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Thermochromic behaviour and cobalt(II) bromide complex equilibrium in low temperature melting acetamide–ammonium nitrate–water mixtures

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ABSTRACT

The absorption spectra of cobalt(II) bromide in molten $NH_4NO_3 \cdot 2.61H_2O$, $NH_4NO_3 \cdot CH_3CONH_2 \cdot 1.61H_2O$ and $NH_4NO_3 \cdot 2.61CH_3CONH_2$ containing variable amounts of ammonium bromide were investigated at different temperatures from 45 to 75 °C. In the absence of bromide the solutions show spectra typical for octahedral co-ordination of cobalt(II). Addition of bromide caused a shift of the absorption maximum toward lower energies and an increase of the overall molar absorption coefficient with the increasing bromide concentration. The position of the absorption maximum and the intensity of absorption indicate tetrahedral or severely distorted octahedral co-ordination. The molar absorption coefficient of the cobalt(II) species changes with temperature as a result of changes in coordination geometry. By an analysis of the spectra with a suitable computer program it was found that the following complexes were formed: $[Co(NO_3)_4]^{2-}$, $[Co(NO_3)_2Br_2]^{2-}$ and $[CoBr_4]^{2-}$. Stability constants of these complexes in $NH_4NO_3 \cdot 2.61CH_3CONH_2$ have been calculated at 45 °C.

1. Introduction

Acetamide and its mixtures with inorganic salts have high values of the latent heat of fusion [1] and have been considered as phase change materials for thermal energy storage [2,3]. On the other hand, it has been shown, that cobalt(II) halide and mixed complexes dissolved in molten salts exhibit a thremochromic effect *i.e.* an increase of the molar absorption coefficient with temperature. The combination of the high latent heat capacity of the phase change material with the reversible optical properties of the dissolved cobalt halide complex has been considered as suitable material for simultaneous control of temperature and insolation of solar heated agricultural greenhouses [4]. Due to some physical properties of acetamide resembling water (*e.g.* relative permittivity, density and dissociation constant), melts of inorganic salts in which water is partially replaced by acetamide are particularly interesting. In order to get more detailed insight into the changes of the optical properties of these melts, occurring with temperature and cobalt(II) and halide concentration, an investigation of the cobalt halide complex forming process is needed.

The stepwise formation of cobalt(II) chloride complexes in molten acetamide has been studied by Tripković et al. [5] and in acetamide–calcium nitrate tetrahydrate melts by Savović et al. [6,7].

In our earlier work [8] the formation of cobalt(II) chloride and mixed complexes in molten $NH_4NO_3 \cdot 2.61CH_3CONH_2$, $NH_4NO_3 \cdot CH_3CONH_2 \cdot 1.61H_2O$ and $NH_4NO_3 \cdot 2.61H_2O$ was investigated. The mixture where acetamide mole ratio is $R(CH_3CONH_2) = 2.61$ was chosen because the system $NH_4NO_3 \cdot 2.61CH_3CONH_2$ is a eutectic mixture, having the lowest melting temperature. The present paper extends our research study to cobalt(II) bromide complexes in the above melt, and in the systems in which the acetamide molecules are partly or completely replaced by water. The data obtained can be used for an additional test of the systems containing several potential ligands (CH_3CONH_2, H_2O, NO_3^- and Br^-) for sites in the co-ordination sphere of cobalt(II) ions. The influence of the ligand exchange can also be analysed.

2. Experimental

All commercial chemicals used were reagent grade *Merck* products. Melts of the desired composition were prepared from weighed amounts of dry reagent grade ammonium nitrate, acetamide and/or water. Ammonium nitrate was dried for 8 h at 105 °C. Acetamide was washed by the mixture of diethyl ether and methanol, and then dried 6 h at 60 °C. The stock solution of cobalt(II) nitrate was prepared by dissolving of cobalt(II) nitrate hexahydrate in a known amount of the solvent melt. The cobalt nitrate content of the commercial cobalt(II) nitrate hexahydrate was determined by the complexometric titration. Cobalt(II) nitrate hexahydrate was used as a source of cobalt(II) in hydrous melts. Anhydrous cobalt(II) nitrate could not be prepared due to its decomposition during the drying process at elevated temperature. Therefore, dehydrated cobalt(II) bromide was used in anhydrous $NH_4NO_3 \cdot 2.61CH_3CONH_2$ system. Since the complexation of cobalt(II) with bromide ions in the studied systems is weak, the presence of

