

Chemical modification of electrolytes for lithium batteries

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Abstract. Modern approaches to modifying chemically electrolytes for lithium batteries are analysed with the aim of optimising the charge-transfer processes in liquid-phase and solid (polymeric) media. The main regularities of transport properties of lithium electrolyte solutions containing complex (encapsulated) ions in aprotic solvents and polymers are discussed. The prospects for the development of electrolytic solvosystems with the chain (ionotropic) mechanism of conduction with respect to lithium ions are outlined. The bibliography includes 126 references.

I. Introduction

Direct energy conversion from chemical to electrical forms is a central problem of modern science and technology. At present, active research is carried out on the development of primary and secondary lithium cells with characteristics (high energy density, low self-discharge rate, applicability at low temperatures, high reliability, *etc.*) that should surpass those of traditional electrochemical systems^{1–6} and displace them in future. The research on lithium chemical power sources (CPS) was, first of all, stimulated by the progress in such industrial fields as electronics, new communication systems and transport (electrical vehicles). Lithium cells and rechargeable batteries are increasingly applied as autonomous power sources in various domestic, medical and computer devices. Special-purpose lithium CPS are used in night-vision devices, guidance systems, space equipment, and new weapon systems. At present, the yearly production of lithium CPS for special equipment and military branches is ~ 30 million cells, which is 3–4 times higher compared with other industrial branches.⁷

Elaboration of highly efficient lithium CPS is largely aimed at the development of electrolytic systems with high conductivities (10^{-3} – 10^{-2} S cm⁻¹) in a wide temperature range (from –50 to +70 °C) and chemical and electrochemical stabilities with respect to lithium and cathodic materials. Such systems should also enable sufficiently fast and reversible electrode processes. Insufficient conductivity of liquid-phase and, particularly, solid poly-

meric lithium electrolytes is a key factor impeding the development of CPS with lithium electrodes.^{8–11} The importance of solving this problem is determined by the fact that the internal resistance of a power source directly governs its main performance characteristics such as the power density and the discharge current.

Most approaches to choosing optimum electrolytic compositions for lithium CPS were based on theoretical concepts of the ion-migration mechanism of charge transfer.^{12–14} Hence, the aim of the latest studies was to create such conditions that would both enhance the migration rates of electrolyte ions as the main charge carriers in solution and in polymers and increase their concentrations. For this purpose, mixed low-viscosity solvents with sufficiently low dielectric constants were used as the electrolytic systems, macrocyclic ligands which can encapsulate lithium cations and different anions were added, lithium salts with low lattice energies which involve large anions with delocalised charges were synthesised, *etc.* It is known that a chain (prototropic) mechanism of conduction is brought about in aqueous solutions of acids and bases used as the electrolytes for traditional CPS, which is responsible for the conductivities of these solutions being 1–2 orders of magnitude higher as compared with solutions with the migration mechanism of charge transfer. It is also known that the ionotropic mechanism of charge transfer can involve not only protons in water and protic solvents but also some other ions in aprotic media. In this connection, the latest studies have considered a possibility of developing highly conductive nonaqueous electrolytes with a conduction mechanism different from the ion-migration one, as well as designing CPS based on such electrolytes with improved performance characteristics.

This survey analyses and generalises the results of studies published in the past 10–15 years and devoted to modifying chemically the conventional electrolytes applied in lithium CPS with the aim of optimising the charge transfer processes in liquid-phase and solid (polymeric) media. The analysis was carried out from the standpoint of dividing the electrolytes according to their phase compositions, *viz.*, liquid-phase and solid (polymeric) electrolytes. The latter type traditionally involves biphasic electrolytes, *i.e.*, gels, composites, *etc.* The survey also includes new systems which do not fit the traditional classification (*e.g.*, electrolytes with polymeric anions and ionic liquids). That is why it seemed reasonable to analyse the results of studies of different polymeric electrolytes according to the examples of concrete chemical modifications that were most interesting from our viewpoint, rather than to consider in detail the classes of electrolytes.

