

## Viscosity of Potassium Trioxalato Complexes of Al(III), Fe(III), Co(III), and Cr(III) in Aqueous Solution Between 15° and 35°C

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Received February 18, 1998

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The viscosity 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, as well as  $K_2(ox) \cdot H_2O$ , were measured between 15 and 35°C. Those of  $CoCl_2 \cdot 6H_2O$ ,  $FeCl_3 \cdot 6H_2O$ ,  $Al_2(SO_4)_3 \cdot 18H_2O$ , and  $CrCl_3 \cdot 6H_2O$  were measured at 25°C. These data were analyzed by the Jones–Dole equation. The ionic  $B$  coefficients of the above complex anions were discussed in terms of ion–solvent interactions and the overall change in  $\Delta B$  associated with complex formation.

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**KEY WORDS:** Viscosity; complex ions; trioxalato complexes; temperature dependence;  $B$  coefficients.

### 1. INTRODUCTION

Determination of viscosities of dilute aqueous solutions have been a useful tool in the elucidation of solute–solvent interactions and the structural behavior of liquid water. In the study of solute molecules, the shape of the molecules and the electrical charge density have been important aspects to which due considerations were given in many of the reported works. The model compounds chosen were the simple electrolytes, quaternary ammonium and phosphonium salts, and the dipolar ions, such as the amino acids and peptides. The above classes of compounds display electrostriction through their polar group and hydrophobic hydration through the apolar group. Recently, interest was focused on the chemistry of complex compounds in

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solution<sup>(1-4)</sup> since they provide a rich source of model compounds with the desired structural symmetry. Complex compounds have characteristics that are particularly favorable for the systematic study of the effect of size and charge of the solute ion on the solvent molecules and the resultant ion-solvent interactions. Reported literature on the chemistry of complex compounds in aqueous solution indicate physicochemical studies mainly aimed at finding the effect of various organic ligands on the neighboring solvent molecules. No significant effort seems to have been made to evaluate the role of the central metal ion. It is known that change of the central metal ion significantly changes the nature of coordination bonding in chelate compounds, which is likely to affect the interactions with neighboring solvent molecules. Therefore, we decided to examine the behavior of a series of mixed complexes with the same ligand and identical crystal structure, but with different central metal ions. In our present paper, we report the viscosity of aqueous solutions of the potassium trioxalato complexes of Al(III), Fe(III), Co(III), and Cr(III) between 15 and 35°C. To our knowledge, a systematic study involving the dilute solution viscosity behavior of the above complexes have so far not been reported. In order to compare the behavior of the complexes with respect to their parent metal and ligand ions, we included the salts  $K_2(ox)\cdot H_2O$ ,  $CoCl_2\cdot 6H_2O$ ,  $FeCl_3$ ,  $Al_2(SO_4)_3\cdot 18H_2O$ , and  $CrCl_3\cdot 6H_2O$ , precise viscosity data for dilute solution of which were not available in literature.

## 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 known methods.<sup>(5)</sup> The purification and handling procedure of the complexes were reported in a previous publication.<sup>(6)</sup>  $K_2(ox)\cdot H_2O$  (Ranbauxy, A.R),  $CoCl_2\cdot 6H_2O$  (Merck, G.R),  $Al_2(SO_4)_3\cdot 18H_2O$  (Merck, G.R), and  $CrCl_3\cdot 6H_2O$  (Merck, extra pure) were used as received without further purification. Anhydrous  $FeCl_3$  (S.D.Fine Chemicals) was used for making solution; the concentration of  $FeCl_3$  in solution was estimated by a volumetric method.

### 2.2. Apparatus and Measurements

Preparation of solutions and measurement of densities were carried out as reported earlier.<sup>(6)</sup> The average uncertainty in the density measurement was within  $\pm 1 \times 10^{-5}$  gm-cm<sup>-3</sup>.

