Nuclear Magnetic Resonance Study of Caesium-133 in Binary Molten Trifluoroacetate Salt Mixtures

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The chemical shifts of Cs^+ in binary melts of caesium trifluoroacetate with lithium, sodium, potassium or thallium trifluoroacetates have been studied as a function of composition. An influence of added foreign cations on chemical shift of caesium nuclei has been found. The nature of the intra- and intermolecular paramagnetic contributions into the shifts of ^{133}Cs is discussed.

Key words: Molten Salts; ^{133}Cs NMR Spectra.

Introduction

The use of molten salts as novel green solvents which may replace conventional media in chemical processes implies a good knowledge of their microscopic structure [1].

As known, high temperature NMR spectroscopy has been applied successfully to molten salts. This technique permits to obtain information about the structure and dynamics of the local environment of most of the nuclei in salt melts [2, 3].

In the present work the chemical shifts ^{133}Cs in molten binary mixtures of caesium trifluoroacetate with lithium, sodium, potassium, and thallium trifluoroacetates have been studied as functions of the composition of these binary melts.

The ^{133}Cs nucleus (natural abundance 100%) has a spin of 7/2 and high NMR receptivity. The moderate chemical shift range of ^{133}Cs is approximately 300 ppm or more [4]. However the NMR studies on these nuclei are rather limited, especially at high temperature.

Experimental

2.1. Materials

Lithium, sodium, potassium, caesium and thallium trifluoroacetates were prepared by the method described in [5, 6]. All salts were free from any water and acid, as evidenced by their IR-spectra. The binary mixtures were prepared by melting the preweighed components under argon. The samples were stored in argon before the measurements.

2.2. ^{133}Cs NMR Studies

The ^{133}Cs NMR spectra were obtained on a Brucker CXP-200 NMR spectrometer at 110 °C (working frequency 26.23 MHz). The compositions of the mixtures studied were in the range 100 - 60mol% caesium trifluoroacetate. The spectra were each characterized by single resonances corresponding to the central transition ($\frac{1}{2} \Leftrightarrow -\frac{1}{2}$), the linewidth being in the range 70 Hz. They are indicative of both the fast quadrupole relaxation and the fast chemical exchange of Cs^+ between different structural groups if such differences exist. The chemical shift, δ, measured at a fixed magnetic field is given by

$$\delta = (\nu_R - \nu_S)/\nu_R, \quad (1)$$

where ν_R and ν_S are the resonance frequencies of the reference and the sample, respectively. A dilute aqueous solution of $CsNO_3$ served as external standard. The estimated uncertainty of the chemical shifts was ± 0.5 ppm.

Results and Discussion

Figure 1 shows the composition dependence of the chemical shifts for the four binary systems studied. The composition range was limited by the high

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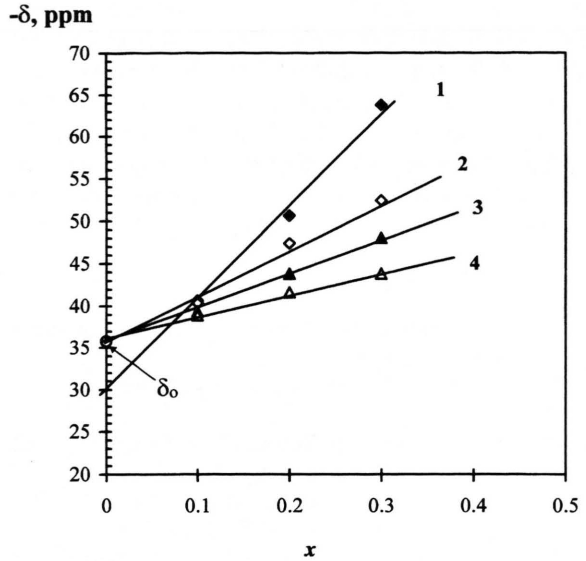

Fig. 1. ^{133}Cs NMR chemical shifts versus the composition of the binary systems at 110 °C. 1: $\{x\ CF_3COOLi + (1-x)\ CF_3COOCs\}$, 2: $\{x\ CF_3COONa + (1-x)\ CF_3COOCs\}$, 3: $\{x\ CF_3COOK + (1-x)\ CF_3COOCs\}$, 4: $\{x\ CF_3COOTl + (1-x)\ CF_3COOCs\}$.

