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**SPECIALTIES OF THE STRUCTURE AND CONDUCTIVITY
OF THE NON-AQUEOUS ELECTROLYTES BASED ON ALKALI METAL
BIS (SALICYL) BORATES AND BIS (OXALATO) BORATES**

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The structure and coordination environment of non-aqueous electrolytes based on bis (salicyl) borates of lithium, sodium and potassium, and bis (oxalato) borates from lithium to cesium using NMR spectroscopy have been investigated. The NMR spectra analysis of ¹³C and ¹¹B found the presence of R-, S-enantiomers in bis (salicyl) borate anion with a labile coordination sphere of boron in the presence of a solvent. This difference affects the final structure of the electrolytes and leads to a change in the thermal dependence of the electrical conductivity of bis (salicyl) borates and the ways of ions transport relatively bis (oxalato) borates in non-aqueous solvents.

K e y w o r d s: non-aqueous electrolyte, alkali metal bis (salicyl) borates, conductivity, structure, labile complex, ion transport.

INTRODUCTION. Electrolytes are the key components of all the modern chemical power sources (CPS). Their main function is to ensure the conductivity between the electrodes, to form the capacity and the ability to cycle. Bis (salicyl) borates and bis (oxalato) borates of alkali metals and organic cations are promising electroconductive components of electrolytes of modern CPS (lithium-, sodium-ion batteries and super-capacitors) [1–4]. In this case it is very necessary to have the representation about solvents influence on the electrolytes structure and conducting properties of salt-solvent system. Some approaches adjust these properties through combinations of solvents with different dynamic viscosities and dielectric permeability values. In particular, high conductivity values are achieved by obtaining a stable electrolyte layer on the anodes surface [5].

Another option of increasing the electrolyte ion conductivity is the using of lithium salts solutions with organic anions in dimethyl sulfoxide (DMSO), propylene carbonate or other aprotic dipolar solvents. However, the modern study have clarified that the main role of the conductivity formation had a specific cluster-based supra-molecular architecture of the electrolyte in case of full salt dissociation [6–10]. Such clusters stabilize due to the equilibrium between the processes of interconversion, and their production rate (including salvato splited or contact pairs) depends on the salt-solvent ratio [6–10].

Thus, the aim of current work is the determination of the relationship between the structures and conductivity of electrolytes based on alkali metals bis (salicyl) borates and bis (oxalato) borates with the solvent nature.

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EXPERIMENTAL PART. The synthesis was done by microwave method by keeping the mixture of stoichiometric components during 10–15 min [11]. The final product was recrystallized from dry isopropanol. The obtained mixture was analyzed using ANANCE 400 spectrometer (Bruker, Germany).

Samples for NMR studies ^{13}C and ^{11}B were prepared by obtaining a saturated solution of *bis*-(saltillo)borate sodium (NaBSB), *bis*(salicyl)borate potassium (KBSS) in dimethyl sulfoxide (DMSO), dimethylformamid (DMFA) and dimethylacetamide (DMAA) in proportion of 0.3–0.4 g per 1 g of the solvent. Boric acid solution in water and tetramethylsilane in DMSO were used as standards for NMR spectra recording. The formation of R-, S-enantiomers was recorded using the ^{13}C NMR spectral chemical shift of the carbon signals in carboxyl group.

Temperature dependences of electrical conductivity were measured on the Metrohm Autolab-30 30 PGSTAT.301N electrochemical module using a 2-electrode isolated 2 cm^3 cell with the platinum electrodes (constant cell value was 24.135 Ohms). The temperature regime was maintained using a thermostat with a measurement error $\pm 1^\circ\text{C}$. Before measurements, the samples have been incubated at respective temperature for 30 min for achieved equilibrium in the solution.

RESULTS AND DISCUSSION. The analysis of ^{11}B NMR spectra have shown that similar to the *bis*(oxalato)borate (BOB^-) spectrum of *bis*(salicyl)borate (BSB^-) anion in dimethyl sulfoxide (DMSO) is characterized by one boron atom signal and has a stronger shift by $\delta = -11.5$ m.d. BSB^- in comparison with BOB^- signal $\delta = -7.1$ m.d. The BSB^- spectra of salts with all three cations have the same δ signal positions and are identical to the spectrum of *bis*(oxalato) and LiBSB. In contrast to the BOB^- there were 6 carbon signals of the benzene ring and one signal of the carboxyl group identified for BSB^- anion in the NMR spectrum. The BSB^- spectra for salts with all three cations have the same δ signal positions and are identical to the *bis*(oxalato) spectrum of lithium borate (LiBSB). In contrast to the BOB^- there were 6 carbon signals of the benzene ring

and one signal of the carboxyl group identified for BSB^- anion in the NMR spectrum. In the ^{13}C NMR spectra of *bis*(oxalato)borate there is only an intense signal at $\delta = 157.36$ ppm, which is responsible for all four carboxyl groups. The two carboxyl groups *bis*(salicyl)borate in the spectrum of the NaBSB solution in DMAA (1 mol/kg) have two separate signals 167 and 162 ppm respectively (Fig. 1, a, b).

