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Conductometric Study of Complex Formation between Benzylbisthiosemicarbazone and Metal Cations in Acetonitrile, Dimethylformamide, and Their Binary Mixtures[1]

Hamideh Sharifi Noghabi[a], Gholam Hossein Rounaghi[a], Mohammad Hossein ArbabZavar[a], and Javad Ebrahimi[b]

[a]Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran
e-mail: ronaghi@um.ac.ir, sharifinoghabi_hamideh@stu.um.ac.ir

[b]Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran

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Abstract—We report on conductometric study of complexation between benzylbisthiosemicarbazone [(2*E*,2'*E*)-2,2'-(1,2-diphenylethane-1,2-diylidene)bis(hydrazine-1-carbothioamide)] with Zn^{2+}, Cr^{3+}, Co^{2+}, and Ni^{2+} cations at different temperatures in acetonitrile–dimethylformamide binary solvents of varied composition. The equilibrium constant and standard thermodynamic parameters ($\Delta_c H^0$ and $\Delta_c S^0$) of the complexes formation have been determined and found to be dependent on the binary solvent composition, the metal ion nature, and temperature.

Keywords: metal cation, benzylbisthiosemcarbazone, acetonitrile, dimethylformamide, binary solvent, conductometry

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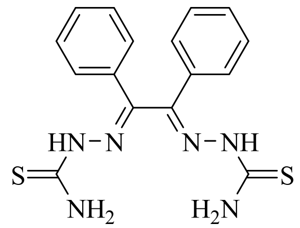
Thiosemicarbazones and their metal complexes have attracted considerable interest due to variety of their biological activities: as antitumor, antiviral, anticancer, antifungal, and antibacterial agents [1–10]. They can serve as useful models in bioinorganic processes study [11] as well. Other peculiar features of the thiosemicarbazones are flexibility, selectivity, and sensitivity to the nature of the complexing ion as well as structural similarity to some natural substances (especially, due to the presence of imino group determining the biological activity [12]). Due to possibility of chelates formation, benzylbisthiosemicarbazone [BTC, (2*E*,2'*E*)-2,2'-(1,2-diphenylethane-1,2-diylidene)bis(hydrazine-1-carbothioamide)] (see Scheme 1) is of special interest among the thiosemicarbazones.

Scheme 1.



BTC

Thermodynamics of metal ions complexes formation in pure and mixed solvents has been studied by a variety of physico-chemical methods such as calorimetry [13], polarography [14, 15], potentiometry [16], NMR spectrometry [17], and conductometry [18]. Among these methods, conductometry has been recognized as a sensitive and cheap technique.

Formation of BTC complexes with selected metal ions in a few pure solvents has been reported [19]. The results have suggested that the solvent plays a crucial part in determination of the complexation mechanism, kinetics, and thermodynamics; selectivity of the complexation reactions can be therefore altered by the choice of the solvent. However, to the best of our knowledge no experimental data has been reported concerning formation of BTC complexes in mixed non-aqueous solvents.

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[1] The text was submitted by the authors in English.

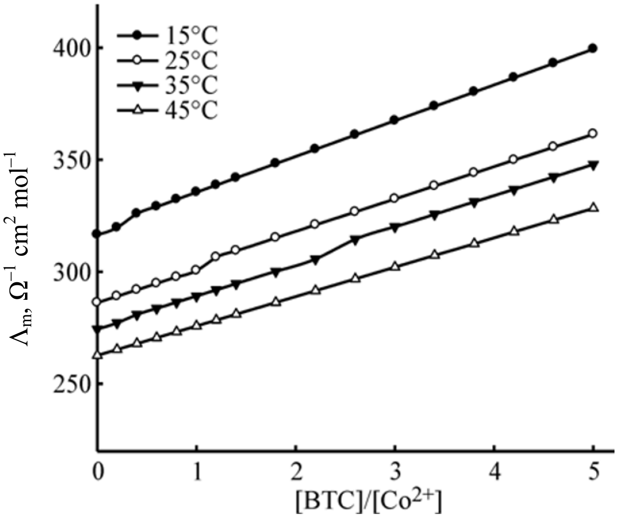

Fig. 1. Conductometric titration curves of complex formation between Co^{2+} and BTC in the binary AN–DMF solvent (75 mol % AN) at different temperatures.

