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ANALYSIS BY DIFFERENTIAL SCANNING CALORIMETRY OF THE KNCS/DIBENZO-18-CROWN-6 SYSTEM: PHASE DIAGRAM AND ENTHALPY CHANGES

ANTONIO BIANCHI, JOLANDA GIUSTI and PIERO PAOLETTI

Chemistry Department, University of Florence, Via. J. Nardi 39, 50132 Florence (Italy)

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ABSTRACT

The phase diagram of the system KNCS/dibenzo-18-crown-6 (DB18C6) was determined by DSC analysis. A 1:1 complex, congruently melting at 245°C, is formed, which is not miscible with the components in the solid phase and is miscible with the crown ether, but not with KNCS, in the liquid phase.

The enthalpies of melting of the complex and of its components were determined and the relative entropy changes were calculated. The enthalpy of formation of the complex from its components in the different states was determined and discussed.

INTRODUCTION

Up to date, a wide number of crown ethers has been synthesized [1]. These ligands form complexes with metal ions both of transition and main groups. Particularly, those complexes with crown ethers containing a number of oxygen donor atoms ranging from five to ten are the most stable [2].

The interest in these ethers has rapidly grown because of their likeness to some naturally occurring cyclic antibiotics. Owing to the ability of these products to control the biological activity of the alkali and alkaline earth metal cations [3], the affinity of crown ethers for these metal ions has also been widely tested [4]. Some interesting solid-state information is available. For instance, crystals of [$KAuCl_4$(valinomycin) [5], [KI(enniatin B)] [6] and [KNCS(nonactin)] [7] have been isolated and their structures have been determined by X-ray analysis. In all three cases the K^+ ions is surrounded by the macrocyclic ligand. In comparison with these complexes, the crystal structure of $[(Rb_{0.55}Na_{0.45})NCS(DB18C6)]_2(DB18C6)$ [8] has been reported. Its unit cell is composed of four complexed molecules and two molecules of free ether. These crystal structures demonstrate the ability of DB18C6 to give, with alkali metals, systems in which the metal salt : ether ratio differs from the simplest 1 : 1. Thus, we have found it interesting to study one of these systems and to determine its phase diagram. The chosen system, KNCS/DB18C6, was investigated by differential scanning calorimetry

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(DSC). This technique also gives interesting information on the heat effects of the system studied.

EXPERIMENTAL

Materials

Dibenzo-18-crown-6 (purum grade, Fluka) and KNCS (RPE-ACS grade, C. Erba) were used without further purification. Their purity was checked by the analysis of the profile of the melting peaks observed in the thermograms [9]. They were 99.9% for dibenzo-18-crown-6 and 99.8% for KNCS.

[K(DB18C6)]NCS was prepared as follows. A solution of KNCS (0.135 g, 1.38 mmol) in 70 cm^3 of boiling ethanol was added to a solution of DB18C6 (0.5 g, 1.38 mmol) in 20 cm^3 of boiling methylene chloride. The resulting solution was reduced to 60 cm^3 and allowed to cool. The crystalline product, formed on cooling, was filtered off, washed with methylene chloride and dried in vacuo at 50°C. The product melts sharply at 245°C. Found: C, 55.2; H, 5.3; N, 3.0%. Calc. for $C_{21}H_{24}NO_6SK$: C, 55.12; H, 5.28; N, 3.06%.

Differential scanning calorimetry

DSC analyses were carried out by using a DSC-2C (Perkin-Elmer) differential scanning calorimeter coupled with a Scanning AutoZero (Perkin-Elmer) and a 56-recorder (Perkin-Elmer). Aluminium volatile sample pans (0219-0062 Perkin-Elmer) were filled with amounts of products ranging from 0.350 to 4.011 mg for DB18C6 and from 0.060 to 1.760 mg for KNCS. The weighings were done on a Cahn Electrobalance Gram model. The sample holder was purged by a flow of nitrogen (UPP grade) which had been dried with a gas filter-dryer.

X-ray diffraction

The powder patterns were run on a Philips automatic diffractometer.

RESULTS

In Fig. 1 we report the phase diagram of the DB18C6/KNCS system obtained from the DSC thermograms of sample mixtures with different molar fractions(x) of ether. This diagram is characterized by the formation of one complex with 1 : 1 stoichiometry ($x = 0.5$) congruently melting at 245°C. The diagram is divided into two parts by the formation of the 1 : 1 compound.

