ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 3, pp. 552–554. © Pleiades Publishing, Ltd., 2014.
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Polythermal Solubility of Chromium(III) and Cobalt(III) Tris(acetylacetonates) in Water–*tert*-Butanol Mixtures

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Received May 14, 2013

Abstract—Solubility data for chromium(III) and cobalt(III) tris(acetylacetonates) in water and water–*tert*-butanol mixtures over a wide range of temperatures and alcohol concentrations were obtained, and thermodynamic parameters of solution were calculated. The dependences of solubility on the concentration of *tert*-butanol have an inversion point corresponding to a change in the hydration mechanism, when the solvent structure changes from water to aqueous alcohol.

DOI: 10.1134/S1070363214030244

In the previous works [1–3] we have studied the thermodynamics of solution of Cr(III) and Co(III) trisacetylacetonates [$Cr(acac)_3$ and $Co(acac)_3$] in mixtures of water with ethanol, propan-1-ol, propan-2-ol, and methanol. Solubility inversion was revealed for $Cr(acac)_3$ and $Co(acac)_3$ at alcohol concentrations 0.025–0.055 mole fraction: at lower concentrations the process was exothermic and at higher concentrations it changed for enndothermic. This phenomenon was explained by structural changes in the water–alcohol mixed solvent. *tert*-Butanol and its mixtures with water are more structured liquids which combine a fairly high polarity with a bulky alkyl alcohol fragment. In the present work we continued research on the polythermal solubility of $Cr(acac)_3$ and $Co(acac)_3$ in water–*tert*-butanol mixtures.

The experiment was performed by the same procedure as in [1]. Therewith, much attention was focused to the range of low *tert*-butanol concentrations (<0.02 mole fraction). Our solubility data in water are fairly consistent with published data [4, 5]. Analysis of errors in the determination of solubility shows that the error in the log molar solubility concentration (log *S*) is no more than 0.01 log units.

The dependences of the molar solubility concentrations of tris(acetylacetonates) on the temperature and the composition of the water–*tert*-butanol mixture (Figs. 1 and 2) are similar to those obtained in [1–3].

Like in [3], the resulting solubility data were processed by Eq. (1) [6] deduced with account for the inter-compensating effect of $\Delta_r H$ and $\Delta_r S^0$.

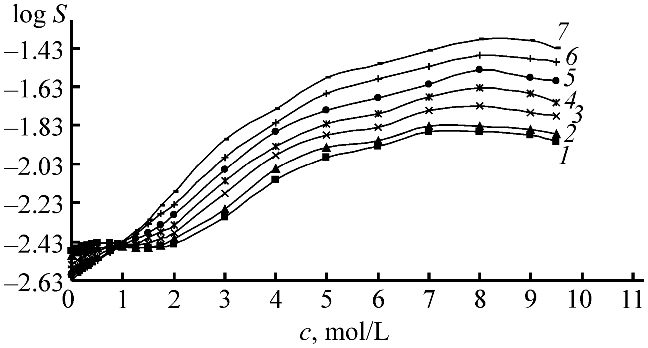

Fig. 1. Dependence of log *S* on the molar concentration of *tert*-butanol for solution of $Cr(acac)_3$ at (*1*) 17.5, (*2*) 20, (*3*) 25, (*4*) 30, (*5*) 35, (*6*) 40, and (*7*) 45°C.

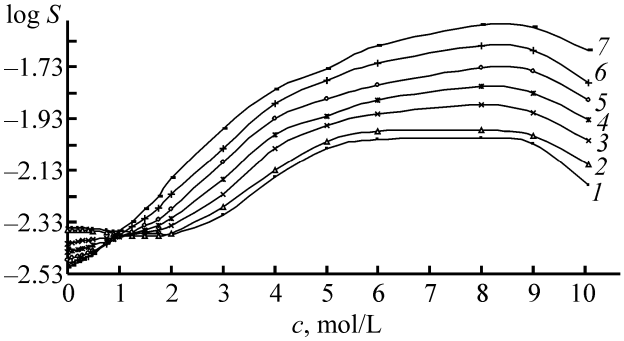

Fig. 2. Dependence of log *S* on the molar concentration of *tert*-butanol for solution of $Co(acac)_3$ at (*1*) 16.5, (*2*) 20, (*3*) 25, (*4*) 30, (*5*) 35, (*6*) 40, and (*7*) 45°C.