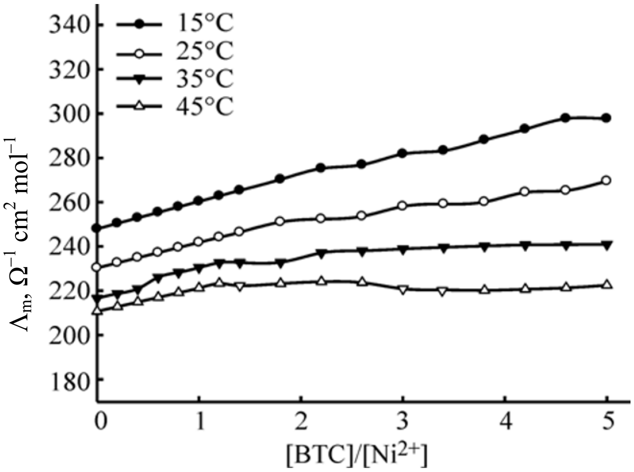

Fig. 2. Conductometric titration curves of complex formation between Ni^{2+} and BTC in the binary AN–DMF solvent (50 mol % AN) at different temperatures.

In the present work, we studied complexation of BTC with Zn^{2+}, Co^{2+}, Ni^{2+}, and Cr^{3+} cations at different temperatures in acetonitrile (AN), dimethylformamide (DMF), and their binary mixtures taking advantage of the conductometry method. Hereafter we report and discuss dependence of stability, selectivity, and thermodynamic parameters of those complexation processes on the solvent nature and composition.

Measurements of the metal salt solution conductivity in the course of stepwise addition of the ligand solution afforded conductometric titration curves in the form of molar conductance (Λ_m) as function of the ligand to cation molar ratio [BTC]/[M]. A representative example is shown in Fig. 1 [titration of the cobalt(II) salt in the AN–DMF solution at 75 mol % of AN]. From data in Fig. 1 it is to be seen that the solution conductivity increased upon addition of the ligand. Eventually, in the organic solution Co^{2+} and NO_3^- ions formed contact or solvent-separated ion pairs that somewhat deteriorated the ionic conductivity of the solution. The complex formed upon addition of BTC was evidently more bulky than Co^{2+} ion; therefore, its interaction with nitrate counterions was shielded, and the solution conductivity increased due to enhanced mobility of the ionic species. Similar behavior was observed in the cases of most of other studied systems.

The absence of steep change of the titration curves slope in Fig. 1 suggested formation of relatively weak BTC complexes with Co^{2+}. From the titration curves fitting results (not shown), their shape coincided well with formation of the 1 : 1 complexes in the cases of most of the studied systems; however, formation of higher complexes could not be absolutely excluded.

The shape of titration curves was, however, different in the cases of nickel(II) nitrate titration in the AN–DMF solvents at 50 mol % (Fig. 2) and 75 mol % (Fig. 3) of AN. As seen from Figs. 3 and 4, addition of the BTC ligand to solution of Ni^{2+} salt in the AN–DMF (3 : 1 or 1 : 1) binary solvent at 35 and 45°C resulted in increase of the molar conductivity up to the $[BTC]/[Ni^{2+}]$ ratio of about 1, further addition of the

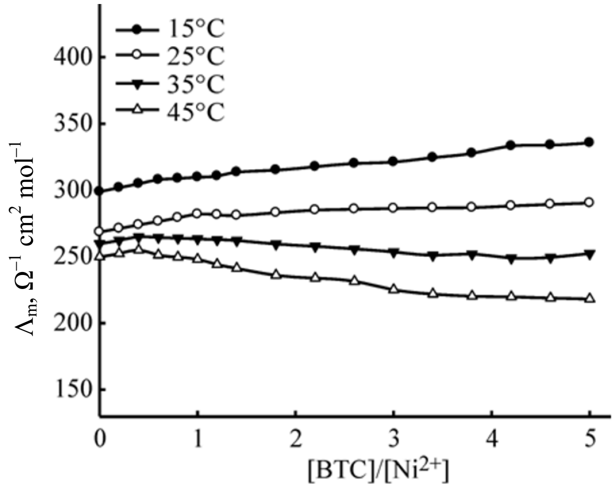

Fig. 3. Conductometric titration curves of complex formation between Ni^{2+} and BTC in the binary AN–DMF solvent (75 mol % AN) at different temperatures.