In the first part, line A corresponds to the $KNCS(I)_{(c)} \rightarrow KNCS(II)_{(c)}$ transition, occurring at 142°C, in the $K(DB18C6)NCS_{(c)}/KNCS(I)_c$ mix-

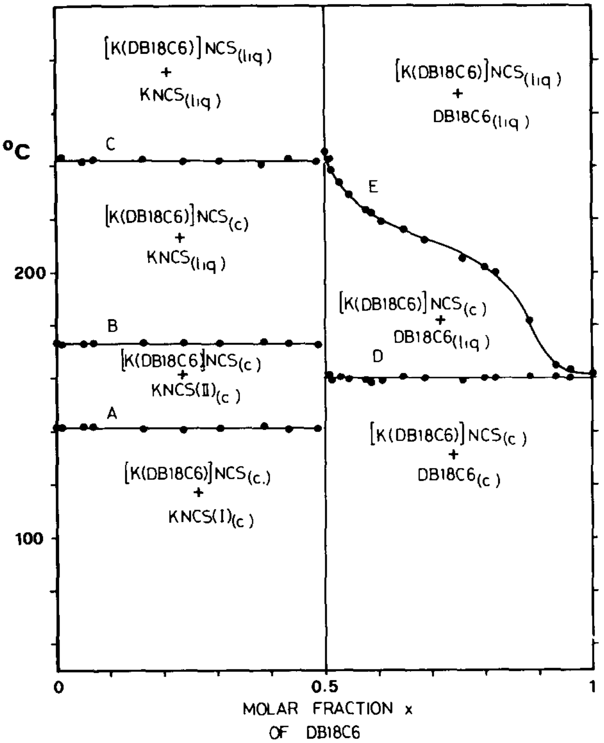


Fig. 1. Phase diagram for the system dibenzo-18-crown-6 (DB18C6)/KNCS determined by differential scanning calorimetry.

ture. Line B (173.5°C) corresponds to the melting of KNCS(II)$_{(c)}$ in the [K(DB18C6)]NCS$_{(c)}$/KNCS(II)$_{(c)}$ mixture, and line C (243°C) to the melting of the complex in the KNCS$_{(liq)}$/[K(DB18C6)]NCS$_{(c)}$ mixture. As we can see from this part of the figure, KNCS and [K(DB18C6)]NCS complexes are completely immiscible both in the solid and in the liquid phases.

On the contrary, in the second part of the diagram, we found a field of miscibility, in the liquid phase, between the complex and the ether. This field is delimited by curve E under which there is a zone of existence of a DB18C6$_{(liq)}$/[K(DB18C6)]NCS$_{(c)}$ mixture. Line D corresponds to the melting of DB18C6$_{(c)}$ in the [K(DB18C6)]NCS$_{(c)}$/DB18C6$_{(c)}$ mixture.

The debyegrams of powdered mixtures of K(DB18C6)NCS both with KNCS and with DB18C6, obtained by cooling the corresponding liquid mixture at room temperature, were compared with the debyegrams of pure complex, KNCS, and ether. The diagrams of the mixtures resulted in a nearly exact superposition of the diagrams of the pure compounds, in agreement with the thermal analysis determination of immiscibility of the components in the solid state.

In Fig. 2 we report a typical thermogram obtained with a KNCS/DB18C6 equimolar ($x = 0.5$) mixture. The small endothermic peak at 142°C corre-

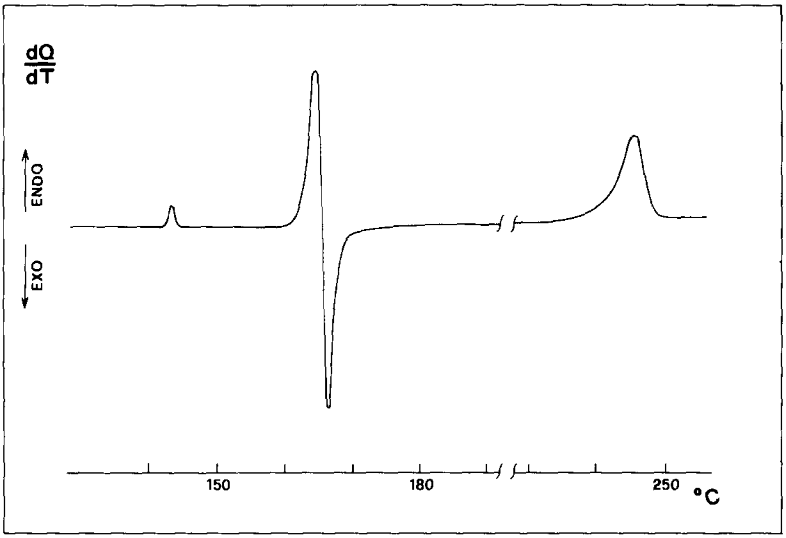


Fig. 2. Typical thermogram obtained for an equimolar mixture of DB18C6/KNCS.

sponds to the transition between crystalline modifications I and II of KNCS. At 161°C the crown ether starts melting (endothermic peak) and the liquid immediately reacts with solid KNCS(II) to give the solid complex (exothermic peak) which melts at 245°C. By integrating the areas of the peaks corresponding to the melting of the ligand and to the complex formation we obtain the enthalpy change for the reaction

$$\mathrm{DB18C6_{(c)} + KNCS(II)_{(c)} = [K(DB18C6)]NCS_{(c)}}$$

at the temperature of incipient melting of the ligand. The complex was then cooled to 25°C and thermal analysis was repeated without any change in the experimental conditions. This second scanning of the temperature from 25 to 180°C reproduced the first baseline quite well, demonstrating that ΔC_{p} for the formation reaction of the complex in the solid state is negligible under these conditions. Furthermore, no peaks due to unreacted starting materials were found by this second scanning. Thus, the correction to be made in transferring the enthalpy change to 25°C consists just of adding the heat of transition of KNCS.