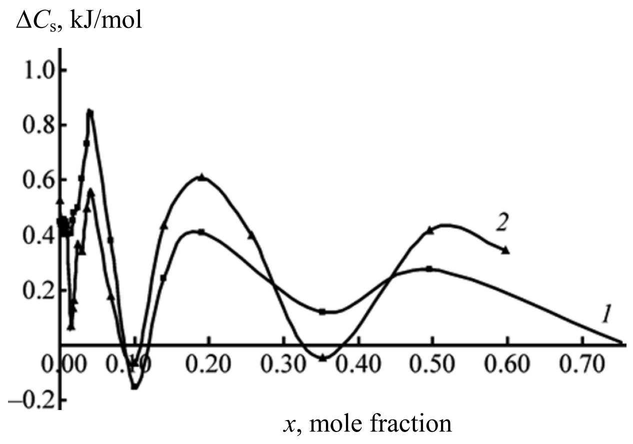

Fig. 3. Dependence of ΔC_s on the molar concentration of *tert*-butanol for solution of (*1*) Co(acac)$_3$ and (*2*) Cr(acac)$_3$.

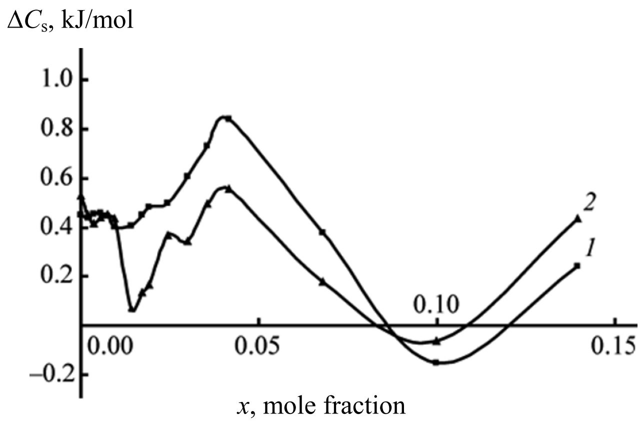

Fig. 4. Dependences of ΔC_s on the composition of the mixed solvent at low alcohol concentrations for (*1*) Co(acac)$_3$ and (*2*) Cr(acac)$_3$.

$$R\ln S = a_0 + a_1(\Delta T/T) + a_2(\Delta T/T)^2. \qquad (1)$$

Here $a_0 = -\Delta_r G^0(10^3/T^*)$, $a_1 = (\Delta_r H^* \times 1000)/T^*$, $a_2 = 2\Delta_r C_s$; T^* is an arbitrarily chosen temperature inside the temperature range in focus; $\Delta_r G^0$, Gibbs energy of solution; and $\Delta_r H$, enthalpy of solution.

The resulting values of thermodynamic parameters (ΔG^0, ΔH, $T\Delta S^0$) are listed in the table.

We also estimated the ΔC_s of solution. As known [7, 8], in most cases, when $|\Delta C_s| > 0$, the temperature effects on ΔH and ΔS^0 are almost completely compensate each other, while ΔC_s takes values close to zero.

Figure 3 shows the dependences of the isobaric heat capacity of solution of Cr(acac)$_3$ and Co(acac)$_3$ on the mole fraction of alcohol (Fig. 4 presents the low concentration range). The obtained dependence is consistent with published data [9]. Figure 5 shows the dependence of the contributions of intermolecular interactions into heat capacity on alcohol concentration [9]. As the alcohol fraction on the system increases, the contribution of intermolecular interaction in *tert*-butanol increases much slower than the contribution of water–*tert*-butanol interaction, which points to strong