Viscosity was measured using a Schott Geräte Ubbelohde viscometer using Schott Geräte AVS 310 measuring unit coupled with a thermostat (CT

1150). The temperature of the thermostat was maintained within  $\pm 0.01^\circ\text{C}$ . The kinetic energy correction term of the viscometer was found to fall within experimental error and, therefore, was neglected. The relative viscosities determined were found to have a precision of 0.05%, which is comparable to that obtained in our earlier work.<sup>(7-10)</sup>

### 3. RESULTS AND DISCUSSION

All the complex compounds studied in the present work are water soluble at normal temperature, with  $\text{K}_3[\text{Al}(\text{ox})_3]$  showing the lowest solubility. The upper concentration range that was available for  $\text{K}_3[\text{Al}(\text{ox})_3]$  at experimental temperatures was about 0.06*m*. In water, these complexes behave as true solutions and, therefore, calculation of their viscosities follow that of simple Newtonian liquid. The relative viscosities of  $\text{K}_3[\text{Al}(\text{ox})_3]\cdot 3\text{H}_2\text{O}$ ,  $\text{K}_3[\text{Fe}(\text{ox})_3]\cdot 3\text{H}_2\text{O}$ ,  $\text{K}_3[\text{Co}(\text{ox})_3]\cdot 3\text{H}_2\text{O}$ ,  $\text{K}_3[\text{Cr}(\text{ox})_3]\cdot 3\text{H}_2\text{O}$ , and  $\text{K}_2(\text{ox})\cdot \text{H}_2\text{O}$  were determined at 15, 25, and  $35^\circ\text{C}$ . The relative viscosities of  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ ,  $\text{Al}_2(\text{SO}_4)_3\cdot 18\text{H}_2\text{O}$ ,  $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$ , and  $\text{FeCl}_3$  were determined at  $25^\circ\text{C}$  only. The value of the relative viscosity  $\eta_r$  was calculated using the relation

$$\eta_r \equiv \frac{\eta}{\eta_0} = \frac{\rho t}{\rho_0 t_0} \quad (1)$$

where  $\eta$ ,  $\rho$ , and  $t$  represent the viscosity, density and flow time, respectively, of the complexes in solution and  $\eta_0$ ,  $\rho_0$ , and  $t_0$  refer to those of pure water. For calculation of relative viscosities of the complex salts, the density values were taken from reported data published earlier.<sup>(6)</sup> The experimental value of the relative viscosity as determined at each concentration is presented in Table I. The experimental relative viscosities of the trioxalato complexes and other salt solutions were evaluated by means of a least-squares fit to the Jones–Dole equation:

$$\eta_r = 1 + AC^{1/2} + BC \quad (2)$$

where  $C$  is the molarity of the solutes in solution. The calculated relative viscosity  $\eta_{r(\text{calc})}$  was obtained by using least square to evaluate the  $A$  and  $B$  coefficients. These data are given at each concentration in Table I. In the absence of stable  $\text{Co}^{3+}$  salts, its  $B$  coefficient was calculated from the  $B$  coefficient found for  $\text{Co}^{2+}$  and the  $B$  coefficient ratio for  $\text{Fc}^{3+}/\text{Fc}^{2+}$ , assuming similar behavior on the basis of close crystal ionic radius (63 and 64 nm for  $\text{Co}^{3+}$  and  $\text{Fe}^{3+}$ , respectively).

The experimental values of the  $A$  and  $B$  coefficients of Eq. (2) and  $\sigma$ , the RMS deviation between the experimental and calculated relative viscosity values for the complexes, are presented in Table II. The coefficient  $A$ , which

Table I. Relative Viscosities Calculated on the Basis of Eq. (1)