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bromide in small amounts does not affect the data evaluation for complex formation. Anhydrous cobalt(II) bromide was obtained in the reaction between the cobalt(II) nitrate and the excess of hydrobromic acid. After evaporation of the HBr excess and HNO_3 produced in the reaction, obtained cobalt(II) bromide was heated and dried 6 h at 140 °C. The composition of the product was determined by analysis for both cobalt(II) (complexometric titration) and bromide (potentiometric titration with standard silver nitrate solution). The experimental results were in a good agreement with the theoretical values (experimental: $\omega(\mathrm{Co})=26.90\%$; $\omega(\mathrm{Br})=73.02\%$; theoretical: $\omega(\mathrm{Co})=26.94\%$; and $\omega(\mathrm{Br})=73.06\%$). Prepared substance was kept in a dry atmosphere of phosphoric(V) oxide.

Due to a high density of the studied mixtures and uncomfortable work with volumetric apparatus at elevated temperature, it is not common to measure volume of the melts. Thus, solutions were prepared by measuring of masses of the components. Concentrations of cobalt(II) and bromide ions were expressed in molalities, m, (mol kg^{-1}). In order to calculate the molar absorption coefficients, all concentrations were converted to molarities (mol dm^{-3}). The density of the melt solutions required for conversion of molalities into molarity scale was determined picnometrically at different temperatures and different ammonium bromide concentrations. The variation of density with the cobalt(II) concentration was negligible in the actual composition range. The densities of the mixtures were determined using a pycnometer having a bulb volume of 10 cm^3. The volume of the pycnometer was calibrated as a function of temperature using distilled water at various temperatures. The pycnometer filled with liquid was kept in a thermostatically controlled and well-stirred water bath maintained at a constant temperature to within 0.5 °C for 15 to 20 min to attain thermal equilibrium. The density measurements were carried out at temperatures of 40, 45, 50, 55, 60, 65 and 75 °C. Each experimental density value is the average of at least three measurements. Repeated experimental measurements showed reproducibility within 1%, and an average value was used in further calculations. The dependence of the density, d, on the ammonium bromide molality, m, and temperature, t, in the range 40–75 °C is presented in Table 1.

The absorption spectra of the melts with variable bromide concentration were recorded in the wavelength range 400–800 nm on a *Secomam Anthelie Advanced 2* spectrophotometer with thermostated cell compartment. For each solvent a series of cobalt(II) concentrations with increasing bromide ratio was studied at different temperatures from 45 to 75 °C. The measuring procedure and the apparatus are identical to those described in our previous papers [8,9]. As the complete results are too extensive to be listed in this paper, only representative sets of spectra with different cobalt(II) and bromide concentrations covering the whole range studied are presented here as examples. The composition of the solutions corresponding to the spectra presented here is given in Table 2. The complete experimental results can be obtained upon request from the authors.

3. Results and discussion

3.1. The absorption spectra

The spectra of cobalt(II) solution in melts without bromide added at 45 and 75 °C are presented in Fig. 1. In this figure the overall molar absorption coefficient ε is plotted against the wavelength. The overall molar absorption coefficient is defined as

$$\varepsilon = A l^{-1} c_{\mathrm{M}}^{-1} \tag{1}$$

where A is the absorbance, l is the light pathway and c_{M} is the total cobalt(II) concentration.

Table 1
Dependence of density of investigated mixtures on ammonium bromide molality, m (mol kg^{-1}) and temperature, t (°C).

System	d/g cm^{-3}
$NH_4NO_3\cdot 2.61CH_3CONH_2+NH_4Br$	$1.227–8.12\cdot 10^{-4}t+(0.0556–7.2\cdot 10^{-5}t)\cdot m$
$NH_4NO_3\cdot CH_3CONH_2\cdot 1.61H_2O+NH_4Br$	$1.283–6.11\cdot 10^{-4}t+(0.0549–4.2\cdot 10^{-5}t)\cdot m$
$NH_4NO_3\cdot 2.61H_2O+NH_4Br$	$1.309–6.43\cdot 10^{-4}t+(0.0555–5.4\cdot 10^{-5}t)\cdot m$

Table 2
The composition of the solutions of which spectra are presented in Figs. 2–4.

