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Solvation of Metal Acetylacetonate in Organic Solvents

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Synopsis. The velocities of ultrasonic waves in solutions of metal acetylacetonate in organic solvents were measured with an ultrasonic interferometer operating at 4MHz at 5 and 15 °C. The solvation behavior was marked in the $[\mathrm{Mg(acac)_2}]$-methanol system. The results are compared with those of such different methods as IR and NMR spectroscopies.

The behavior of metal acetylacetonates in organic solvents has been the subject of considerable interest in various areas. Many of the experimental results of the metal acetylacetonates in solution have been interpreted on the basis of the hydrogen-bonding between the complexes and the solvent, or of the hydration/solvation of the complexes.[1—4] For example, Yamamoto *et al.* have related the heat of solution of cobalt(III) acetylacetonate in alcohols and in water to solvation phenomena of the solute.

In relation to our previous study of the hydration of cobalt and iron complexes in aqueous media,[5] metal acetylacetonates attract our attention because of the following facts; they are large complexes without electric charge and the acetylacetones coordinated to the central metal atom sterically hinder the approach of the solvent molecules. The lack of electric charge and the steric hindrance are the unfavorable factors for electrostrictive solvation.

The present study deals with the determination of the degree of solvation of such acetylacetonates as $[\mathrm{Be(acac)_2}]$, $[\mathrm{Mg(acac)_2}]$, and $[\mathrm{Co(acac)_3}]$ in various organic solvents. The same study in aqueous solutions will also be necessary, but is impossible owing to the insufficient solubility of the complexes. The degree of solvation was determined from the adiabatic compressibilities of the solutions. It should be kept in mind that in the present method the term "solvation" means the existence of a certain incompressible region in the solution, while the bulk solvents in solution are assumed to be compressible.

All of the metal acetylacetonates are those commercially available and were used without further purification, except for $[\mathrm{Be(acac)_2}]$, which was purified once from a solution in acetone. The organic solvents used were acetone, acetylacetone, benzene, methanol, and chloroform. The first three solvents were purified by distillation after suitable treatments. Methanol and chloroform were of guaranteed and spectral grades, respectively.

The adiabatic compressibilities of the solutions were obtained by measurement of the ultrasonic velocities using an ultrasonic interferometer operating at 4 MHz. Details of the experimental apparatus and the method of determination of the solvation number are essentially the same as before.[5,6] Preliminary experiments revealed that as expected, $[\mathrm{Co(acac)_3}]$ is not solvated in benzene at 30 °C. Measurements were therefore carried out at 15 and 5 °C. But the experiments at 5 °C were very limited by the low solubilities of the metal acetylacetonates at this temperature.

The results are summarized in Table 1, where K_m is the (relative) partial molar compression of the solute and the subscript zero refers to infinite dilution. For $K_\mathrm{m}>0$, K_m becomes the molar solvation volume (cm^3/mol). For $K_\mathrm{m}<0$, it signifies the non-existence of an incompressible region in the solution and in this case, the values of K_m represent the quantities related to the compressibility of the solute in solution.[7] In the present paper, however, the cases of negative values of K_m0 will be excluded from the discussion below.

TABLE 1. K_m0 (ml/mol) FOR THE METAL ACETYLACETONATES

		$[\mathrm{Be(acac)_2}]$	$[\mathrm{Co(acac)_3}]$	$[\mathrm{Mg(acac)_2}]$
5 °C	$\mathrm{CH_3OH}$	10	35	102
	$\mathrm{CH_3COCH_3}$	(−66)	—	—
	$\mathrm{CHCl_3}$	(−113)	(−199)	—
15 °C	$\mathrm{CH_3OH}$	(−11)	0	53
	$\mathrm{CH_3COCH_3}$	(−17)	0	—
	$\mathrm{CHCl_3}$	(−154)	(−160)	—
	$\mathrm{CH_3COCH_2COCH_3}$	(−143)	(−96)	—
	$\mathrm{C_6H_6}$	(−122)	−126)	—

Table 1 shows that only methanol can solvate with metal acetylacetonates and that solvation to $[\mathrm{Mg(acac)_2}]$ is more marked than to $[\mathrm{Be(acac)_2}]$ and $[\mathrm{Co(acac)_3}]$. The solvation numbers calculated from the posivite values of K_m0 are shown in Table 2.

TABLE 2. SOLVATION NUMBER IN METHANOL (mol/mol)

	$[\mathrm{Be(acac)_2}]$	$[\mathrm{Co(acac)_3}]$	$[\mathrm{Mg(acac)_2}]$
5 °C	0.2	0.8	2.6
15 °C	N.S.	N.S.	1.3

N.S.: non-solvated

The results for the solutions in benzene are reasonable, since benzene can hardly solvate under ordinary conditions.

The present results in methanol and in chloroform are compared with those given by the different methods. The IR spectra obtained by Davis and Fackler,[2] using deuteriochloroform ($\mathrm{CDCl_3}$) in carbon tetrachloride and methanol in carbon tetrachloride as the solvents, give an indication that no or very weak hydrogen-bonding occurred with the tetrahedral bis metal ketoenolate complexes, like $[\mathrm{Be(acac)_2}]$, that stronger hydrogen-bonding to the planar bis complexes occurred and that for tris complexes the interaction occurred with both deuteriochloroform and methanol. In addition, from NMR techniques, the hydrogen-bonding interaction of [Co(acac)$_3$] and [Cr(acac)$_3$] with the solvent in the mixture of chloroform and carbon tetrachloride was observed.[3] The vapor pressure measurement showed that the rareearth acetylacetonates form disolvate with methanol but not with chloroform.[8]

For the solvent methanol, all of these results, together with the present work, agree with one another, whereas some disagreements exist for [Co(acac)$_3$] and the solvent chloroform. These disagreements arise partially from the fact that the hydrogen-bonding interactions detected by IR and NMR spectroscopies are not always strong enough to correspond to the formation of an incompressible region in the solution or of the solvate in solid form.

The solvation numbers for [Mg(acac)$_2$] given in Table 2 suggest that the solvated methanol occupies the two vacant sites on the opposite side of the planar structure of the complex. According to the model of Davis and Fackler,[2] chloroform and methanol can form hydrogen-bonding to the oxygen atoms of the chelate in bis metal β-ketoenolate, but the present work does not give any direct information of the position of the solvated methanol.

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