$c^a$	$\eta_r$	$\eta_{r(\text{calc})}$	$c^a$	$\eta_r$	$\eta_{r(\text{calc})}$
$K_3[Al(ox)_3] \cdot 3H_2O$			$K_3[Fe(ox)_3] \cdot 3H_2O$		
15°C					
0.01061	1.0066	1.0066	0.01775	1.0101	1.0099
0.02159	1.0122	1.0121	0.03401	1.0176	1.0176
0.03191	1.0169	1.0170	0.04407	1.0222	1.0222
0.04454	1.0229	1.0229	0.06361	1.0305	1.0309
0.05479	1.0277	1.0278	0.07720	1.0374	1.0369
0.06747	1.0355	1.0334	0.09524	1.0448	1.0448
			0.10919	1.0508	1.0508
25°C					
0.01247	1.0082	1.0082	0.01553	1.0097	1.0097
0.02477	1.0150	1.0148	0.03062	1.0176	1.0176
0.03463	1.0198	1.0200	0.04564	1.0251	1.0252
0.04606	1.0253	1.0257	0.06159	1.0331	1.0331
0.05623	1.0315	1.0310	0.07034	1.0373	1.0373
0.06660	1.0363	1.0363	0.08398	1.0440	1.0440
			0.10708	1.0551	1.0551
35°C					
0.01244	1.0088	1.0088	0.01549	1.0104	1.0104
0.02470	1.0161	1.0161	0.03052	1.0191	1.0189
0.03452	1.0217	1.0217	0.04548	1.0268	1.0271
0.04592	1.0280	1.0281	0.06138	1.0356	1.0356
0.05605	1.0337	1.0337	0.07010	1.0404	1.0403
0.06639	1.0394	1.0394	0.08370	1.0474	1.0475
			0.10672	1.0597	1.0595
$K_3[Co(ox)_3] \cdot 3H_2O$			$K_3[Cr(ox)_3] \cdot 3H_2O$		
15°C					
0.02051	1.0096	1.0096	0.01728	1.0082	1.0082
0.03922	1.0168	1.0167	0.03473	1.0147	1.0148
0.05541	1.0225	1.0226	0.04947	1.0204	1.0203
0.07415	1.0296	1.0294	0.06559	1.0259	1.0261
0.09204	1.0352	1.0357	0.07932	1.0313	1.0310
0.10502	1.0405	1.0405	0.09336	1.0357	1.0359
25°C					
0.01359	1.0074	1.0075	0.01724	1.0092	1.0091
0.02603	1.0129	1.0129	0.03260	1.0156	1.0157
0.04066	1.0190	1.0190	0.04243	1.0196	1.0198
0.05508	1.0247	1.0248	0.05430	1.0245	1.0247
0.06718	1.0299	1.0297	0.06347	1.0283	1.0284
0.08119	1.0351	1.0352	0.07416	1.0326	1.0327
0.09038	1.0389	1.0388	0.08425	1.0371	1.0367
35°C					
0.01355	1.0080	1.0079	0.01705	1.0096	1.0096
0.02596	1.0139	1.0138	0.03240	1.0169	1.0168