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II. Liquid-phase electrolytes

The main factors that affect the charge migration rate in electrolytes are the solvent viscosity and the processes of solvation and association. One of the first approaches to optimising electrolytic systems in lithium CPS consisted in the use of complex lithium compounds with low lattice energies, which involve weakly solvated and easily polarisable anions. This provided solutions with enhanced conductivities and higher concentrations of electrolyte ions. Within this approach, lithium electrolytes with coordinatively saturated fluorine-containing anions AsF_6^- , PF_6^- , BF_4^- and also with ClO_4^- , Ph_4B^- , all of which exhibited sufficiently high electrochemical stability, were extensively used.^{2, 8–11, 15–17} Moreover, the use of fluorine-containing salts allowed one to reduce the corrosion of cathodes with aluminium current leads at high positive potentials. However, the performance of power sources with the electrolytes mentioned entailed quite a number of problems. For example, lithium perchlorate is thermally unstable, and its solutions are explosive, especially, in ether-like solvents; lithium hexafluorophosphate can decompose in solution to give poorly soluble lithium fluoride and a Lewis acid PF_5 , which initiates polymerisation of cyclic ethers; hexafluoroarsenate ions are reduced electrochemically to give AsF_5 and As^0 which are environmentally hazardous; lithium tetrafluoroborate solutions do not provide a sufficient conductivity level and, moreover, BF_4^- ions initiate polymerisation of cyclic ethers. Therefore, the search for new lithium electrolytes which would exhibit better compatibility with solvents and electrode materials is still in progress.

Lithium salts with anions such as CF_3SO_3^- , $\text{B}_{10}\text{Cl}_{10}^-$, $\text{B}_{12}\text{Cl}_{12}^-$ and BMe_4^- turned out to be more stable but their solutions possessed low conductivities. Recently, new lithium electrolytes with large anions and minor polarisability have been proposed: $\text{Li}[(\text{CF}_3\text{SO}_2)_2\text{N}]$ (**1**) and the corresponding cyclic imides $\text{Li}[\text{N}(\text{SO}_2)(\text{CF}_2)_n(\text{SO}_2)]$ ($n = 1–3$) (**2**), lithium methanide $\text{Li}(\text{CF}_3\text{SO}_2)_3\text{C}$ (**3**), the family of lithium chelatoborates of the general formula $\text{Li}[\text{BR}_2]$ (**4–6**) (where bidentate ligands R are aliphatic or aromatic diols), and the corresponding lithium phosphates $\text{Li}[\text{PR}_3]$ which are highly stable chemically and electrochemically, well soluble ($> 1 \text{ mol litre}^{-1}$) and weakly associated.^{9, 18–25} The charge distribution in anions strongly affects the electrolyte association. With addition of electron-acceptor substituents such as F, CF_3 , COOR, SO_2OR and nitrogen atoms, which can delocalise the negative charge in anions, the association constants of lithium electrolytes decreased by several orders of magnitude. The effects mentioned favour the increase in the conductivity and extend the electrochemical window of solvents. Thus the specific conductivity of 1 M solutions of lithium

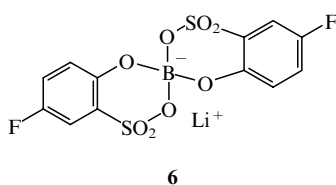
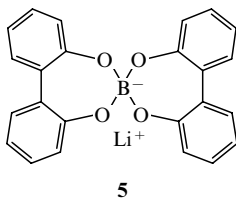
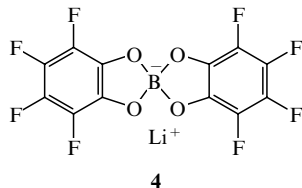
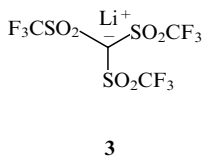
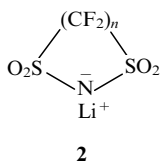
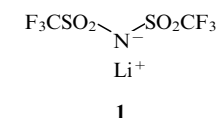
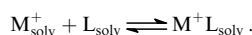
chelatorborates $\text{Li}[\text{B}(\text{C}_6\text{H}_x\text{F}_{4-x}\text{O}_2)_2]$ ($1 < x < 4$) in 1,2-dimethoxyethane (DME) increased by a factor of 4.4 at 25 °C and by a factor of 2.4 at –45 °C with substitution of fluorine atoms for four hydrogen atoms. A linear correlation between the limiting potentials of anodic oxidation of lithium borates and the energies of higher occupied molecular orbitals of anions, which was estimated using semiempirical quantum-mechanical methods AM1 and MNDO,^{9, 19} indicates that the electrochemical stability of these electrolytes depends on the degree of delocalisation of the negative charge in anions.