N°	Fig. 2		Fig. 3		Fig. 4	
	$c(Co^{2+})\cdot 10^2$/ moldm^{-3}	$c(Br^-)$/ moldm^{-3}	$c(Co^{2+})\cdot 10^2$/ moldm^{-3}	$c(Br^-)$/ moldm^{-3}	$c(Co^{2+})\cdot 10^2$/ moldm^{-3}	$c(Br^-)$/ moldm^{-3}
1	4.025	0.08050	0.709	0.7085	3.494	0.6998
2	3.463	0.4373	0.686	1.3726	3.378	1.3555
3	2.222	0.5286	0.675	1.6896	3.277	1.9667
4	1.559	0.8121	0.665	1.9938	0.668	2.6783
5	2.881	0.7730	0.660	2.1136	0.683	2.7325
6	1.082	1.0865	0.656	2.2337	0.674	2.9708
7	3.160	0.9233	0.652	2.3528	0.650	3.1381
8	1.018	1.0841	0.648	2.4611	0.644	3.2819
9	0.708	1.1183	0.644	2.5741	0.635	3.5200
10	0.991	1.1380	0.598	2.5744	0.645	3.6865

In the $NH_4NO_3\cdot 2.61H_2O$ melt the spectra of cobalt nitrate solution show an absorption maximum at 514 nm, very close to 510 nm, ascribed to octahedral hexa-co-ordinated cobalt(II) aqua-complexes in aqueous solutions [10]. In $NH_4NO_3\cdot CH_3CONH_2\cdot 1.61H_2O$ and in $NH_4NO_3\cdot 2.61CH_3CONH_2$ the absorption maxima appeared at 522 and 538 nm, respectively. These values are between 510 nm in aqueous solutions and 550 nm in anhydrous $(K,Li)NO_3$ eutectics [11–13], and they are in good agreement with 525 nm in acetamide–calcium nitrate melts [6] and 545 nm in pure acetamide [7]. A small blue shift of the λ_{max} values in aqueous melts from the value in anhydrous melt indicates simultaneous coordination by water and nitrate ion. The position of the maximum and the values of the overall molar absorption coefficient indicate octahedral co-ordination, as suggested earlier [10,13–16]. The overall molar absorption coefficient increases with temperature as expected for octahedral co-ordination. An increase of the absorption intensity with the replacement of water by acetamide suggest that acetamide is much weaker bounded to cobalt(II) than water molecules, giving a greater chance to nitrate ions to occupy sites in co-ordination sphere of cobalt(II).

Addition of ammonium bromide caused an appearance of a new absorption band with three maxima, at 640, 665 and 696 nm, and a

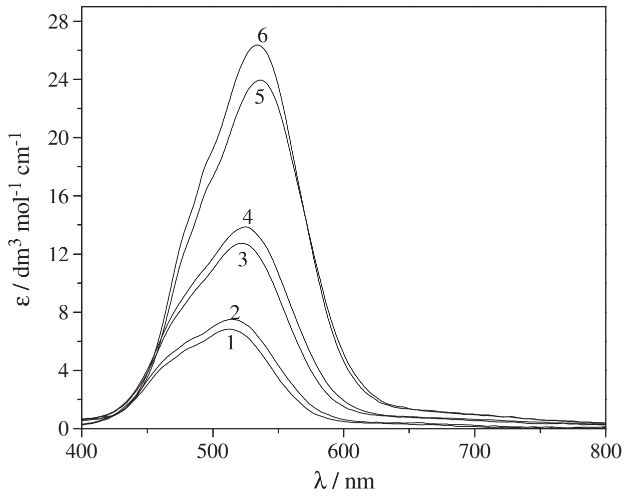

Fig. 1. Absorption spectra of cobalt(II) nitrate in different melts at 45 (1, 3, and 5) and 75 °C (2, 4, and 6). 1,2-$NH_4NO_3\cdot 2.61H_2O$; 3,4-$NH_4NO_3\cdot CH_3CONH_2\cdot 1.61H_2O$; 5,6-$NH_4NO_3\cdot 2.61CH_3CONH_2$.