Table I. Continued

$c^a$	$\eta_r$	$\eta_{r(\text{calc})}$	$c^a$	$\eta_r$	$\eta_{r(\text{calc})}$		
0.04054	1.0203	1.0205	0.04243	1.0210	1.0212		
0.05491	1.0266	1.0269	0.05410	1.0267	1.0265		
0.06697	1.0322	1.0322	0.06326	1.0302	1.0306		
0.08094	1.0383	1.0382	0.07395	1.0351	1.0353		
0.09010	1.0424	1.0422	0.08403	1.0401	1.0397		
$c$	$\rho$	$\eta_r$	$\eta_{r(\text{calc})}$	$c$	$\rho$	$\eta_r$	$\eta_{r(\text{calc})}$
$\text{K}_2(\text{COO})_2 \cdot \text{H}_2\text{O}$ 15°C				$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ 25°C			
0.02294	1.00200	1.0060	1.0064	0.01487	0.99879	1.0073	1.0073
0.03432	1.00339	1.0093	1.0088	0.02898	1.00040	1.0132	1.0132
0.04461	1.00465	1.0111	1.0109	0.04299	1.00203	1.0187	1.0188
0.05588	1.00603	1.0131	1.0131	0.05501	1.00341	1.0237	1.0236
0.06759	1.00746	1.0154	1.0153	0.06794	1.00489	1.0286	1.0286
0.07918	1.00887	1.0172	1.0175	0.08090	1.00639	1.0337	1.0337
$\text{K}_2(\text{COO})_2 \cdot \text{H}_2\text{O}$ 25°C				$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ 25°C			
0.02291	0.99986	1.0071	1.0073	0.01812	0.99936	1.0140	1.0143
0.03427	1.00123	1.0102	1.0101	0.03601	1.00157	1.0270	1.0266
0.04454	1.00247	1.0127	1.0127	0.05141	1.00348	1.0371	1.0370
0.05579	1.00383	1.0154	1.0152	0.06785	1.00551	1.0481	1.0479
0.06749	1.00524	1.0180	1.0179	0.08314	1.00740	1.0582	1.0579
0.07905	1.00663	1.0200	1.0205	0.09851	1.00930	1.0672	1.0680
$\text{K}_2(\text{COO})_2 \cdot \text{H}_2\text{O}$ 35°C				$\text{FeCl}_3$ 25°C			
0.02284	0.99682	1.0080	1.0080	0.01555	0.99920	1.0137	1.0133
0.03416	0.99817	1.0110	1.0111	0.03095	1.00127	1.0243	1.0248
0.04440	0.99939	1.0140	1.0139	0.04678	1.00339	1.0363	1.0367
0.05561	1.00072	1.0168	1.0168	0.06260	1.00550	1.0479	1.0480
0.06728	1.00212	1.0199	1.0198	0.07884	1.00765	1.0595	1.0597
0.07880	1.00349	1.0227	1.0228	0.09700	1.01000	1.0733	1.0726
$c$	$\rho$	$\eta_r$	$\eta_{r(\text{calc})}$				
$\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ 25°C							
0.00919	1.00029	1.0234	1.0231				
0.01785	1.00323	1.0417	1.0422				
0.02591	1.00598	1.0592	1.0595				
0.03397	1.00871	1.0765	1.0767				
0.04229	1.01153	1.0944	1.0943				
0.05045	1.01425	1.1121	1.1115				

<sup>a</sup>Molarity, mol·L<sup>-1</sup>.

**Table II.** *A* and *B* coefficients of Eq. (2) for the Complexes at Three Temperatures

	$K_3[A(ox)_3]$	$K_3[Fe(ox)_3]$	$K_3[Cr(ox)_3]$	$K_3[Co(ox)_3]$	$K_2(ox)$
15°C					
<i>A</i>	0.022	0.021	0.020	0.022	0.019
<i>B</i>	0.412	0.401	0.319	0.316	0.154
$10^4\sigma$	0.82	2.42	1.78	2.27	3.00
25°C					
<i>A</i>	0.022	0.022	0.022	0.023	0.020
<i>B</i>	0.461	0.447	0.361	0.355	0.189
$10^4\sigma$	2.86	0.38	2.16	1.07	2.40
35°C					
<i>A</i>	0.023	0.023	0.022	0.022	0.020
<i>B</i>	0.503	0.489	0.398	0.394	0.218
$10^4\sigma$	0.41	1.51	2.74	1.69	0.82
25°C					
	$CoCl_2$	$CrCl_3$	$FeCl_3$	$Al_2(SO_4)_3$	
<i>A</i>	0.016	0.023	0.022	0.050	
<i>B</i>	0.361	0.616	0.678	1.985	
$10^4\sigma$	0.58	4.13	4.30	3.74	

results from ion-ion interactions, falls between 0.016 to 0.050 for all solutions of the complex salts and the other divalent and trivalent electrolytes. Despite using the least-squares method for evaluation of the experimental *A* coefficients, no trend in its variation with temperature could be obtained, possibly due to limitations in experimental precision. Therefore, a discussion of the *A* coefficients of individual complexes and their variation are not attempted here.

The *B* coefficient measures the size and shape effects of the solutes as well as structural modifications induced by solute-solvent interactions and is the major contributor to relative viscosity above concentrations of 0.005 mol-dm<sup>-3</sup>. In structured solvents, a solute with or without a primary solvation shell can apparently affect the orientation of the solvent molecules in relatively large distances, thereby, influencing the *B* coefficient and its variation. It is seen from Table II that coefficient *B* of all the above complexes and other simple electrolytes are positive and large and increase with a rise in temperature.

