$  ion the value  $V_2^0(\text{K}^+) = 3.62 \text{ cm}^3\text{-mol}^{-1}$  at  $25^\circ\text{C}$  by converting the conventional partial ionic volume data compiled by Millero<sup>(11)</sup> to the absolute scale on the basis of  $V_2^0(\text{H}^+) = -5.4 \text{ cm}^3\text{-mol}^{-1}$ . The  $V_2^0$  (ion) for the complex anions thus obtained are listed in Table IV.

The volume change associated with formation of the complex anions may be calculated as

$$\Delta V_2^0(\text{ion}) = V_2^0([\text{M}(\text{ox})_3]^{3-}) - V_2^0(\text{M}^{3+}) - 3V_2^0(\text{ox}^{2-}) \quad (7)$$

where, for the oxalate ion  $V_2^0(\text{ox}^{2-}) = 10.59 \text{ cm}^3\text{-mol}^{-1}$ . The calculated values of  $\Delta V_2^0$  (ion) for all the complex anions at  $25^\circ\text{C}$  are presented in Table IV.

Millero<sup>(11)</sup> has compiled the conventional partial ionic volumes of  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Cr}^{3+}$  at  $25^\circ\text{C}$ . On the basis of  $V_2^0(\text{H}^+) = -5.4$ , the absolute partial ionic volumes of the above ions are  $-47.60$ ,  $-49.10$  and  $-44.90 \text{ cm}^3\text{-mol}^{-1}$  for  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Cr}^{3+}$ , respectively. In the absence of literature data, the absolute partial ionic volume for  $\text{Co}^{3+}$  is calculated to be  $-47.1 \text{ cm}^3\text{-mol}^{-1}$  from its ionic radius of  $68.5 \text{ nm}$ .<sup>(12)</sup> It is very interesting to note that although the absolute partial ionic volumes of the triply charged bare metal ions in aqueous solutions are rather similar, the absolute partial ionic volumes of their trioxalato complexes in aqueous solution are somewhat different. The increase in partial ionic volume due to complex formation,  $\Delta V_2^0$  (ion), as

**Table IV.** Partial Ionic Volumes and Partial Ionic Adiabatic Compressibilities and Hydration Numbers of Ions at  $25^\circ\text{C}$ <sup>a</sup>

Ions	$V_2^0$ (ion)	$\Delta V_2^0$ (ion)	$10^4 K_s^0$ (ion)	$n_H$
$[\text{Al}(\text{ox})_3]^{3-}$	156.38	172.18	-45.88	5.7
$[\text{Fe}(\text{ox})_3]^{3-}$	167.25	184.55	-40.43	5.0
$[\text{Co}(\text{ox})_3]^{3-}$	183.64	198.94	-34.07	4.2
$[\text{Cr}(\text{ox})_3]^{3-}$	183.18	196.38	-33.50	4.1

<sup>a</sup>See Tables I and II for units.



presented in Table IV is very large and follows the order  $[\text{Co}(\text{ox})_3]^{3-} > [\text{Cr}(\text{ox})_3]^{3-} > [\text{Fe}(\text{ox})_3]^{3-} > [\text{Al}(\text{ox})_3]^{3-}$ . The large value of  $\Delta V_2^\circ$  (ion) results from (a) an increase in intrinsic volume associated with complex formation, (b) a decrease in total electrical charge associated with metal and ligand through coordinate bond formation, and (c) a decrease in charge density due to a larger surface area of the complex and resulting in decreased electrostriction. The differences observed in the  $\Delta V_2^\circ$  (ion) with the change in the central metal of the complexes, however, demands further scrutiny since in all the above cases, the decrease in electrical charge due to bond formation and increase in intrinsic volume due to complex bond formation are more or less equal. Crystal data on the complexes<sup>(13-15)</sup> suggest identical distorted octahedral crystal structures for all the complexes. The dimensions of the unit cells suggest a very close crystal molecular volumes for all the complexes with less than  $1 \text{ cm}^3\text{-mol}^{-1}$  variation in the overall dimensions in the crystalline state. The differences in solution volume can, therefore, be attributed to differences in residual charges of the complexes due to partial ionic character of the coordinate bonding which again depends on the nature of the central metal atom. Kawaizumi *et al.*,<sup>(9)</sup> from a study of the several nitroammoniumcobalt (III) ions, suggested that the charges of the complex ions are distributed on the periphery and are not confined to central metal ion itself. We agree with their view since the effect of the minor differences in residual charges would be annulled by the shielding effect of the protruded ligands if the charges were located on the central metal atom.