Table 1. Formation constants of the 1 : 1 complexes between BTC and Ni^{2+}, Co^{2+}, Zn^{2+}, and Cr^{3+} as function of temperature and the solvent used

Solvent (mol:mol)	$\log K_c \pm SD$[a]			
	15°C	25°C	35°C	45°C
		$[BTC\cdot Co]^{2+}$		
AN	2.66 ± 0.06	2.73 ± 0.12	2.83 ± 0.07	2.80 ± 0.09
AN–DMF 3 : 1	2.77 ± 0.11	2.79 ± 0.10	2.72 ± 0.14	2.73 ± 0.14
AN–DMF 1 : 1	2.81 ± 0.11	2.84 ± 0.09	2.69 ± 0.14	2.72 ± 0.14
AN–DMF 1 : 3	2.83 ± 0.10	2.72 ± 0.17	2.72 ± 0.15	2.69 ± 0.13
DMF	2.71 ± 0.12	2.70 ± 0.14	2.78 ± 0.09	2.71 ± 0.16
		$[BTC\cdot Zn]^{2+}$		
AN	2.83 ± 0.08	3.06 ± 0.21	2.72 ± 0.13	2.70 ± 0.15
AN–DMF 3 : 1	2.73 ± 0.14	2.69 ± 0.13	2.69 ± 0.13	2.77 ± 0.09
AN–DMF 1 : 1	3.09 ± 0.06	2.91 ± 0.07	2.97 ± 0.07	2.76 ± 0.14
AN–DMF 1 : 3	2.76 ± 0.09	2.71 ± 0.12	2.75 ± 0.10	2.75 ± 0.10
DMF	2.69 ± 0.13	2.82 ± 0.08	2.80 ± 0.09	2.76 ± 0.11
		$[BTC\cdot Cr]^{3+}$		
AN	2.71 ± 0.15	2.73 ± 0.17	2.77 ± 0.09	2.71 ± 0.13
AN–DMF 3 : 1	2.78 ± 0.11	2.79± 0.10	2.73 ± 0.15	2.73 ± 0.15
AN–DMF 1 : 1	2.69 ± 0.13	2.74 ± 0.14	2.69 ± 0.13	2.71 ± 0.15
AN–DMF 1 : 3	2.69 ± 0.13	2.69 ± 0.13	2.69 ± 0.14	2.69 ± 0.13
DMF	2.82 ± 0.10	2.82 ± 0.10	2.69 ± 0.13	2.69 ± 0.13
		$[BTC\cdot Ni]^{2+}$		
AN	3.30± 0.14	2.79 ± 0.13	3.44 ± 0.12	[b]
AN–DMF 3 : 1	2.62 ± 0.34	4.26 ± 0.12	[b]	[b]
AN–DMF 1 : 1	2.88 ± 0.11	3.32 ± 0.10	4.27 ± 0.08	[b]
AN–DMF 1 : 3	2.86 ± 0.10	2.82 ± 0.13	3.26 ± 0.08	3.83± 0.09
DMF	2.77 ± 0.09	2.80 ± 0.07	2.83 ± 0.06	2.90 ± 0.08

[a] SD, standard deviation. [b] Data could not be fitted or produced too high error.

ligand causing decrease in the molar conductivity. Seemingly, the 1 : 1 complex formation in that case was followed by appearance of other complexes (1 : 2 or even oligomeric ones). The complexes of stoichiometry other than 1 : 1 were likely less mobile and/or caused association of nitrate ions, thus decreasing the solution conductivity. Additionally, the noticeable change of the titration curves slope could be due to formation of the somewhat stronger complexes with the studied ligand in the case of Ni^{2+} ion (noteworthily, this was in line with data in Table 1, see discussion below).

Hence, the predominant stoichiometry of the complexation reactions between the studied metal cations and the BTC ligand could be altered by changing the composition of the binary mixed solvent as well as temperature.

Assuming formation of the 1 : 1 complexes between BTC and the studied metal cations at least at early stages of the titration, we calculated their formation constants at different temperatures and in different solvents by processing the molar conductivity curves with GENPLOT software [20]. The results are summarized in Table 1.

Data reported in Table 1 revealed noticeable changes of the complexes stability constant as function of the solvent nature. The observed effect was the most prominent in the case of Ni^{2+} and Zn^{2+} at lower temperatures; whereas in the cases of Cr^{3+} and Co^{2+} (within the whole studied temperature range) as well as of Ni^{2+} and Zn^{2+} (upon heating) the observed variation of the stability constant with the change of the solvent composition was within the fitting error. When the solvent nature effect was clearly observed, the

Table 2. Thermodynamic parameters of the 1 : 1 complex formation between BTC and Ni^{2+}, Co^{2+}, Zn^{2+}, and Cr^{3+} as function of the solvent used

