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Dielectric Properties of Some Metal 1,3-Diketonates and Their Molecular Complexes with Iodine: Evidence of Solute-Solvent Interaction

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ABSTRACT

The dipole moment values of M(acac)$_n$, [M = Be(II), Al(III), Fe(III), Cr(III), VO(IV), Co(III), Zr(IV), and Th(IV)], M(X-acac)$_n$ [X = Cl, Br, I], M(BA)$_n$ [M = Cu(II), Al(III), Cr(III), and Co(III)], M(DBM)$_n$ [M = Cu(II), Pd(II), and Al(III)] and their molecular complexes with iodine have been determined in different solvents by Guggenheim, refractive index, and dielectric titration plot methods. The dielectric titration technique indicates a 1:1 stoichiometry of these complexes. The interaction between these donors with solvents (CCl_4 and C_6H_6) has also been obtained by calculating U_{ind} by ($U_{ind} = U_{sol} - U_{inert}$). These data show that the molecular interaction between polar solutes and nonpolar aromatics is governed by dipole-induced dipole electrostatic attraction. The dipole moment obtained

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by charge-transfer (μ_{DA}) has also been calculated and it was found that its value increases with an increase in the extent of interaction between donor and acceptor. These data further support the pseudoaromatic character of the metal 1,3-diketonate chelate ring.

INTRODUCTION

We have reported through spectrophotometric [1], conductometric [2], refractometric [3], and differential refractometric [4, 5] methods that some metal 1,3-diketonates form molecular complexes with iodine by the donation of π-electrons of these chelate rings to the σ^*-orbital of iodine. Recently Sahai and Badon [6] and Sahai and Verma [7] studied the dielectric properties of Be(II), Al(III), Cr(III), Co(III), Cu(II), Zr(IV), and Th(IV) acetylacetonates [$M(acac)_n$] and some of their nitro derivatives. They also studied the interaction of $M(acac)_n$ with I_2 in carbon tetrachloride using the refractive index method. In this paper an attempt is made to study the dielectric behavior of metal 1,3-diketonates, their γ-substituted nitro and halogen derivatives, and their molecular complexes with iodine using the Guggenheim [8] and refractive index methods in order to investigate the geometry and the nature of solute-solvent interactions.

EXPERIMENTAL AND DATA ANALYSIS

Acetylacetonates of Be(II) [9], Al(III) [10], Fe(III) [11], Cr(III) [12], VO(IV) [11], Co(III) [13], Zr(IV) [14], and Th(IV) [15]; benzoylacetonates [16] of Cu(II), Al(III), Cr(III), and Co(III); and dibenzoylmethanates [16] of Cu(II), Pd(II), and Al(III) were prepared and purified as reported in the literature. AR grade iodine was resublimed before use. All the solvents were of AR grade and were purified as reported in the literature [17].

The apparatus used and the method of experimentation are essentially the same as reported earlier [8]. The dipole moments of $M(acac)_n$, M(X-acac), $M(BA)_n$, and $M(DBM)_n$ have been calculated using the Guggenheim method [8]. The dipole moments of $M(acac)_n$-I_2, $M(BA)_n$-I_2, and $M(DBM)_n$-I_2 complexes have also been calculated by the Guggenheim method [8] by calculating a_ϵ and a_n parameters as described earlier [7].

RESULTS AND DISCUSSION

From Table 1 it is evident that acetylacetone has a greater dipole moment than chelated metal acetylacetonates. This may be due to the nonplanar (assymmetric) structure of acetylacetone. However, the decrease in the dipole moment after chelation may be due to the enhanced symmetry in the structure of the chelate. The similar order of magnitude of the dipole moment of Al(III), Cr(III), and Co(III) may be due to the similar symmetry (octahedral structure). The slight difference in dipole moment values may be due to differences in their respective electronegativities and may also be due to M(dπ)-O(pπ) bonding in some of these chelates. From Table 1 it is also clear that γ-substituted de-

TABLE 1. Dipole Moment (μ) of Some Metal 1,3-Diketonates and Their γ-Substituted Derivatives in CCl_4 at 30°C

	$\mu \times 10^{18}$ esu		
	Refractive index method	Guggenheim method	Dielectric titration plot of the metal 1,3-diketonate-I_2 complex
H(acac)	2.63	2.68	
$Be(acac)_2$	0.88	0.76	0.71
$Be(Cl\text{-}acac)_2$	0.92	0.84	
$Be(Br\text{-}acac)_2$	0.90	0.79	
$Cu(acac)_2$	0.82	0.80	0.76
$Cu(Cl\text{-}acac)_2$	1.10	1.20	
$Cu(Br\text{-}acac)_2$	0.89	0.91	
$Al(acac)_3$	1.30	1.35	1.31
$Al(Cl\text{-}acac)_3$	1.58	1.65	
$Al(Br\text{-}acac)_3$	1.22	1.20	
$Fe(acac)_3$	0.92	0.95	0.90
$Fe(Cl\text{-}acac)_3$	1.28	1.39	
$Fe(Br\text{-}acac)_3$	1.10	1.10	

(continued)