Thermodynamic parameters of solution of Cr(III) and Co(III) acetylacetonates in water–*tert*-butanol mixtures (*c*, mol/L)

c_{alc}, mol/L	Co(acac)$_3$				Cr(acac)$_3$			
	ΔC_s	ΔG^0	ΔH	$T\Delta S^0$	ΔC_s	ΔG^0	ΔH	$T\Delta S^0$
0	0.449 ± 0.109	13.77 ± 0.02	–13.18 ± 0.70	–27.0 ± 0.7	0.525 ± 0.042	14.52 ± 0.01	–12.34 ± 0.27	–26.9 ± 0.3
0.1	0.440 ± 0.097	13.75 ± 0.02	–12.22 ± 0.62	–26.0 ± 0.6	0.451 ± 0.059	14.40 ± 0.01	–11.14 ± 0.38	–25.5 ± 0.4
0.2	0.456 ± 0.082	13.73 ± 0.01	–11.67 ± 0.53	–25.4 ± 0.5	0.414 ± 0.066	14.33 ± 0.01	–10.48 ± 0.43	–24.8 ± 0.4
0.3	0.457 ± 0.099	13.72 ± 0.02	–11.04 ± 0.64	–24.8 ± 0.7	0.437 ± 0.033	14.28 ± 0.01	–9.86 ± 0.21	–24.1 ± 0.2
0.4	0.447 ± 0.088	13.71 ± 0.01	–10.02 ± 0.57	–23.7 ± 0.6	0.450 ± 0.058	14.23 ± 0.01	–9.34 ± 0.38	–23.6 ± 0.4
0.5	0.403 ± 0.057	13.69 ± 0.01	–9.01 ± 0.37	–22.7 ± 0.4	0.435 ± 0.036	14.18 ± 0.01	–8.10 ± 0.24	–22.3 ± 0.2
0.75	0.407 ± 0.046	13.65 ± 0.01	–5.61 ± 0.30	–19.3 ± 0.3	0.069 ± 0.042	14.03 ± 0.01	–3.41 ± 0.27	–17.4 ± 0.3
0.9	0.451 ± 0.025	13.64 ± 0.01	–3.56 ± 0.16	–17.2 ± 0.2	0.135 ± 0.072	14.01 ± 0.01	–1.59 ± 0.47	–15.6 ± 0.5
1.0	0.481 ± 0.046	13.62 ± 0.01	–2.53 ± 0.30	–16.2 ± 0.3	0.164 ± 0.084	13.99 ± 0.01	0.23 ± 0.54	–13.8 ± 0.6
1.25	0.500 ± 0.076	13.58 ± 0.01	0.09 ± 0.49	–13.5 ± 0.5	0.366 ± 0.091	13.99 ± 0.01	3.83 ± 0.58	–10.2 ± 0.6
1.5	0.606 ± 0.090	13.55 ± 0.01	2.64 ± 0.58	–10.9 ± 0.6	0.341 ± 0.136	13.90 ± 0.02	7.87 ± 0.88	–6.0 ± 0.9
1.75	0.731 ± 0.105	13.50 ± 0.02	5.32 ± 0.68	–8.2 ± 0.7	0.495 ± 0.086	13.79 ± 0.01	11.15 ± 0.55	–2.6 ± 0.6
2.0	0.840 ± 0.115	13.41 ± 0.02	9.05 ± 0.74	–4.4 ± 0.3	0.553 ± 0.104	13.63 ± 0.02	13.85 ± 0.67	0.2 ± 0.7
3.0	0.379 ± 0.069	12.68 ± 0.01	19.08 ± 0.45	6.4 ± 0.8	0.177 ± 0.231	12.52 ± 0.04	23.97 ± 1.49	11.4 ± 1.5
4.0	0.153 ± 0.134	11.72 ± 0.02	22.86 ± 0.87	11.1 ± 0.9	–0.064 ± 0.225	11.39 ± 0.04	22.94 ± 1.45	11.5 ± 1.5
5.0	0.242 ± 0.167	11.21 ± 0.03	18.71 ± 1.08	7.5 ± 1.1	0.436 ± 0.148	10.78 ± 0.02	23.42 ± 0.95	12.6 ± 1.0
6.0	0.409 ± 0.120	10.95 ± 0.02	20.77 ± 0.78	9.8 ± 0.8	0.607 ± 0.100	10.49 ± 0.02	24.27 ± 0.64	13.8 ± 0.7
7.0	–	–	–	–	0.399 ± 0.135	10.04 ± 0.02	24.72 ± 0.87	14.7 ± 0.9
8.0	0.120 ± 0.142	10.76 ± 0.02	27.24 ± 0.91	16.5 ± 0.9	–0.046 ± 0.147	9.86 ± 0.02	31.57 ± 0.95	21.7 ± 1.0
9.0	0.275 ± 0.087	10.91 ± 0.01	27.55 ± 0.56	16.6 ± 0.6	0.415 ± 0.111	10.04 ± 0.02	29.79 ± 0.71	19.7 ± 0.7
9.5	–	–	–	–	0.345 ± 0.221	10.19 ± 0.04	29.86 ± 1.42	19.7 ± 1.5
10.06	0.008 ± 0.388	11.57 ± 0.06	31.09 ± 2.50	19.5 ± 2.6	–	–	–	–