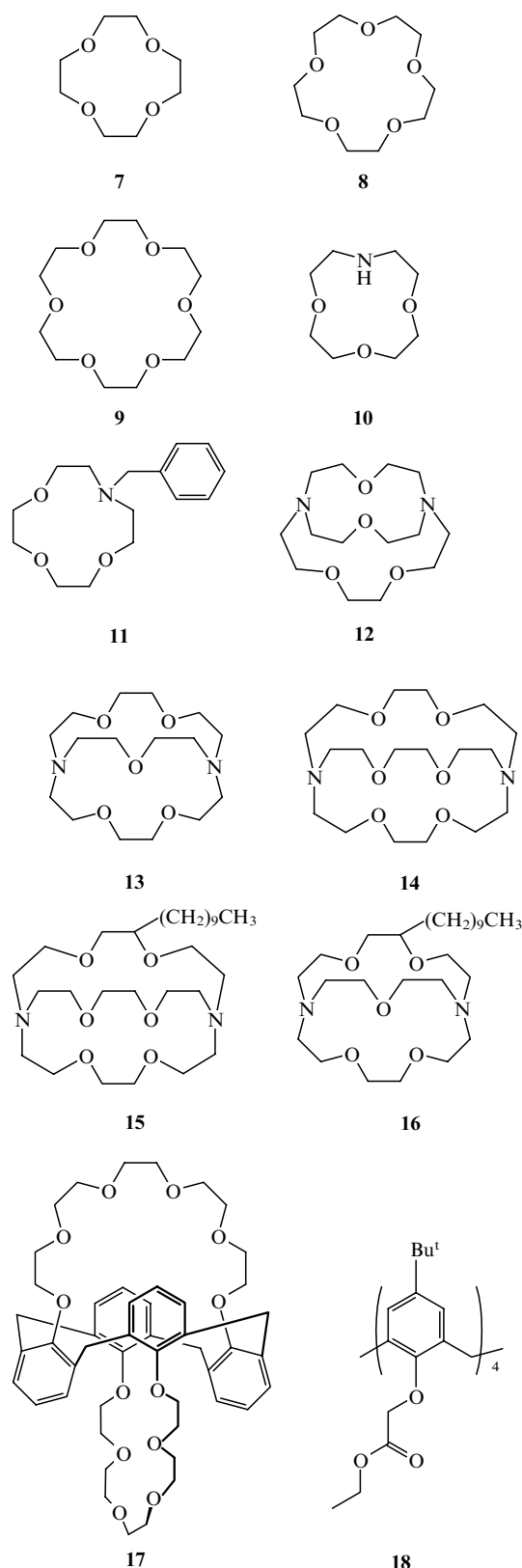
Lithium CPS most often employ cyclic and linear ethers and esters, *viz.*, DME, propylene carbonate (PC), γ -butyrolactone (γ -BL), tetrahydrofuran (THF) and inorganic sulfur compounds (SO_2 , SOCl_2 , SO_2Cl_2) as the solvents.^{2, 26–28} Solutions of lithium salts in such solvents demonstrated sufficiently high conductivities but often exhibited an enhanced activity with respect to both the lithium anode and cathodes. To enhance the stability of electrode materials, it was proposed to add dialkyl carbonates to solutions. In this case, due to a protective film formed on the anode and consisting mainly of solvent oxidation products, the cycling stability substantially increased. At present, the electrolytes for lithium power sources involve, as a rule, binary and ternary compositions based on PC or ethylene carbonate with addition of a certain low-viscosity solvent (DME, THF, *etc.*). At low temperatures, mixed solvents with low viscosities and sufficiently high dielectric constants proved to be most efficient.^{9, 10} Moreover, the possibility of using certain strongly associated and sufficiently viscous liquids, *viz.*, sulfones,^{29–31} sulfamides $\text{R}^1\text{R}^2\text{NSO}_2\text{NR}^3\text{R}^4$ and glymes (dimethyl ethers of polyethylene glycol) $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ (see Refs 32–34), which allow preparing solutions of lithium salts with conductivities of an order of magnitude of $(0.8–2.5) \times 10^{-3} \text{ S cm}^{-1}$, was discussed.