Repeated heating–cooling cycles around the temperature of fusion of the complex demonstrate that this is a fully reversible process.

Complexes of DB18C6 with lanthanides undergo ligand dissociations at temperatures ranging from 224 to 270°C in a nitrogen atmosphere [10], and also the corresponding complex with yttrium dissociates at 285°C [11]. All these dissociation reactions have well-defined, positive enthalpy changes [10,11]. In the present case, [K(DB18C6)]NCS is thermally stable up to 290°C; at a higher temperature an exothermic decomposition occurs which is not well defined.

TABLE 1

Thermal data determined for the system dibenzo-18-crown-6 (DB18C6)/KNCS by differential scanning calorimetry

	KNCS	DB18C6	[K(DB18C6)]NCS
Transition temp. (°C)	142	–	–
Melting point (°C)	173.5	161	245
$\Delta H^0_{\mathrm{tran}}$ (kcal mol^{-1})	0.34(2) [a,b]	–	–
ΔH^0_{m} (kcal mol^{-1})	2.89(2) [c]	14.5(2)	14.3(2)
ΔH^{d}_1 (kcal mol^{-1})	–	–	5.4(1)
ΔH^{e}_2 (kcal mol^{-1})	–	–	2.0(2)
$\Delta S^0_{\mathrm{tran}}$ (cal mol^{-1} K^{-1})	0.8	–	–
ΔS^0_{m} (cal mol^{-1} K^{-1})	6.5	33.4	27.6

[a] Values in parentheses are standard deviations of the last significant figure.

[b] Kinsho et al. [15] report 0.61 kcal mol^{-1}.

[c] Pascal [16] reports values ranging from 3.03 to 3.39.

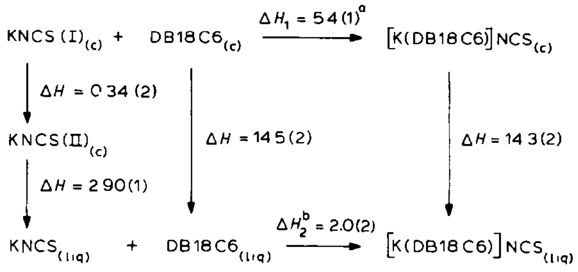
[d] Related to the reaction: $\mathrm{KNCS_{(c)} + DB18C6_{(c)} = [K(DB18C6)]NCS_{(c)}}$ in Scheme 1.

[e] Related to the reaction: $\mathrm{KNCS_{(liq)} + DB18C6_{(liq)} = [K(DB18C6)NCS_{(liq)}}$ in Scheme 1.

In Table 1 we report all the experimentally obtained thermal data for the system studied. In the same table we also report the value of the enthalpy change, for the formation reaction of the complex in the liquid phase, obtained from the thermodynamic cycle given in Scheme 1.

DB18C6 and [K(DB18C6)] NCS present fairly high heats of fusion and, rather surprisingly, they are equal within the experimental error. On the other hand, the complex has an entropy of fusion about six units smaller than that of the ligand, though they are both very high. Flexible molecules exhibit a rapid rise in entropy of fusion with molecular weight [12], but the presence of the cation in the complex causes a stiffening of the ligand molecule, leading to a smaller entropic gain.

A noteworthy aspect of this experience is that the DSC technique directly gives the enthalpy change for a reaction (the complex formation in the solid



Scheme 1. Thermodynamic cycle assembled for the complex formation between KNCS and dibenzo-18-crown-6 (DB18C6) in solid and liquid phases. All enthalpy values are in kcal mol^{-1}. [a] Values in parentheses are standard deviations of the last significant figure. [b] Value not experimentally determined.

state) which, as a matter of fact, does not take place. The enthalpy change, found for this hypothetical reaction, is 5.4 kcal mol^{-1}. By subtracting from this value the heat of fusion of DB18C6 we obtain the enthalpy change for the reaction actually occurring between liquid DB18C6 and solid KNCS to give the solid complex, which is -9.1 kcal mol^{-1}. This reaction may be interpreted as a three-step reaction. The first step is represented by the dissolution of solid KNCS in liquid DB18C6. In the second step complex formation occurs, with a process that may be considered as exothermic as demonstrated by calorimetry in solution ($\Delta H^0 = -9.58$ kcal mol^{-1} in MeOH [13] and $\Delta H^0 = -5.5$ kcal mol^{-1} in DMSO [14]). The last step consists of the crystallization of the complex for which an enthalpy change of -14.3 kcal mol^{-1} was found. Such considerations allow us to conclude that the heat of dissolution of solid KNCS in liquid DB18C6 should be rather endothermic.

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