In order to evaluate the various factors contributing to the *B* coefficient, it is necessary to calculate the ionic *B* coefficient of the individual complex anions. This can be carried out by assuming the ionic *B* coefficient of K<sup>+</sup> and Cl<sup>-</sup> ions to be equal, as proposed by Kaminsky,<sup>(11)</sup> This assumption is based on the fact that the K<sup>+</sup> and Cl<sup>-</sup> ions have nearly the same mobility indicating a comparable size for the two ions in solution and *B* coefficients

are known to be size-dependent. Although the method of Kaminsky for splitting the  $B$  coefficient is not beyond criticism, it may be accepted for the present systems, since  $B$  coefficients of the trivalent metal ions and the complex anions are much larger compared to the  $B$  coefficients of either  $K^+$  or  $Cl^-$  ions and an error associated with the method of splitting of the  $B$  coefficient will not appreciably change the general discussions in the present case. The values of the ionic  $B$  coefficient for the complex anions and the trivalent metal ions thus obtained are listed in Table III.

From Table III it can be seen that the  $B$  coefficient of all the complex anions are positive and large but smaller compared to the trivalent parent metal ions. In addition, since  $(ox)^{2-}$  has a positive and large  $B$  coefficient, it is clear that complex formation is associated with a reduction in the magnitude of the  $B$  coefficient. The change associated in the  $B$  coefficient due to complex formation  $\Delta B$  can be calculated as

$$\Delta B = B_{ion}\{[M(ox)_3]^{3-}\} - B_{ion}[(M)^{3+}] - 3B_{ion}[(ox)^{2-}] \quad (3)$$

The numerical values calculated are presented in Table III. It can be seen that the values of  $\Delta B$  are all negative and large and are nearly the same irrespective of the differences in the  $B$  coefficient of the parent metal ions

**Table III.** Ionic  $B$  Coefficients and Related Quantities

Ions	°C	$B_{ion}$	$\Delta B_{ion}^a$	$(B_{ion} - 2.5 V_2^0 \times 10^{-3})$
[Al(ox) <sub>3</sub> ] <sup>3-</sup>	15	0.472		0.079
	25	0.482	-0.829	0.091
	35	0.489		0.090
[Fe(ox) <sub>3</sub> ] <sup>3-</sup>	15	0.462		0.045
	25	0.468	-0.819	0.050
	35	0.477		0.051
[Cr(ox) <sub>3</sub> ] <sup>3-</sup>	15	0.379		-0.079
	25	0.382	-0.843	-0.076
	35	0.383		-0.088
[Co(ox) <sub>3</sub> ] <sup>3-</sup>	15	0.376		-0.079
	25	0.376	-0.835	-0.083
	35	0.379		-0.089
Ox <sup>2-</sup>	15	0.174		0.046
	25	0.196		0.064
	35	0.213		0.080
Co <sup>2+</sup>	25	0.375		0.329
Al <sup>3+</sup>	25	0.723		0.839
Fe <sup>3+</sup>	25	0.699		0.822
Co <sup>3+</sup>	25	0.623		0.741
Cr <sup>3+</sup>	25	0.637		0.749

<sup>a</sup>See Eq. (3).

in the complexes. In a previous communication, we showed that  $\Delta V_{2(\text{ion})}^{\circ}$ , the change in partial ionic volume due to complex formation, was positive and large for all the complex anions. It was considered that the large positive  $\Delta V_{2(\text{ion})}^{\circ}$  resulted from (1) a net decrease in the sum total of the electrical charges of the ligands and bare metal ion prior to complex formation, (2) an increase in intrinsic volume through complex formation, and (3) a decrease in the electrical charge density due to factors (1) and (2). The same factors seem to be responsible for a large negative  $\Delta B$  in the present cases. The positive contribution is due to an increase in intrinsic volume to viscosity being negligible compared to the negative contribution due to decrease in electrical charge density resulting in reduced ion-solvent interactions.

