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HEATS OF SOLUTION OF COBALT(III) ACETYLACETONATE IN ALCOHOLS AND WATER

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Heats of solution of cobalt(III) acetylacetonate in alcohols and water were measured and the results were related to the number of hydroxyl groups and the cohesive energy densities of solvents. Heats of solution of the same chelats were also measured in dilute carbon tetrachloride solutions of alcohols. From the results, it was found that alcohols can exist completely as monomer at an extremely low concentration range.

Behavior of trivalent metal acetylacetonates in various nonaqueous solvents has been investigated by some authors. It was proposed1,2) that there exists a high degree of hydrogen-bonding interaction between cobalt acetylacetonate and chloroform. It was also shown that rare-earth acetylacetonates form solvates of methanol3). Mechanism of hydration to aluminum(III), chromium(III) and rhodium(III) has also been discussed1).

Here in this work, the interaction of cobalt(III) acetylacetonate with methanol, ethanol, 2-propanol, 1-butanol and water was investigated through the measurements of heats of solution in relation to the solvation phenomena of acetylacetonates. Linear relationships were observed (1) between the heats of solution and the relative number of oxygen atoms of solvents in unit volume and (2) between the heats of solution and cohesive energy densities of solvents.

Experimental

Cobalt(III) acetylacetonate from Dojindo Co., Ltd. was used without purification. The purity was checked by analysis at Chemical Analysis Center of Kyoto University (found: C, 50,86; H, 6.00, calcd: C, 50.57; H, 5.94 %). All the alcohols used were of the purest reagent grade from Hayashi Pure Chemical Industries, Ltd. The refractive indice at 20° by the specification were, methanol: 1.329, ethanol: 1.361, 2-propanol: 1.377 and 1-butanol: 1.399, and the reported values are 1.329, 1.361, 1.377 and 1.398, respectively. Carbon tetrachloride of analytical reagent grade was dehydrated over calcium chloride and was distilled under reflux.

A homemade calorimeter was used for the measurement, the detailed description of which is presented elsewhere.4) To 100 ml of a solvent in a Dewar, was added a suitable amount of the sample (50 - 80 mg) in the form of a very fine powder and the temperature change was then measured. Measurement was repeated at least five times.

Results and Discussion

Heats of solution of cobalt(III) acetylacetonate in water, alcohols and carbon tetrachloride are shown in Table 1.

Table 1. Heat of Solution of $Co(acac)_3$ at 25°

Solvent	ΔH(solution) kcal/mol	cohesive energy density, cal/cc	OH concentration mol/l
water	-5.0 ± 0.2	551	55.4
methanol	5.1 ± 0.2	205	24.6
ethanol	6.5 ± 0.2	162	17.0
2-propanol	7.5 ± 0.3	134	13.0
1-butanol	7.8 ± 0.3	129	10.8
CCl_4	3.2 ± 0.2	74	-

The heat of solution can be regarded as resulting from three stages. (1) the complex is split into monomeric molecules. (2) A cavity of the size of a monomeric molecule is formed in a solvent. (3) A molecule of the complex is placed in the cavity.

The heat absorbed in stage (1) can be represented by the heat of solution of the complex in carbon tetrachloride which can be regarded as an inert solvent.

As a measure of cavity formation, cohesive energy densities of the solvents were calculated from the heats of vaporization at 25° and molar volumes $(H^V - RT)/V$ (cf. Table 1). The heats of solution were plotted against this value and a straight line was obtained as shown in Fig. 1.

When the complex molecule is placed in the cavity, there will be an interaction between the solute and the solvent molecules. Hopkins and Douglas[1)] proposed that water molecules hydrate metal acetylacetonate through the oxygen atoms of their hydroxyl group. According to them, the electron cloud on cobalt is displaced by the approach of the electrons on the oxygen of water molecule and therefore a strong hydration is made possible, while for chromium(III) with only three d-electrons the electronic polarizability is smaller and so it is less hydrated. As for the solvation of chloroform they suggest the interaction between hydrogen of chloroform and carbonyl group of acetylacetone.

In either case, the solvating power must be related to the number of hydroxyl group available for solvation. Thus, the heats of solution were plotted against the relative number of OH groups in 1 litre of the solvents which is given by dividing the weight of 1 litre of each solvent by its molecular weight (cf. Table 1).

A straight line was obtained for alcohols as shown in Fig. 2 though water is a little deviated from the line. The larger the number, the smaller was the heat of solution

It is now shown through the discussion on Fig. 1 and Fig. 2 that the heat of solution in this system is a function of the interactions, (1) between the solvent molecules themselves (i.e., energy of cavity formation) and (2) between the solute and the hydroxyl group of the solvents.