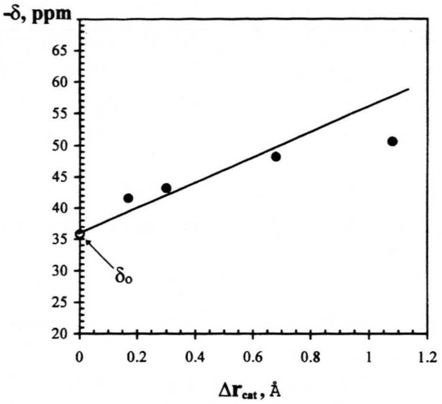

Fig. 2. Dependence of ^{133}Cs NMR chemical shifts on the difference in cationic radii (Δr_{cat}) for binary mixtures $\{x\ CF_3COOM + (1-x)\ CF_3COOCs\}$ with $x = 0.20$ at 110 °C, where M = Li, Na, K, Tl and $\Delta r_{cat} = r_{Cs} - r_M$. The values of Shannon were taken for the cationic radii [12].

melting temperatures of second component rich mixtures. The observed shifts increase in diamagnetic (high field) direction almost linearly with the mole fraction x of the foreign cation.

In general the changes of δ are due to the common effect of the diamagnetic δ_d and paramagnetic δ_p contributions, i. e.

$$\delta = \delta_d + \delta_p. \qquad (2)$$

However the diamagnetic contribution, δ_d, being known [7] to be little sensitive to the character of the cation-anion interaction (bonding) and the change of δ with composition, $\Delta\delta$ may be interpreted by only the change of the paramagnetic contribution i. e. $\Delta\delta \cong \Delta\delta_p$. In the overlap model of Kondo and Yamashita [8] and the polarization model of Hafner and Nachtrieb [9] the relative change of the chemical shift for $^{133}Cs^+$ with composition may be given as [10]

$$\Delta\delta/\delta_0 \cong \Delta\Lambda/\Lambda_0 \cong (-C_0\Delta R - R_0\Delta C)x, \qquad (3)$$

where the subscript 0 denotes the pure caesium trifluoroacetate, Δ denotes the change of the parameters of the pure caesium trifluoroacetate with composition in substituting Cs^+ by a foreign cation, x is the foreign cation mole fraction, Λ and C are overlap parameters, and R is interionic distance between Cs^+ and the anion.

It should be noted that only the intramolecular paramagnetic contribution to the change of the chemical shift is taken into consideration by (3).

As seen in Fig. 1 the composition dependencies of δ^{133}Cs on x are linear and pass through the δ_0 for binaries with sodium, potassium and thallium, which implies that $\Delta C = 0$, i. e. these cations don't vary electronic donor capability of the anion towards the caesium cation.

In the system of caesium with lithium trifluoroacetes the straight line passes beneath δ_0. The lithium cation has the same effect on the electronic donor properties of the anion as other alkali cations, that is $\Delta C = 0$. Thus a positive (paramagnetic) shift of the linear dependence of δ^{133}Cs on the mole fraction of lithium trifluoroacetate relative to δ_0 may imply an additive intermolecular paramagnetic contribution to the shifts of ^{133}Cs. Indeed, as known [11], only lithium cations may form in the melt stable anionic dimers such as $[A^-\text{-}Li^+\text{-}A^-]$, and so Cs^+ plays a role of an outerspheric cation. In this case the Cs^+ is bound to be in the perpendicular position about the main symmetry axis of the anionic dimer. This causes the nuclei of Cs^+ to be exempted from shielding effect of inducted circulation of electrons around the valent bonds of trifluoroacetate anions and hence leads to an additive intermolecular paramagnetic shift of ^{133}Cs.

In Fig. 2 the dependence of δ^{133}Cs on the difference in cationic radii (Δr_{cat}) for binary mixtures with

$x = 0.20$ can be seen. Since for the binary salt mixtures with common anion $\Delta R = \Delta r_{\text{cat}}$ [9], the linearity of this dependence agrees well with (3) and supports the proposed mechanisms of changes of the inter- and intramolecular paramagnetic contributions to the shifts of ^{133}Cs.

Thus, NMR spectra give the possibility to estimate and elucidate the extent and nature of the composition effect on the character of the interionic interactions in binary salt melts. This investigation has shown that chemical shift of $^{133}Cs^+$ in the trifluoroacetate melts may be described by a complex function of the composition and reflects both the character of the cation-anion bonding and the ionic association in the second coordination sphere of caesium cation.

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