In terms of the contribution of the primary and secondary hydration and the structure broken region of the ionic cosphere of the Frank and Wen<sup>(12)</sup> model of ionic hydration, large positive  $B$  coefficients could be observed when

$$\eta^{\text{obs}} + \eta^{\text{sec}} \gg \eta^{\text{st}}$$

(cf. Stokes and Mills<sup>(13)</sup>), where  $\eta^{\text{obs}}$  is the positive viscosity increment due to the size of the ion, including its primary hydration shell, and  $\eta^{\text{sec}}$  is viscosity increment due to the less strongly held secondary hydration of multiply charged ions.  $\eta^{\text{st}}$  is the negative contribution to viscosity  $B$  coefficient due to structure-breaking in the ionic cosphere.

It is seen from the Table III, that the  $B$  coefficient of all the complex anions show increases with a rise in temperature. It is known that the hydrodynamic contribution due to  $\eta^{\text{obs}}$  is not affected by change of temperature. Therefore, a significant increase in  $B$  coefficient with a rise in temperature is possible only when  $\eta^{\text{sec}} \ll \eta^{\text{st}}$ , since, with rise in temperature, the positive contribution of  $\eta^{\text{sec}}$  would disappear and the negative contribution from  $\eta^{\text{st}}$  would become less negative due to less structural order at higher temperatures. On the other hand, when  $\eta^{\text{sec}} \approx \eta^{\text{st}}$ , the decrease in  $\eta^{\text{sec}}$  due to a rise in temperature is annulled by the decrease in negative contribution due to  $\eta^{\text{st}}$ , and the  $B$  coefficient is only marginally affected. In the present study, the anions  $[\text{Al}(\text{ox})_3]^{3-}$  and  $[\text{Fe}(\text{ox})_3]^{3-}$  seems to fall in the former class and the anions  $[\text{Cr}(\text{ox})_3]^{3-}$  and  $[\text{Co}(\text{ox})_3]^{3-}$  fall in the latter category, showing only marginal increase in the  $B$  coefficient with a rise in temperature.

In a previous communication<sup>(6)</sup> we showed that on the basis of  $K_s^{\circ}$  and  $V_2^{\circ}$  the degree of interactions between complex anions and water molecules follow the order  $[\text{Al}(\text{ox})_3]^{3-} > [\text{Fe}(\text{ox})_3]^{3-} > [\text{Co}(\text{ox})_3]^{3-} > (=) [\text{Cr}(\text{ox})_3]^{3-}$ . If the magnitude of ionic  $B$  coefficient is taken as the criteria for ion-solvent interactions, then, with marginal difference, the same sequence seems to follow for all the experimental temperatures in the present study.



For ideal spherical suspensions without structural interactions with solvent molecules, the hydrodynamic volume  $V_h$  could be calculated from the  $B$  coefficient by the Einstein equation

$$B = 0.0025 V_h$$

The quantity  $V_h$  comprises the intrinsic volume of the solute ions, together with any solvent molecules, which are immobilized by the solute ions and can be considered as a part of the mobile entity. This, however, should be considered as a minimum estimate for ions associated with a significant amount of electrostriction. Desnoyers and Perron<sup>(14)</sup> have suggested that the deviation from ideal behavior could be used to classify ions on the basis of  $B - 0.0025 V_2^0$ , where  $V_2^0$  is the partial molar volume of the solute ion at infinite dilution. According to these authors, a positive value of  $B - 0.0025 V_2^0$  would correspond to overall structure-making; a negative value would indicate structure-breaking. For large ions, such as the complexes in the present study, the Einstein relation could be considered as a fair approximation in terms of spherical suspension and, therefore, Desnoyers–Perron method of classification could suitably be applicable. Values of  $B - 0.0025 V_2^0$  for the complex anions and also for the ligand and trivalent bare metal ions are given in Table III. It is seen that for the trivalent bare metal ions very large positive deviations are obtained followed by small positive deviation for the ligand ion. For the complex anions  $[\text{Al}(\text{ox})_3]^{3-}$  and  $[\text{Fe}(\text{ox})_3]^{3-}$ , small positive deviations are observed, while for  $[\text{Co}(\text{ox})_3]^{3-}$  and  $[\text{Cr}(\text{ox})_3]^{3-}$  small negative deviations are observed in all the experimental temperatures.

