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NMR study of the dynamic behaviour of the system 2-ethylhexylsodium-2-ethylhexyllithium in heptane

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Abstract

Mixtures of 2-ethylhexylsodium and 2-ethylhexyllithium are studied by ^{1}H- and ^{13}C-NMR spectroscopy in the temperature range from 20 to -50°C in hydrocarbon solutions. Characteristic temperature-dependent spectra obtained are indicative of dynamic exchange processes taking place in the system. The following activation parameters are found: $\Delta H^{\neq} = 31.7 \pm 2.7$ kJ mol^{-1}; $\Delta G^{\neq}_{313} = 58.7 \pm 0.6$ kJ mol^{-1}; $\Delta S^{\neq} = -86.37 \pm 10.8$ J mol^{-1} K^{-1}. The negative value of the activation entropy indicates that the exchange proceeds through the associative mechanism. The participation in exchange reactions of aggregates, containing both sodium and lithium derivatives, is suggested. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Alkylsodium; Alkyllithium; DNMR

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1. Introduction

Literature data on reactions between alkali metal alkyls are mostly limited to lithium compounds. There are several reviews on the subject [1–4]. All RLi compounds exhibit line-shape changes in their NMR spectra reflecting equilibrium exchange reactions [3,5]. It is shown that alkyllithiums which are known to exist in solutions in the form of bridged aggregates, are capable of intra and intermolecular exchange reactions [3,6]. By the study of ^{13}C-NMR spectra for branched-chain alkyllithiums enriched in ^{6}Li such as isobutyllithium–^{6}Li and (2-ethylbutyl)lithium–^{6}Li, it was shown that these compounds are fluxional aggregates where slow intermolecular exchange reactions take place [6]. Rapid exchange reactions between CH_3Li and C_2H_5Li in ether were investigated in detail [7]. In hydrocarbons, exchange reactions in the systems C_4H_9Li–$(CH)_3SiCH_2Li$ [8] and C_4H_9Li–C_2H_5Li [9] were studied. Slow intermolecular exchange is observed.

Reactions with the participation of alkyl derivatives of heavier alkali metals are practically unstudied due to their poor solubility in hydrocarbons. 2-Ethylhexylsodium (2-EtHexNa) is one of a few alkylsodiums soluble in hydrocarbons in contrast to straight-chain alkylsodium isomers, but when 2-EtHexNa is mixed with a straight-chain alkyllithium compound in hydrocarbons, a rapid exchange reaction proceeds, corresponding alkylsodium precipitating. If, however, 2-ethylhexyllithium is taken as a second component, the system remains homogeneous which makes it possible to use spectroscopic methods for the study of mixed systems. It seemed of interest to study dynamic processes in this system by multinuclear NMR.

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Table 1
Chemical shifts of the –CH_2Mt group (Mt = Na, Li) in ^{1}H-NMR spectra of 2-EtHexNa–2-EtHexLi mixtures at various Li/Na ratios[a]

Concentration (mol l^{-1})		Na (mol%)	Li (mol%)	δ (ppm)	$^3J_{HH}$ (Hz)
Na	Li				
–	0.392	0	100	-0.831	6.6
0.0773	0.220	26	74	-0.847	5.3
0.134	0.130	51	49	-0.866	4.8
0.155	0.0597	72	28	-0.916	5.6
0.0784	–	100	0	-0.883	5.8

[a] Deuterocyclohexane, 20°C.

2. Results and discussion

As it was shown earlier [10], in the ^{1}H-NMR spectrum of 2-EtHexNa, the resonance of –CH_2Na group protons is in the higher field (δ -0.88 ppm) in comparison with that of the –CH_2Li group of 2-EtHexLi ($\delta - 0.83$ ppm). This fact may be accounted for by the greater polarity of the C–Na bond as compared with that of C–Li one. The same conclusion was made in the work by Shcheglova et al. [11], where it had been shown that the absorption maximum in the UV spectra of polyisoprenylsodium in heptane (PINa) is shifted to the long-wave region ($\lambda_{max} = 304$ nm) in comparison with that in the spectrum of polyisoprenyllithium (PILi) ($\lambda_{max} = 270$ nm).

All this is in accordance with the opinion that chemical shifts of –CH_2 group resonance in ^{1}H-NMR spectra of such organometallic compounds correlate with electronegativities of metal atoms [12] (0.93 and 0.98 for Na and Li, respectively [13]). However, it should be noted that some authors consider sodium more electronegative than lithium [14].