With the purpose of further investigating the solvation behavior of alcohol molecules, very dilute solutions of alcohol in carbon tetrachloride were prepared and heats of solution of $Co(acac)_3$ were measured in them. Results are shown in Fig. 3. For every case, a depression well is seen in the concentration range of 0 - 1.6 ml of alcohol/100 ml of CCl_4 at 25°. This must be due to the solvation of the cobalt complex with monomeric alcohol molecules produced through hydrogen bond rupture by CCl_4. Depth of the depression is roughly in the order of heats of solution in pure alcohols, for example, methanol shows the deepest depression and the smallest heat of solution of all the alcohols tested.

Alcohol can exist as monomeric molecules in carbon tetrachloride only when the concentration is lower than about 0.4 ml for methanol, 0.5 ml for ethanol, 0.8 ml for 2-propanol and 1.0 ml for 1-butanol in 100 ml of CCl_4, which are about 0.01 in mole fraction for every alcohol. At a concentration higher than this, the effect of aggregation already appears.

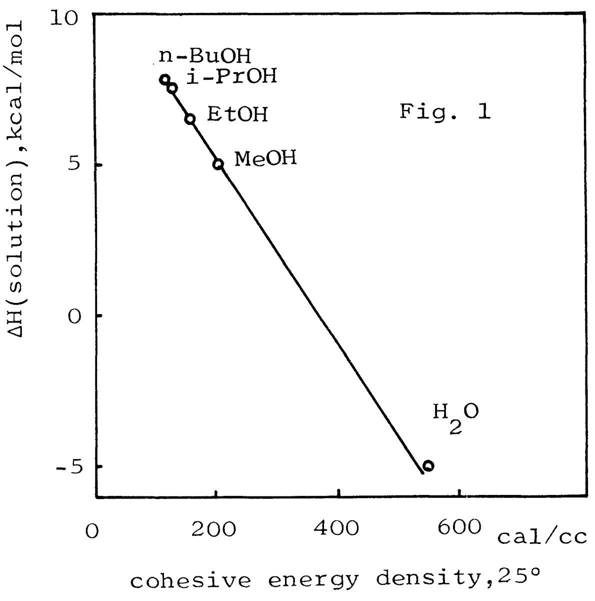

Fig. 1

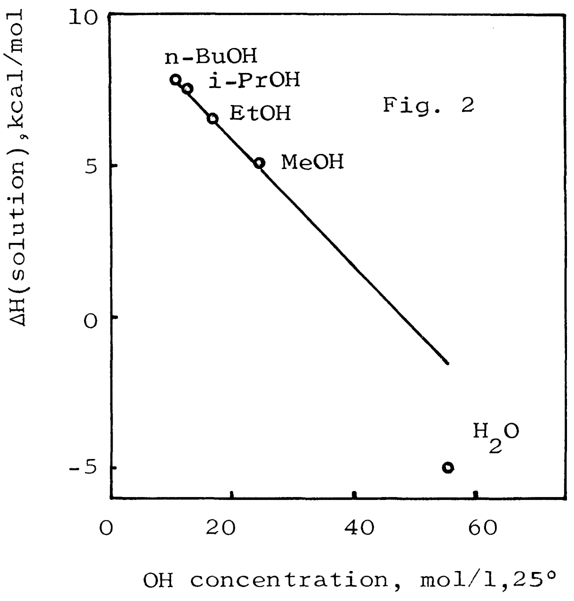

Fig. 2

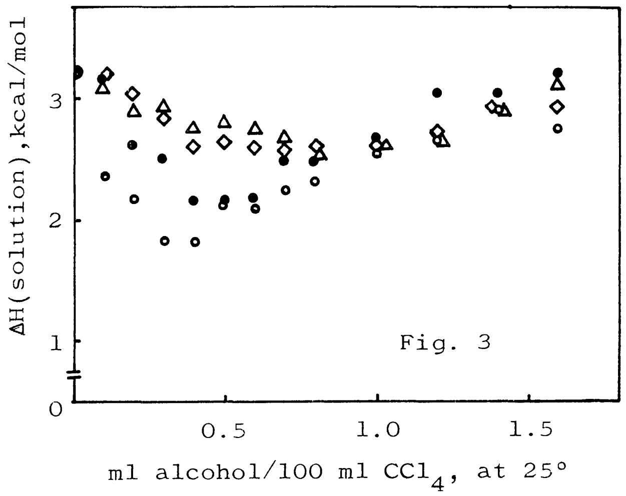

Fig. 3

Fig. 1: Heats of solution of $Co(acac)_3$ vs. cohesive energy density of solvents.

Fig. 2: Heats of solution of $Co(acac)_3$ vs. OH concentration.

Fig. 3: Heats of solution of $Co(acac)_3$ in alcohol/CCl_4.

Open circle: methanol

Filled circle: ethanol

Triangle: 2-propanol

Square: 1-butanol

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