1. Electrolytes with molecularly encapsulated lithium ions

The maximum conductivity and prevention of concentration polarisation during the discharge, were achieved if concentrated (1.5–3 M) electrolyte solutions were used in lithium CPS. However under these conditions, many lithium salts in solvents of low and medium dielectric constants dissociated incompletely to form ion pairs and other associates which cannot conduct current.³⁵ Insufficient solubility of lithium electrolytes also limited their practical application. The solubility and conductivity of lithium electrolytes could be enhanced by introducing macrocyclic compounds which contain oxygen or nitrogen atoms possessing appreciable affinity towards lithium ions into solutions. Several groups of mono- and bicyclic oxo- and aza(oxo)-ligands which form stable lithium complexes with the 1:1 composition are known. These comprise crown ethers: 12-crown-4 (**7**), 15-crown-5 (**8**), 18-crown-6 (**9**), 1,4,7-trioxo-10-azacyclododecane (**10**), *N*-benzyl-1,4,7-trioxo-10-azacyclododecane (**11**), *etc.*; cryptands: cryptand 211 (**12**), cryptand 221 (**13**), cryptand 222 (**14**); cryptand 222D (**15**), cryptand 221D (**16**), *etc.*; calixarenes: 25,27,26,28-bis[1,4,7,10,13,16-hexaoxa(hexadecamethylene)]calix[4]arene (**17**), 4,10,16,22-tetra-*tert*-butyl-25,26,27,28-tetrakis-(ethoxycarbonylmethoxy)calix[4]arene (**18**), *etc.*^{36–43} Tricyclic ligands with cylindrical cavities can also form binuclear complexes with the composition 2:1 at high $\text{Li}^+ : \text{L}$ ratios.⁴²

Among all macrocyclic compounds known, cryptands form the most stable inclusion complexes (cryptates) with alkali metal ions. Such ligands have a spheroidal cavities that can encapsulate cations of suitable sizes, virtually screening the latter from interactions with solvent molecules and counterions.^{36, 37, 43–63} Due to their unique complexing properties, cryptands and crown-ethers favour the dissolution of metal salts and weaken their association in low-polarity media. The solubility increases due to a decrease in the free energy of ions as a result of their encapsulation in the ligand's internal cavity



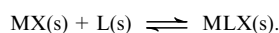


This effect and the solvation of hydrophobic groups of the ligand by organic solvent molecules compete with the increase in the free energy of ions as their radii increase upon complexing. By the example of cryptand **14**, it was shown that complexing of salts with macrocyclic ligands results in a decrease in the solubility of salts well soluble in this solvent and its increase for poorly soluble salts. For a given cryptate salt, the solubility increased with the transition to less polar media in which this salt is more strongly associated.

Table 1. Standard enthalpies of formation for lithium electrolytes in acetonitrile (AN) and propylene carbonate (PC) at 298.15 K.^{45–49}

Electrolyte	$\Delta H^\circ / \text{kJ mol}^{-1}$	
	AN	PC
LiBF ₄	–14.57	–15.55
[Li(7)]BF ₄	4.74	9.69
[Li(8)]BF ₄	4.18	7.29
[Li(10)]BF ₄	0.85	3.73
[Li(11)]BF ₄	11.33	12.35
[Li(14)]BF ₄	6.7	—
[Li(18)]BF ₄	–21.0	—
LiClO ₄	–43.26	—
[Li(7)]ClO ₄	1.27	6.51
[Li(11)]ClO ₄	10.23	9.62
[Li(14)]ClO ₄	20.9	—
[Li(18)]ClO ₄	–9.17	—
LiCF ₃ SO ₃	–15.99	–12.50
[Li(7)]CF ₃ SO ₃	15.69	—
[Li(8)]CF ₃ SO ₃	9.17	13.34
[Li(10)]CF ₃ SO ₃	14.66	18.74
[Li(11)]CF ₃ SO ₃	18.96	22.50
[Li(14)]CF ₃ SO ₃	18.4	—
[Li(18)]CF ₃ SO ₃	–14.0	—
LiAsF ₆	–18.45	–15.14
[Li(7)]AsF ₆	7.17	14.92
[Li(8)]AsF ₆	10.62	13.19
[Li(10)]AsF ₆	3.72	4.84
[Li(11)]AsF ₆	8.75	13.91
[Li(18)]AsF ₆	–22.5	—

The strategy of choosing complex electrolytes for lithium CPS, which has been put forward in Refs 45–49, is based on studying the processes of complex formation and solvation in lithium salt solutions. The experimentally determined enthalpies of dissolution ΔH° for a number of lithium electrolytes in acetonitrile and PC (Table 1) showed that, as a rule, a lithium ion in the free state is much more strongly solvated ($\Delta H^\circ < 0$) than that incorporated into a complex with macrocyclic ligands ($\Delta H^\circ > 0$). A decrease in the degree of solvation due to complexing, which leads to an increase in the conductivity, was observed in less polar media. A number of lithium electrolytes with complex cations involving crown ethers, cryptands and calix[4]arenes as the ligands were isolated as solids. Studies of solvation of simple (M^+X^-) and complex ($[ML]^+X^-$) electrolytes as well as ligands (L) allowed the estimating of the changes in the enthalpy for solid-state complexing processes