The 2-ethylhexyl derivatives under investigation as well as 2-methylbutyllithium (2-MeBuLi) have asymmetric carbon atoms, which may result in the disappearance of the magnetic equivalence of –CH_2Mt protons. Indeed, in the ^{1}H-NMR spectrum of 2-MeBuLi, the non-equivalence of –CH_2Li group protons had been observed [15]. The difference in their chemical shifts is about 0.3 ppm. In the case of 2-EtHexNa and 2-EtHexLi, corresponding protons seem to be equivalent in the whole temperature range studied. They contain a methylene group at the asymmetric carbon atom instead of a methyl group in the case of 2-MeBuLi. So, the near surrounding of the asymmetric carbon atom in 2-EtHexMt consists of a hydrogen atom and three methylene groups containing, however, different substituents. This fact, apparently, facilitates a noticeable decrease in the splitting resonances of –CH_2Mt group protons in the spectra of 2-EtHexMt. Therefore, their non-equivalence is not detected since it is lower than the experimental detection level.

^{1}H-NMR spectra of a 2-EtHexNa and 2-EtHexLi mixture in deuterocyclohexane were measured at 20°C. At all Na/Li ratios, the resonance of the –CH_2Mt group is a doublet, but not a superposition of the spectra of the components, the resonance location being almost within the range between chemical shift values characteristic of the –CH_2Na and –CH_2Li groups of these compounds (Table 1). A slight shift beyond this range may be accounted for the complexation between sodium and lithium compounds which will be discussed later. Such behaviour of the system indicates that the exchange process between metal atoms of 2-EtHexNa and 2-EtHexLi takes place.

^{1}H-NMR spectra of the equimolar 2-EtHexNa–2-EtHexLi mixtures in heptane are also recorded within the temperature range -40 to $+30$°C. Experimental spectra of methylene protons bound with Na and Li are presented in Fig. 1. At low temperatures, two sets of resonances are observed: a doublet related to –CH_2Li and an unresolved resonance of –CH_2Na. The substantial broadening of the latter is, probably, accounted for by the poor solubility of 2-EtHexNa in heptane at low temperatures. With increasing temperature, the multiplicity of the –CH_2Li resonance disappears, too, its lines broadening significantly. A further increase in the temperature results in merging –CH_2Na and –CH_2Li resonances. At temperatures higher than 10°C, only one narrow doublet with the average constant $^3J_{HH} = 5.5$ Hz is observed.

The line shape of the resonance related to the –CH_2Li group of 2-EtHexLi alone in heptane does not change substantially with increasing temperature in the interval from -50 to $+20$°C, as can be seen in Fig. 2. Spectra of 2-EtHexNa could not be measured at low temperatures due to the precipitation of the substance.

Changes taking place in the ^{1}H-NMR spectra of 2-EtHexNa–2-EtHexLi mixtures with lowering temperature indicate that there is a dynamic process in the system caused by the mutual transition between 2-EtHexNa and 2-EtHexLi. Calculations of the full shape of the ^{1}H-NMR spectrum lines within the temperature range -40 to $+10$°C have been performed and constants of the exchange rate between two forms:

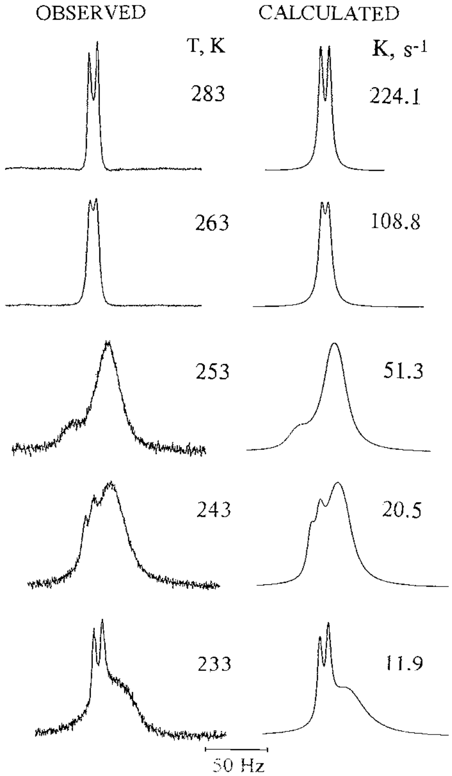

Fig. 1. Proton resonances of $-CH_2Mt$ groups (Mt = Li, Na) of the 2-EtHexNa (0.185 mol l^{-1}) and 2-EtHexLi (0.193 mol l^{-1}) mixtures in heptane at different temperatures with calculated line shapes and exchange rate constants (K).