TABLE 1 (continued)

	$\mu \times 10^{18}$ esu		
	Refractive index method	Guggenheim method	Dielectric titration plot of the metal 1,3-diketonate-I_2 complex
Co(acac)$_3$	1.25	1.20	1.10
Co(Cl-acac)$_3$	1.40	1.45	
Co(Br-acac)$_3$	1.35	1.29	
Cr(acac)$_3$	1.44	1.10	1.05
Cr(Cl-acac)$_3$	1.51	1.35	
Cr(Br-acac)$_3$	1.49	1.20	
VO(acac)$_2$	0.80	0.89	0.80
VO(Cl-acac)$_2$	1.10	1.13	
VO(Br-acac)$_2$	0.95	1.10	
Cu(BA)$_2$	1.36	1.32	1.20
Al(BA)$_3$	1.98	1.93	1.84
Cr(BA)$_3$	1.62	1.58	1.40
Co(BA)$_3$	1.38	1.32	1.20
Cu(DBM)$_2$	1.38	1.32	1.20
Pd(DBM)$_2$	1.69	1.64	1.32
Al(DBM)$_3$	1.75	1.67	1.40

rivatives possess greater dipole moments than chelated metal acetylacetonates. This may be explained as follows.

When hydrogen in the γ-position of the acetylacetonate ring is replaced by a chloro or bromo atom, a shift in electron density away from the ring takes place due to the inductive effect of the halogen, leaving a net positive charge on the ring. The halogen group acts as a π-acceptor. Thus, there is a slight change in the overall geometry of the chelate ring, resulting in a change in the dipole moment. The greater dipole moment of these γ-substituted halogen derivatives confirms the greater asymmetric nature of these chelates. The greater dipole moment of M(Cl-acac)$_n$ than of M(Br-acac)$_n$ may be explained on the basis of the electronegativity scale. The greater electronegativity of the Cl group causes a greater π-electron shift toward the Cl atom. This leads to a greater asymmetric nature of the chelate which causes a higher dipole moment of $M(Cl\text{-}acac)_n$ than of $M(Br\text{-}acac)_n$.

The dipole moment of $M(acac)_n\text{-}I_2$, $M(BA)_n\text{-}I_2$, and $M(DBM)_n\text{-}I_2$ complexes are recorded in Tables (2 and 3). From these tables it is evident that there was an appreciable increase in dipole moment after complexation. From this increase it may be interpreted that $M(acac)_n$, $M(BA)_n$, and $M(DBM)_n$ form the charge-transfer complexes with iodine. This is in support of earlier spectrophotometric [1], conductometric [2, 18], and refractometric [3-5] studies. The stoichiometry of $M(acac)_n\text{-}I_2$ complexes has been determined by using the dielectric titration technique. From Fig. 1 it is clear that these have a 1:1 stoichiometry. From these titration plots the dipole moment of complexes and their polar components [$M(acac)_n$, $M(BA)_n$, and $M(DBM)_n$] can also be calculated by using the method of Price [19, 20]. Dipole moment data thus calculated are recorded in Tables 1-3. These are consistent with the data calculated by other methods. The dipole moment due to donor-acceptor interaction ($\underline{\mu}_{DA}$) has been calculated from

$$\underline{\mu}_C = \underline{\mu}_D + \underline{\mu}_A + \underline{\mu}_{DA} \qquad (1)$$

where D refers to the donor and A to the acceptor and $\underline{\mu}_C$ is the overall dipole moment of the complex [19]. In the present complexes, the dipole moment of acceptor I_2 is zero. $\underline{\mu}_{DA}$ and the equilibrium constant (K_1) of $M(acac)_n\text{-}I_2$ complexes are listed in Table 2. From Table 2 it is evident that $\underline{\mu}_{DA}$ of $Al(acac)_3\text{-}I_2$ is greater than that of $Be(acac)_2\text{-}I_2$. This indicates that the interaction of $Al(acac)_3\text{-}I_2$ is stronger than that of the $Be(acac)_2\text{-}I_2$ complex. This is consistent with the K_1 values of these complexes obtained from the spectrophotometric method by Singh and Sahai [1].

It has been noted that when some $M(acac)_n$, $M(BA)_n$, and $M(DBM)_n$ are dissolved in CCl_4 and C_6H_6 separately, they possess different dipole moments (Table 4). The dipole moment in CCl_4 was found to be less than in benzene. This difference in dipole moment may result from the molecular interaction between solute and nonpolar aromatics (benzene). Thus the dipole moment induced as a result of molecular interaction (μ_{ind}) can be calculated as $\mu_{ind} = \mu_{sol} - \mu_{inert}$ where μ_{sol} and μ_{inert} are the dipole moments of solute in the interacting solvent (ben-

TABLE 2. Dipole Moment of the Complex (μ_C), Dipole Moment Due to Charge-Transfer Interaction (μ_{DA}) of $M(acac)_n$-I_2 Complexes, and Equilibrium Constant (K_1) of These Interactions Calculated by Different Methods in Carbon Tetrachloride at 30°C