Solvent (mol:mol)	$\Delta_c G^0$ ± SD[a] (25ºC), kJ mol^{-1}	$\Delta_c H^0$± SD[a], kJ mol^{-1}	$\Delta_c S^0$± SD[a], J mol^{-1} K^{-1}
$[BTC·Co]^{2+}$			
AN	–15.56 ± 0.69	~0	52.19 ± 2.31
AN–DMF 3 : 1	–15.90 ± 0.58	~0	53.33 ± 1.88
AN–DMF 1 : 1	–16.18 ± 0.50	~0	54.27 ± 1.68
AN–DMF 1 : 3	–15.55 ± 0.95	~0	52.15 ± 3.19
DMF	–15.40 ± 0.82	~0	51.65 ± 2.75
$[BTC·Zn]^{2+}$			
AN	–17.44 ± 1.18	~0	58.49 ± 3.96
AN–DMF 3 : 1	–15.36 ± 0.75	~0	51.52 ± 2.52
AN–DMF 1 : 1	–16.60 ± 0.40	[b]	[b]
AN–DMF 1 : 3	–15.48 ± 0.69	~0	51.92 ± 2.31
DMF	–16.09 ± 0.48	~0	53.97 ± 1.61
$[BTC·Cr]^{3+}$			
AN	–15.57 ± 0.96	~0	52.22 ± 3.22
AN–DMF 3 : 1	–15.97 ± 0.59	~0	53.56 ± 1.98
AN–DMF 1 : 1	–15.65 ± 0.78	~0	52.49 ± 2.62
AN–DMF 1 : 3	–15.37 ± 0.75	~0	51.55 ± 2.52
DMF	–16.08 ± 0.59	~0	53.93 ± 1.98
$[BTC·Ni]^{2+}$			
AN	–15.92 ± 0.76	[b]	53.40 ± 2.55
AN–DMF 3 : 1	–24.31 ± 0.67	[b]	81.54 ± 2.25
AN–DMF 1 : 1	–18.96 ± 0.56	125.96 ± 25.44	[b]
AN–DMF 1 : 3	–16.07 ± 0.58	[b]	[b]
DMF	–15.98 ± 0.42	7.40 ± 0.83	28.78 ± 2.40

[a] SD, standard deviation. [b] Data could not be fitted or produced too high error.

complexes stability constants were not monotonous functions of the solvent composition. Probably, the complex behavior observed in the cases of binary solvents was due to the changes in interactions between the mixed solvent molecules, causing changes in the solvent structure and therefore affecting the solvation number of the cations, the ligand, and the resulting complex. Studies of the interaction between AN and DMF molecules reported elsewhere [21, 22] suggested strong dipolar interaction occurring between the solvent molecules; that was further supported by the observed negative values of excess adiabatic compressibility (β^E) and excess intermolecular free length (L^E_f) over the whole range of AN–DMF binary mixtures composition [23]. As far as the effect of metal ion nature is concerned, the complexes with Ni^{2+} were somewhat stronger. The complexes formation selectivity was different depending on the solvent nature; however, detailed analysis of the effect was complicated due to relatively small variation of the stability constants.

Assuming negligible change of the systems heat capacity with temperature, we calculated the standard thermodynamic parameters of the complexes formation from the temperature dependence of the complexes stability constant. The calculated $\Delta_c G^0_{298}$, $\Delta_c H^0$, and $\Delta_c S^0$ values corresponding to the studied systems are summarized in Table 2. In most cases the changes in the standard enthalpy of the complexation reaction was negligible (the complex formation was athermic); therefore, formation of the complexes was entropy-driven. That was in line with the observed increase of the solutions conductivity explained above by liberation of nitrate ions from the ion pairs with the metal ions. Furthermore, the entropy increase could be associated with disruption of the solution structure accompanied with certain disordering of the systems.

Similarly to the above-discussed stability constants, the standard entropy of the complexation reactions was not a monotonous function of the solvent composition.

EXPERIMENTAL

Cobalt(II) nitrate (Merck), zinc(II) nitrate (Riedel), nickel(II) nitrate (Merck), and chromium(III) nitrate (Merck) were used without further purification. Acetonitrile and dimethylformamide (both from Merck) of the highest available purity were used. (2*E*,2'*E*)-2,2'-(1,2-Diphenylethane-1,2-diylidene)bis(hydrazine-1-carbothioamide) (BTC) was prepared as described elsewhere [26].

Conductivity of the solutions was measured using the Jenway 4510 digital conductometer at 1 kHz. The alternating potential was applied at 1 kHz to the cell constructed of two platinum electrodes; the cell constant was of 0.98 cm^{-1}. Constant temperature (± 0.1°C) was maintained during the measurement using the constant-temperature circulating water bath (LAUDA).

In order to determine the stability constant of the complexes, 20 mL of the studied metal salt solution (1.0×10^{-4} mol/L) was placed to the instrument cell, and the solution conductivity of solution was measured. Then, the BTC ligand solution (2.0×10^{-3} mol/L) in the same solvent was added portionwise to the metal salt solution using a microburet, and the mixture conductivity was measured. The titration curve was thus obtained in the form of the solution conductivity as function of the ligand to metal molar ratio.

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