$A_2X \leftrightarrows A_2'X'$

where $A_2 = -C\underline{H}_2Na$, $A_2' = -C\underline{H}_2Li$, $X \Rightarrow\ > C\underline{H}CH_2Na$, and $X' \Rightarrow\ > C\underline{H}CH_2Li$, have been determined. Since the location of the $>CH-$ group resonance in the spectrum does not affect the calculation results, in order to simplify matters, it is taken that $X = X'$. Theoretical spectra presented in Fig. 1 show the satisfactory coincidence with experimental ones. The Eyring plot of the constants obtained against the temperature is presented in Fig. 3. The following activation parameters of the dynamic process are determined:

$\Delta H^{\neq} = 31.7 \pm 2.7$ kJ mol^{-1}

$\Delta G^{\neq}_{313} = 58.7 \pm 0.6$ kJ mol^{-1}

$\Delta S^{\neq} = -86.37 \pm 10.8$ J mol^{-1} K^{-1}

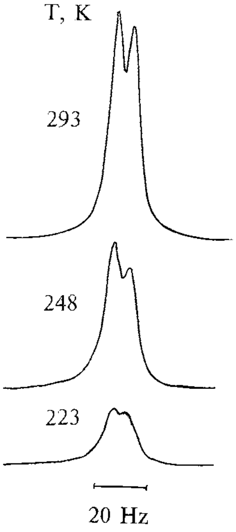

Fig. 2. Proton resonances of the $-CH_2Li$ group of 2-EtHexLi (0.140 mol l^{-1}) in heptane at different temperatures.

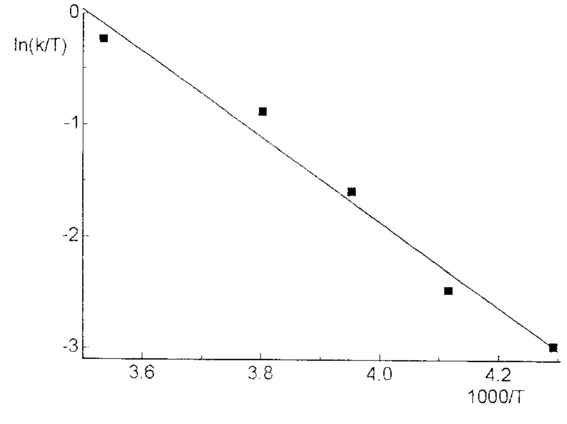

Fig. 3. Eyring plot of ln(k/T) vs. $1/T$ for 2-EtHexNa-EtHexLi exchange from ^{1}H-NMR. k, rate constant, T, temperature in K.

The high negative value of the activation entropy allows us to conclude that the exchange between 2-EtHexNa and 2-EtHexLi proceeds through formation in the transition state of the aggregates between these compounds. The same conclusion was made in the work by Fraenkel et al. [16] where they studied exchange processes in solutions of n-propyllithium, existing in hydrocarbons in the aggregated form similarly to other alkyllithiums [1]. The negative value of entropy (-36 e.u.) found in the study of this dynamic process by ^{13}C- and ^{6}Li-NMR was attributed to the proceeding of the exchange through the formation in the transition state of dodecameric aggregates which have fewer degrees of freedom than original hexameric aggregates.

2-EtHexNa and 2-EtHexLi are, apparently, aggregated too, though their aggregation degrees are not known. According to the literature data [15], the aggregation degree of their close lithium analogue 2-MeBuLi in cyclopentane changes from 3 to 6, depending on the temperature and concentrations. As for alkylsodiums, their aggregation degrees in hydrocarbons are not measured due to their poor solubility in such media. It is known, however, that polybutadienylsodium in heptane has an aggregation degree close to 3 [17].

Accordingly, the exchange reaction may proceed between the aggregates of 2-EtHexNa and 2-EtHexLi (Eq. (1)) or between cross-aggregates, containing Na and Li atoms formed as a result of fast exchange (Eq. (2)).

$$R_mLi_m + R_nNa_n \rightleftarrows [R_{(m+n)}Li_mNa_n]^{\neq} \leftrightarrows R_mLi_m^* = R_nNa_n^* \quad (1)$$

$$2R_{m+n}Li_mNa_n \leftrightarrows [R_{2(m+n)}Li_{2m}Na_{2n}]^{\neq} \leftrightarrows 2(R_{m+n}Li_mNa_n)^* \quad (2)$$

The negative activation entropy value obtained gives evidence that the exchange proceeds by the associative mechanism. Intramolecular exchange with zero activation entropy is not ruled out, but apparently its contribution in the general thermodynamics of the process is not principle.