	$M(acac)_n$-I_2, $\mu \times 10^{18}$ esu						
	Be(II)	Al(III)	Cr(III)	Co(III)	Ni(II)	Fe(III)	VO(IV)
Refractive index method	1.54	2.14	2.40	2.45	1.75	1.97	2.12
Guggenheim method	1.50	2.20	2.42	2.52	1.80	2.00	2.21
Dielectric titration plot method	1.55	2.23	2.50	2.58	1.85	1.95	2.12
μ_{DA}	0.75	0.84	1.32	1.32	1.00	1.05	1.32
	Equilibrium Constant, K_1 (L/mol)						
Spectrophotometric values	10.0 [1]	76.10 [1]	-	-	-	-	-
Differential refractometric values	20.0 [4]	172.41 [4]	833.33 [4]	1176.47	-	256.41 [4]	952.38 [4]

TABLE 3. Dipole Moment of the Complex (μ_C) and Dipole Moment Due to Charge-Transfer Interaction (μ_{DA}) of $M(BA)_n$-I_2 and $M(DBN)_n$-I_2 Complexes Calculated by Different Methods in Carbon Tetrachloride at 30°C

	$\mu \times 10^{18}$ esu						
	$M(BA)_n$-I_2				$M(DBM)_n$-I_2		
	Cu(II)	Al(III)	Cr(III)	Co(III)	Cu(II)	Pd(II)	Al(III)
Refractive index method	2.80	3.20	3.18	3.56	3.80	3.01	3.92
Guggenheim method	2.68	3.02	3.00	3.20	3.40	2.92	3.25
Dielectric titration plot method	2.85	3.20	3.18	3.52	3.82	3.04	3.98
μ_{DA}	1.56	1.27	1.60	2.30	2.50	1.60	2.31
	Equilibrium Constant K_1 (L/mol)						
Differential refractometric method	320	270	906	1241	1505.04	785.94	1080

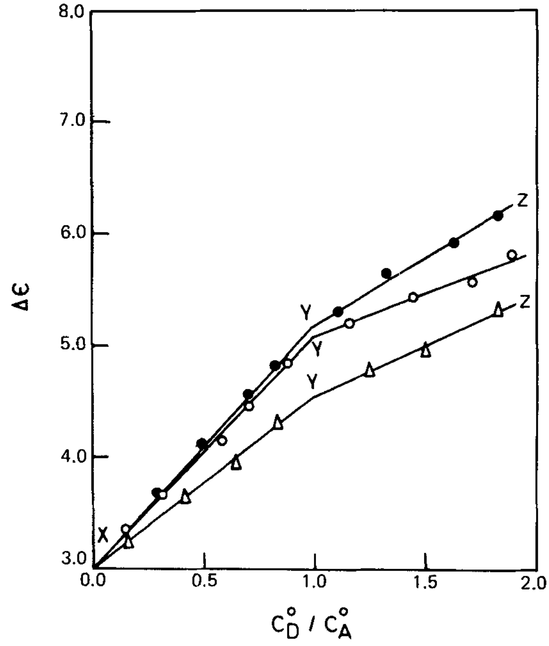

FIG. 1. Dielectric titration plots for the interaction of some metal-acetylacetonates with iodine in CCl_4 at 30°C: $Al(acac)_3$-I_2 (●), $VO(acac)_2$-I_2 (○), $Be(acac)_2$-I_2 (△).

zene) and in the inert solvent, respectively [21]. Similar observations on the metal 1,3-diketonates-solvent interactions were made using differential refractometric and conductometric techniques [5]. Calculated μ_{ind}, μ_{sol}, and μ_{inert} are recorded in Table 4. It is generally considered that the more polar the solute, the larger is the expected increase in its dipole moment values. This is clear from the dipole moment values of solutes (μ_{inert}). Hence it is concluded that the nature of the interaction in $M(acac)_n$, $M(BA)_n$, and $M(DBM)_n$ with benzene is governed by dipole-induced electrostatic attraction.

TABLE 4. Dipole Moment Data of Some Metal 1,3-Diketonates in Different Solvents and Induced Dipole Moment at 30°C.

	$\mu \times 10^{18}$ esu		
Solute	μ_{inert} (CCl_4)	μ_{sol} (benzene)	μ_{ind}[a]
$Be(acac)_2$	0.86	0.96	0.10
$Cu(acac)_2$	0.80	0.90	0.10
$Fe(acac)_3$	0.95	1.10	0.15
$Cr(acac)_3$	1.05	1.27	0.22
$Co(acac)_3$	1.10	1.39	0.29
$Al(acac)_3$	1.35	1.68	0.33
$Cu(BA)_2$	1.32	1.52	0.20
$Al(BA)_3$	1.93	2.24	0.31
$Cr(BA)_3$	1.58	1.81	0.23
$Co(BA)_3$	1.32	1.47	0.15
$Cu(DBM)_2$	1.32	1.47	0.15
$Pd(DBM)_2$	1.64	1.89	0.25
$Al(DBM)_3$	1.67	1.96	0.29

[a] $\mu_{ind} = \mu_{sol} - \mu_{inert}$.

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