To obtain partial ionic adiabatic compressibilities  $K_s^\circ$  for the complex anions, the corresponding value for the  $\text{K}^+$  ion at  $25^\circ\text{C}$  was taken as  $-26.5 \times 10^{-4} \text{ cm}^3\text{-mol}^{-1}\text{-bar}^{-1}$  as reported by Mathieson and Conway.<sup>(10)</sup> The  $K_s^\circ$  (ion) values for all the trioxalato anions thus obtained are listed in Table IV. It is seen from Table IV that  $K_s^\circ$  (ion) is negative for all the complex anions. With the exception of very soft ions such as  $\text{I}^-$  or the hydrophobic tetraalkylammonium ions, ionic solutes generally have negative  $K_s^\circ$ , reflecting the influence of the ions on the cosphere solvent molecules. On the basis of  $K_s^\circ$  (ion), the strength of interactions between complex ions and water molecules follow the order  $[\text{Al}(\text{ox})_3]^{3-} > [\text{Fe}(\text{ox})_3]^{3-} > [\text{Co}(\text{ox})_3]^{3-} > [\text{Cr}(\text{ox})_3]^{3-}$ , which is the same as that found for the limiting apparent molal volumes. What is noteworthy from Tables III and IV is the general similarity in the variation of  $K_s^\circ$  and  $V_2^\circ$  of the complex ions with change of central metal species.

Kawaizumi *et al.*,<sup>(1)</sup> tried to classify ions broadly into two groups. Ions belonging to the first group are ordinary cations and anions, and ligands, both simple and complex, characterized by negative  $K_s^\circ$  values resulting from strong electrostriction which become less negative with increasing  $V_2^\circ$ . The second group of ions contain large complex ions and tetraalkylammonium

ions larger than  $\text{Et}_4\text{N}^+$ . The main factor determining the solute–solvent interactions of these ions is their size rather than their charge. The  $K_s^\circ$  values of this class of ions show positive or small negative values depending on  $V_2^\circ$ . In the present case all the complex anions have large negative  $K_s^\circ$  and therefore, belong to the first group of ions.

The hydration numbers  $n_H$  of the ions at 25°C were calculated from  $K_s^\circ$  (ion) by the method of Millero *et al.*,<sup>(16)</sup> using the relation

$$n_H = -K_s^\circ(\text{electrostriction})/\beta_{s,1}V_1^\circ \quad (8)$$

where  $\beta_{s,1}$  is the compressibility of bulk water,  $V_1^\circ$  is molar volume of water, and  $K_s^\circ(\text{electrostriction}) = [K_s^\circ(\text{ion}) - K_s^\circ(\text{intrinsic})]$  is assumed to be equal to  $K_s^\circ(\text{ion})$  since  $K_s^\circ(\text{intrinsic})$  is negligibly small. Thus, the hydration numbers of the complex anions, listed in Table IV, are proportional to  $K_s^\circ$ .

Of the four complex anions included in the present study, the solution behavior of trioxalato aluminate and trioxalato ferrate differ significantly from that of trioxalato cobaltate and trioxalato chromate. The former two complex anions are characterized by smaller  $V_2^\circ$  (ion) and larger negative  $K_s^\circ$  (ion). The  $V_2^\circ/dT$  for potassium trioxalato aluminate ( $0.281 \text{ cm}^3\text{-mol}^{-1}\text{-K}^{-1}$ ) and potassium trioxalato ferrate ( $0.339 \text{ cm}^3\text{-mol}^{-1}\text{-K}^{-1}$ ) are relatively small compared to the corresponding values for potassium trioxalato cobaltate ( $0.425 \text{ cm}^3\text{-mol}^{-1}\text{-K}^{-1}$ ) and potassium trioxalato chromate ( $0.436 \text{ cm}^3\text{-mol}^{-1}\text{-K}^{-1}$ ). This suggests that the central metal atoms which dictate the nature of the chelate ring might play a vital role in deciding the solution behavior of these complexes.

Study of exchange rates with radioactive oxalate group in the above metal oxalate chelate complexes showed<sup>(17)</sup> that in the case of potassium trioxalato aluminate and potassium trioxalato ferrate, the ligand exchange is rapid whereas in trioxalato cobaltate and trioxalato chromate no exchange reaction takes place. A rapid rate of exchange is usually taken as evidence<sup>(18)</sup> for “partial ionic” bonding in the chelate ring while slow exchange rates are presumed to be indicative of “essentially covalent” character. The results of Duffield and Calvin<sup>(19)</sup> indicate that highly chelating complexes with covalent character are more stable and, therefore, slow to exchange, since the exchange reaction involves chelate ring opening and closing through intermediate formation of a higher-member activated complex.<sup>(20)</sup>

It is, therefore, reasonable to assume that due to partial ionic character and also due to ring opening and closing, the residual surface charge density in trioxalato aluminate and trioxalato ferrate is higher than in the trioxalato cobaltate and trioxalato chromate, giving rise to stronger ion dipole interactions with resultant smaller  $V_2^\circ$  and larger negative  $K_s^\circ$  values. A highly stable chelate ring with equal surface area has reduced interactions with cosphere solvent molecules as in the case of trioxalato cobaltate and trioxalato chromate

in the present study. Physicochemical similarities between cobalt and chromium complexes are widely recognized.<sup>(21)</sup> Interaction parameters in solution for trioxalato cobaltate and trioxalato chromate as seen from Tables III and IV are identical, confirming the above view.

## 5. CONCLUSION

There is a regular trend in the observed values of  $V_2^\circ$  and  $K_s^\circ$  for the potassium trioxalato complexes of Al(III), Fe(III), Co(III), and Cr(III). The contribution of the ligands and metal ions to  $V_2^\circ$  and  $K_s^\circ$  are different before and after coordination bond formation. The nature of the chelate bond and stability of the chelate ring influence the ion solvent interactions of the complex molecules.

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