The exchange according to Eq. (2) is the most probable. Formation of cross-aggregates is well known in the mixtures of alkyllithiums. For example, ethyllithium, which is insoluble in benzene, dissolves upon addition of *n*- or *tert*-butyllithium [18,19], their IR spectra undergoing changes. Some complexes of phenyl and *p*-tolyl derivatives of different alkali metals, such as PhNa · PhLi or PhNa · PhK, were obtained by Wittig [20] in ether solutions.

The thermal stability and solubility of 2-EtHexNa in heptane increases substantially upon addition of 2-EtHexLi. At concentrations of 0.1–0.2 mol l^{-1}, no precipitate is observed even at −40°C while 2-EtHexNa alone precipitates already at 5°C. This fact apparently indicates that these compounds interact with the formation of complexes, presumably of the type $(RLi)_m \cdot (RNa)_n$.

It is interesting to note that the ^{7}Li-NMR spectrum of 2-EtHexLi, which consists of a single line at δ 2.83 ppm ($\Delta\nu = 0.441$ ppm at 20°C) [10], changes slightly upon addition of the equivalent amount of 2-EtHexNa. It narrows to $\Delta\nu = 0.28$ ppm with some change in the chemical shift (δ 3.08 ppm).

The system 2-EtHexNa–2-EtHexLi has also been studied by ^{13}C-NMR in heptane. Spectra of 2-EtHexNa and 2-EtHexLi contain resonances at δ 20.2 and 18.9 ppm, respectively, relating to the carbon atoms of $-CH_2Na$ and $-CH_2Li$ groups of these compounds. They are close to those of the $-CH_3$ group of the corresponding hydrocarbon $CH_3(CH_2)_3CH(CH_3)CH_2$-CH_3 (δ 19.3 ppm) [22]. The assignment of resonances was performed with the use of the pulse sequence DEPT. Spectra of equimolar mixtures of 2-EtHexNa and 2-EtHexLi at −50°C contain resonances close to those of individual compounds (δ 20.1 and 18.9 ppm, respectively), while when the temperature is raised to 42°C only one resonance at δ 19.3 ppm is observed. Such behaviour of the system also indicates the exchange reaction proceeding in the hydrocarbon solution of alkyl derivatives of sodium and lithium.

Mixtures of 2-EtHexNa and 2-EtHexLi were earlier used as initiators of diene monomer polymerizations [11,21]. The results obtained are also an indirect corroboration of the cross-aggregation possibility in the systems studied. Data on molar masses and microstructures of polymers could not be explained by polymerization under the separate action of sodium and lithium initiators. Formation of complex active species of the type $(PNa)_m \cdot (PLi)_n$ was suggested to take place.

3. Conclusion

Thus, characteristic temperature-dependent ^{1}H- and ^{13}C-NMR spectra of 2-EtHexNa–2-EtHexLi mixtures obtained are indicative of dynamic exchange processes taking place in this system in hydrocarbon media. The negative value of the activation entropy gives evidence that the exchange reactions proceed by the associative mechanism. Since many examples show that cross-aggregate formation is thermodynamically favoured for alkyl and aryl derivatives of alkali metals, the participation in exchange reaction of aggregates containing both sodium and lithium derivatives seems most plausible.

4. Experimental

Syntheses of 2-EtHexNa and 2-EtHexLi were carried out by the reaction of 2-EtHexCl with sodium dispersion and lithium chips, respectively, in vacuo as described in our earlier paper [10].

Heptane and deuterocyclohexane were purified by standard procedures and then dried with *n*-butyllithium.

Preparation of samples for NMR and polymerization experiments were performed in all-glass systems under vacuum conditions (10^{-3}–10^{-4} mmHg) with the use of the conventional break-seal technique.

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AMX-400 spectrometer with working frequencies of 400.13 and 100.58 MHz, respectively, and internal stabilization by deuterium within the temperature range from −40 to +30°C. Chemical shifts of ^{1}H nuclea were measured in deuterocyclohexane or heptane and referred to $SiMe_4$. ^{7}Li-NMR spectra were taken on a Bruker-200-SY spectrometer at 77.775 MHz. ^{13}C- and ^{7}Li-NMR spectra were measured in heptane solutions, $CDCl_3$ and 10% solution of LiCl in water, respectively, being used as external standards.

The calculation of the full shape of the ^{1}H-NMR spectrum line was performed with the use of the modified version of the DNMR5 program [23]. Activation parameters of the dynamic process were determined from the Eyring plot of rate constants found against the temperature [24]. Calibration of the thermostabilization system was performed by the registration of ^{1}H-NMR spectra of methanol and ethylene glycol standard samples.

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