The carbon atoms of carboxylic groups ex-

Fig. 1. Spectrum ^{13}C -NMR: a — NaBSB in DMAA 1 m 20°C ; b — LiBOB in DMSO 1 m 20°C .

press by two signals in the spectra of solutions of LiBSB and NaBSB in dimethylacetamide, which points to the presence of R-S-isomers of complex ions (Fig. 2). Conformational lability of the coordination sphere of the sodium bis(salicyl) borate upon dissolution in DMAA leads to the doubling of the integrated intensity of singlet carboxyl groups compared with the signals of the carbon atoms in fragments of another functional group at delays of the time between RF pulses in range 2–15 seconds.

Fig. 2. Optical isomerism of *bis*(salicyl)borate ion *a* (R), *b* (S).

It is well known that the R-enantiomer of such salts take part in the formation of the contact ion pairs in DMSO, that means it could have tendency to form supramolecular structures [6–10]. In the dimethylformamide solution of tetramethylammonium salt, as well as for alkali metal salts, two signals of carbon atoms of the carboxyl group are observed, while the value of chemical shifts of the carbon atoms 4, 5 and 3, 6 signals are significantly separated, which can be explained by the ability to form the salt-solvent hydrogen bonds due to steric effect [6–10] (table 1).

The existence of an intermolecular hydrogen bonds system is a condition for the implementation of the relay mechanism. Therefore, the probability of realization of the relay charge transfer in electrolytes with the corresponding architecture increases. Thus, the electrical conductivity measured at different temperatures has been dependent on the salt concentration. These conductivities of the sodium and potassium bis(salicyl)borates solutions in DMFA were identified in a wide

Table 1

The ^{13}C NMR signals spectrum classification (δ_{BSB}^- ppm)

LiBSB	NaBSB	Me ₄ NBSB		Carbon atoms
DMAA		DMFA	DMAA	
166.92	167	172.917	171.5	C ¹ =O
162.35	162	171.73	—	C ^{1*} =O
137.12	137	137	137	C ⁷ -O
132	132	133.44	133.2	C ³ -C ⁶
131.98	131.9			
121.17	120.67	133.35	133.2	C ⁴ -C ⁵
120.68	121.17	133.32		
118.53	119	—	—	C ² -C

Fig. 3. Temperature dependence of electrical conductivity of KBSB solutions in DMFA: 1 — 0.5; 2 — 0.77; 3 — 0.985; 4 — 1.7; 5 — 3; 6 — 4 mol/kg

Fig. 4. The temperature dependence of electrical conductivity of NaBSB solutions in DMFA: 1 — 0.5; 2 — 0.75; 3 — 1.0; 4 — 2.0 mol/kg.

concentration and temperature range (Fig. 3, 4). The maximum electrical conductivity of solutions in DMFA is reached at concentrations close to 0.75 mol/kg (for KBSB) and 0.77–1 mol/kg (for NaBSB). This means, that in this case a new system is able to ion transfer through relay mechanism (Fig. 2, *b*). This concentration range is wider for sodium ions than for potassium ions with similar values of their solubility (table 2). Such dependence was not found for salts with BOB-anions, since they (except for lithium salts) have weak solubility, low electrical conductivity and no isomers (table 3). Sodium BOB dissolves well in DMFA and DMSO but its solubility is much weaker in acetonitrile and

Table 2

The solubility of bis(salicyl)borates of sodium and potassium (NaBSB and KBSB) in amide solvents and DMSO

Solvent	NaBSB	KBSB
Carbamide	1 mol : 10 mol	1 mol : 10 mol
Acetamide	1 mol : 10 mol	1 mol : 10 mol
DMSO	~ 1.1 M	~ 1.1 M
DMFA	~ 4 M (1:2.92)	~ 3.94 M (1:3.3)
N-methyl acetamide	~ 2.3 M (1:5.62)	0.69 M
N-methyl acetamide	~ 4 M (1:2.92)	Not identified
Propylene carbonate	—	0.73 M