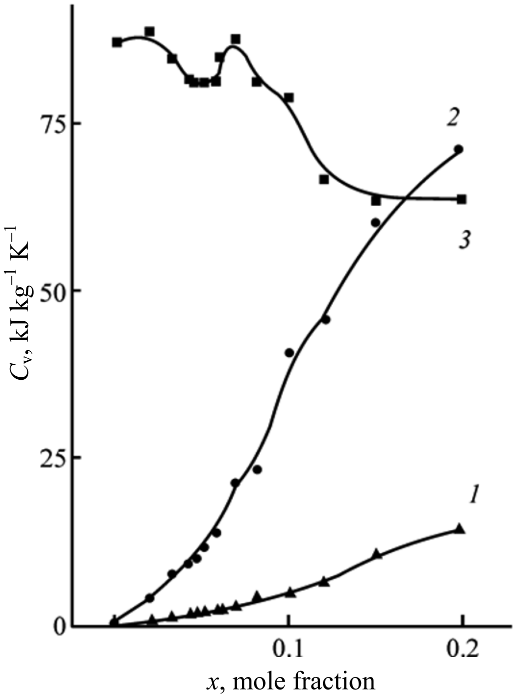

Fig. 5. Dependences of the contributions of (*1*) water–water, (*2*) water–*tert*-butanol, and (*3*) *tert*-butanol–*tert*-butanol intermolecular interactions into C_v on the molar fraction of alcohol.

alcohol–water interaction and fairly uniform distribution of *tert*-butanol molecules in the system. The dependence for the contribution of water–water interactions has an extreme behavior with its minimum falling on ca. 0.05 mole fraction of alcohol, which corresponds to a maximum heat capacity (Fig. 5).

In our studied systems we can recognize three concentration ranges: cubic water structure, mixed structure with prevalence of a “disordered phase,” and chain–cyclic alcohol structure [10, 11]. This allows the patterns of the dependences in Figs. 3 and 4 to be explained in terms of the globular structure of water [12]. According to this model, water globules are separated by a layer of partially hydrophobized water molecules residing on globule boundaries and have hydrogen bonds pointing inside globules. First portions of alcohol added to water initially enter these layers. As the alcohol concentration and temperature increase, the fraction of the “disordered phases” increases, and water–water hydrogen bonds get weaker. At high alcohol concentrations, the system acquires the chain structure of alcohol, and, therewith, the molecular packing gets denser, and the “disordered structure” disappears. The heat capacity increases as the alcohol concentration increases up to 0.05 mole fraction, which is explained by the fact that alcohol molecules fill voids in the water structure. The minimum heat capacity is observed at $x = 0.1$ mole fraction, probably, because at this concentration all voids have already been filled and hydrophobic hydration has a maximum effect [9]. Further change of heat capacity is associated with the destruction of the carcass formed by water molecules. In this range, the heat capacity and enthalpy should be most temperature-dependent because of the lowest density and regularity of molecular packing.

Thus, the ΔC_s can hardly be estimated with an acceptable accuracy, especially at medium and high concentrations of the organic component. For a higher accuracy, more experimental data should be included in the calculations.

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