It is interesting to note that the  $B$  coefficients of  $[\text{Co}(\text{ox})_3]^{3-}$  and  $[\text{Cr}(\text{ox})_3]^{3-}$  are much smaller compared to  $[\text{Al}(\text{ox})_3]^{3-}$  and  $[\text{Fe}(\text{ox})_3]^{3-}$  ions. Since, size of the ions are so important in determining the magnitude of the viscosity  $B$  coefficient, it is necessary to look at the crystal molecular volume of the complexes. In our earlier communication,<sup>(6)</sup> we pointed out that the crystal data for the complexes<sup>(15–17)</sup> suggest distorted octahedral identical crystal structure for all the complexes with less than  $1 \text{ cm}^3\text{-mol}^{-1}$  variation in the overall dimension in the crystalline state. It is, therefore, not possible to explain the large differences observed in the  $B$  coefficient of the complex anions from the dimension and shape in the crystalline state. The differences in partial molar volume and in adiabatic compressibility of these complexes were explained by us as due to differences in the residual charges of the complexes distributed on the periphery of the complex anions. The observed differences in the  $B$  coefficient of the above complexes strengthen our earlier view.

Of the four complex anions included in the present study, the viscosity behavior of trioxalato aluminate and trioxalato ferrate differ significantly

from those of trioxalato cobaltate and trioxalato chromate. The former two complex anions are characterized by a larger  $B_{\text{ion}}$  and  $\Delta B_{\text{ion}}/\Delta T$  ( $0.85 \times 10^{-3}$  and  $0.75 \times 10^{-3} \text{ dm}^3\text{-mol}^{-1}\text{-K}^{-1}$  for aluminate and ferrate, respectively), whereas the later two complex anions are characterized by a smaller  $B_{\text{ion}}$  and  $\Delta B_{\text{ion}}/\Delta T$  ( $0.20 \times 10^{-3}$  and  $0.15 \times 10^{-3} \text{ dm}^3\text{-mol}^{-1}\text{-K}^{-1}$  for chromate and cobaltate, respectively). Since orientation of the ligands in the crystalline state and the crystal volume of all of the above triply charged complex anions are identical, it is only reasonable to assume that the nature of the chelate ring plays a vital role in deciding the viscosity behavior of these complex anions in solution.

As we have pointed out,<sup>(6)</sup> earlier studies<sup>(18)</sup> indicated rapid ligand exchange in the case of potassium trioxalato aluminate and potassium trioxalato ferrate due to their partial ionic character,<sup>(19)</sup> which is absent in the case of highly chelating complexes,<sup>(20)</sup> such as trioxalato chromate and trioxalato cobaltate, where formation of an intermediate activated complex through ring opening and closing is restricted due to stability of the complex.<sup>(21)</sup>

It is, therefore, reasonable to assume that due to their partial ionic character and ring opening and closing, the residual surface charge densities of trioxalato aluminate and trioxalato ferrate are higher than those of trioxalato chromate and trioxalato cobaltate, giving rise to stronger ion-dipole interactions with solvent molecules, which results in larger  $B_{\text{ion}}$  and  $\Delta B_{\text{ion}}/\Delta T$  values. A highly stable chelate ring with equal surface area has less surface charge density, resulting in reduced interactions with cosphere solvent molecules, as in the case of trioxalato chromate and trioxalato cobaltate in the present study. Physicochemical similarities between cobalt and chromium complexes observed earlier<sup>(22)</sup> is reflected in the viscosity  $B$  coefficient and its variation with temperature of the trioxalato chromate and trioxalato cobaltate in the present study.

#### 4. CONCLUSION

Interaction between complex ions and solvent molecules are reflected in the magnitude of their viscosity  $B$  coefficient of the Jones-Dole equation. For mixed complexes, the  $B$  coefficient and its temperature variation depends not only on the size of the complex ions but also on the central metal ion, which influences the nature of the chelate bond and the stability of the chelate ring.

#### ACKNOWLEDGMENTS

The authors wish to thank Director R. R. L. Jorhat for his cooperation in the publication of this paper.

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