Table 3

The electrical conductivity value of LiBOB and LiBSB 0.6 mol/kg

LiBSB ¹		LiBSB ²		LiBOB ³	
<i>t</i> , °C	σ , mS/cm	<i>t</i> , °C	σ , mS/cm	<i>t</i> , °C	σ , mS/cm
20	0.62	26	1.25	17	3.58
25	0.74	43	1.83	24	4.16
39	1.14	61	2.62	25	4.20
57	1.52			31	4.74

¹ LiBSB of propylene carbonate; ² LiBSB of ethylene carbonate-dimethyl carbonate; ³ LiBOB of ethylene carbonate-dimethyl carbonate.

Fig. 5. Impedance spectra of 0.75 mol/kg DMFA solutions in Nyquist coordinates in the temperature range 25–70 °C: *a* — KBSB, *b* — NaBSB.

carbonate esters, which effects the solutions conductivity of the following salts [12, 13].

Further analysis of impedance spectra of these salts approved the existence of an area that has maximum electrical conductivity and is characterized by a 45° slope angle of spectral curves in Nyquist coordinates in the low-frequency range. According to literature data, such spectrum proves the existence of diffusion phenomena in the electrochemical system [14]. The angle slopes of the curves decrease with the temperature rising (Fig. 5, *a,b*), which could be explained by a decreasing of the part of ions diffusion transport. However, the following increase of electrical conductivity reveals the existence of a second ion transport path-

Table 4

The values of frequency dependencies of EIS solutions KBSB in DMFA and NaBSB in DMFA at the room temperature

$C_{\text{salts}}, \text{mol/kg}$	Electrolyte	$\varphi, ^\circ$	f, Hz	$a(f), ^\circ$
0.5	KBSB + DMFA	80	10^3	30
		65	10^{-1}	
0.6	KBSB + DMFA	80	$10^{1.5}$	55
0.77	KBSB + DMFA	80	10^2	45
0.98	KBSB + DMFA	83	$10^{1.5}$	35
1.7	KBSB + DMFA	83	$10^{0.3}$	30
3.0	KBSB + DMFA	80	10^3	55
		71	10^{-2}	
4.33	KBSB + DMFA	74	$10^{1.5}$	55
		63	10^{-2}	
0.5	NaBSB + DMFA	80	10^3	45
0.75	NaBSB + DMFA	80	10^2	45
1.0	NaBSB + DMFA	80	10^2	45
2.0	NaBSB + DMFA	80	$10^{1.5}$	45
		71	10^{-2}	

Note: φ_{max} — maximum shift in the phase angle; f — maximum frequency of the phase angle shift; $a(f)$ — the angle of the spectrum inclination.

way, based on the relay mechanism. On the other hand, a significant phase angle shift is typical for all the studied systems. According to the AC theory, this indicates the presence of two wave forms of electric current in the system and the corresponding difference between the cycles of these waves [15] (table 4). In accordance with what was stated above, there are two streams of charge carriers in the system.

Only one maximum shift in phase angle at a frequency of 10^2 Hz is possible for the systems with a maximum conductivity value and it would be equal to two salts with a similar concentration. The presence of two BSB conformations and two wave forms according to the ^{13}C NMR spectra suggests the formation of a labile borate complex with a solvent that has the maximum electrical conductivity and depends on the salt concentration. Knowing the recorded activity in the coordination sphere of *bis*(salicyl)borate and that the relay mechanism is implemented to transfer the

boron between neighboring coordination nodes during migration through the sulfocation membrane, let us assume the existence of a pseudo-dimensional structure of electrolyte solutions based on *bis*(salicyl)borate anion [16]. Then, it allows the implementation of the relay charge transfer mechanism [17, 18]. Also, the results prove the assumption [19] about the existence of a certain ratio between the fragments of supramolecular formations, that is, the effect of R- and S-enantiomers of *bis*(salicyl)borate-anion with a labile coordination environment of boron on the formation of conductive properties of the electrolyte and the formation of an additional ion transport channel due to the implementation of the relay mechanism.

CONCLUSIONS. The ^{13}C and ^{11}B NMR spectra studies by varying the time delay between the radiofrequency pulses of non-aqueous electrolytes based on *bis*(salicyl)borates and *bis*(oxalato)borate lithium have established that the carboxyl groups atoms are not equal in the *bis*(salicyl)borate-anion due to the emergence of two enantiomers in *bis*(salicyl)borate-anion with labile coordination environment of boron. Based on the electrical conductivity measurements and the spectroscopy data of electrochemical impedance, we suggest two charge transfer pathways in the electrolytes based on *bis*(salicyl)borates: diffusion and the relay, which is in concordance with the results of NMR spectra studies. Based on the data comparison of NMR, CEI and concentration dependences of electrical conductivity in the obtained electrolyte system, the possibility of forming a pseudopolymer labile complex due to the formation of hydrogen bonds between the investigated borates and the solvent was established.

ОСОБЛИВОСТІ БУДОВИ ТА ЕЛЕКТРОПРОВІДНОСТІ НЕВОДНИХ ЕЛЕКТРОЛІТІВ НА ОСНОВІ БІС(САЛІЦИЛО)БОРАТІВ ТА БІС(ОКСАЛАТО)БОРАТІВ ЛУЖНИХ МЕТАЛІВ

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Досліджено структуру та координаційне середовище неводних електролітів на основі бис(салицило)боратів літію, натрію, калію, тетраметиламонію (MeBSB) і бис(оксалато)боратів від літію до цезію (MeBOB) за допомогою ЯМР-спектроскопії. Бис(салицило)борати (BSB) і бис(оксалато)борати (BOB) лужних металів і органічних катіонів розглядаються як перспективні електропровідні компоненти електролітів сучасних хімічних джерел струму (літій та натрій іонних первинних та вторинних батарей і суперконденсаторів). Солі синтезували методом НВЧ-випромінювання. Дослідженням спектрів ЯМР ^{13}C та ^{11}B визначили наявність симетричної структури в аніоні BOB та двох оптичних конформацій аніона BSB з лабільним координаційним середовищем бору. Оптична активність BSB є результатом формування іонних контактних пар. У разі катіона тетраметиламонію наявність оптичної активності залежить від реактивної складової середовища. Конформаційна лабільність координаційної сфери NaBSB, розчиненого в DMAA, пов'язана з підвищенням інтегральної інтенсивності сигналів карбоксильних груп щодо сигналів атомів вуглецю в фрагментах іншої функціональної приналежності, коли затримка між радіочастотними імпульсами змінюється протягом 2–15 секунд. Різниця в структурі цих аніонів призводить до зміни температурної залежності електропровідності BSB і транспорту іонів у неводних розчинниках. Максимальна електропровідність розчинів солей у ДМФА досягається при близьких концентраціях 0.75 моль/кг для KBSB і 0.77–1 моль/кг для NaBSB. Розчинність для солей BSB в амідах та інших АДР краща, ніж для солей BOB. Причому розчинність для BSB практично незмінна від Li^+ до K^+ , а для BOB різко спадає від Li^+ до K^+ і далі незмінна до Cs^+ . На основі вимірювань електропровідності та даних спектроскопії електрохімічного імпедансу (кут нахилу спектрів у координатах Найквіста в низькочастотному діапазоні, кут нахилу фази при частоті) запропоновано існування двох способів транспорту іонів і зарядів в електролітах: дифузійний і естафетний транспорт. Встановлена можливість утворення лабільного сольового комплексу з розчинником за рахунок водневих зв'язків.

Ключові слова: неводний електроліт, бис(салицил)борати лужних металів, провідність, структура, лабільний комплекс, транспорт іонів.

ОСОБЕННОСТИ СТРОЕНИЯ И ЭЛЕКТРОПРОВОДНОСТИ НЕВОДНЫХ ЭЛЕКТРОЛИТОВ НА ОСНОВЕ БИС(САЛИЦИЛО)БОРАТОВ И БИС(ОКСАЛАТО)БОРАТОВ ЩЕЛОЧНЫХ МЕТАЛЛОВ

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Исследована структура и координационное окружение неводных электролитов, состоящих из бис(салицило)боратов лития, натрия, калия и бис(оксалато)боратов от лития до цезия с использованием ЯМР-спектроскопии. Анализ спектров ЯМР ^{13}C и ^{11}B установил присутствие двух конформаций в бис(салицило)борат-анионе с лабільным координационным окружением бора в присутствии растворителя. Это различие в структуре анионов влияет на конечное строение электролитов и приводит к изменению термической зависимости электропроводности бис(салицило)боратов и путей переноса ионов относительно бис(оксалато)боратов в неводных растворителях.

Ключевые слова: неводный электролит, бис(салицил)бораты щелочных металлов, проводимость, структура, лабильный комплекс, транспорт ионов.

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