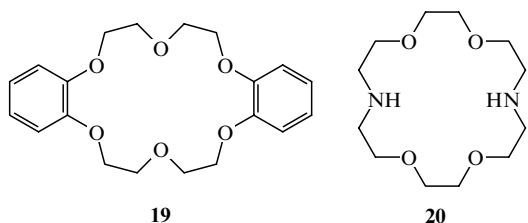
These values can be considered as the characteristics of complex formation in media with low dielectric constants.^{45–49} As was shown, the association of a complex cation with an anion in cryptand-containing solid electrolytes is weaker as compared with electrolytes containing crown ethers and calixarenes. For lithium salts (LiX), the coordination process becomes less exothermic with a decrease in the polarisability in the following sequence of anions: $I^- > ClO_4^- > Br^- > CF_3SO_3^- > AsF_6^- > BF_4^-$. In propylene carbonate at 298.15 K, the complexing of Li^+ with crown ethers resulted in a substantial increase in the ionic mobility (Table 2). Similar results were obtained for lithium complexes with **9** in PC and 2-cyanopyridine and complexes with **9** and **14** in a PC–dichloromethane mixed solvent.^{50, 51}

Studies of the molar conductivity (Λ) of a 1 M LiBF₄ solution in γ -BL as a function of the [L]:[LiBF₄] ratio [L designates crown ethers **8** and **9** and dibenzo-18-crown-6 (**19**)] have shown⁵² that Λ increases with an increase in the crown ether content and reaches its maximum at the equimolar ratio. An electrolyte based on crown ether **8** which forms the most stable complex with a lithium

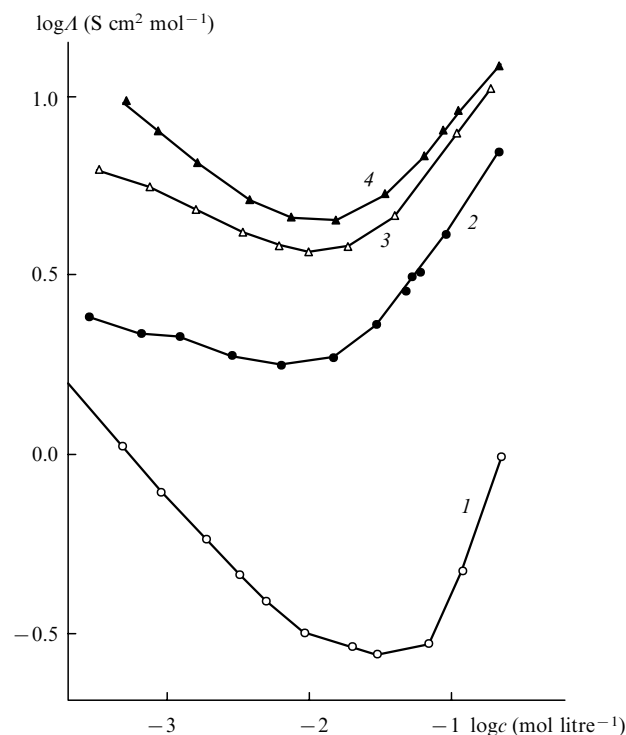
Table 2. Limiting mobility ($S\text{ cm}^2\text{ mol}^{-1}$) of Li^+ and $[\text{LiL}]^+$ cations at 298.15 K.

Cation	A_{LiL^+}	Ref.	Cation	A_{LiL^+}	Ref.
Solvent — PC			Solvent — nitromethane		
Li^+	7.86	46	Li^+	41.4	58
$[\text{Li}(7)]^+$	10.02	46	$[\text{Li}(8)]^+$	29.3	58
$[\text{Li}(8)]^+$	10.50	46	Solvent — AN		
$[\text{Li}(9)]^+$	8.41	50	Li^+	69.5	64
$[\text{Li}(10)]^+$	10.25	46	$[\text{Li}(7)]^+$	68.68	61
$[\text{Li}(11)]^+$	11.99	46	$[\text{Li}(8)]^+$	65.10	61
Solvent — methanol			$[\text{Li}(13)]^+$	63.20	64
Li^+	39.61	62	$[\text{Li}(14)]^+$	60.0	64
$[\text{Li}(7)]^+$	37.53	61	$[\text{Li}(15)]^+$	45.6	64
$[\text{Li}(8)]^+$	38.20	61	$[\text{Li}(16)]^+$	45.1	64
$[\text{Li}(14)]^+$	38.60	62			

ion exhibited the maximum conductivity ($1.1 \times 10^{-2}\text{ S cm}^{-1}$). The use of **8** enhanced the battery power. A possibility of using substances capable of forming charge-transfer complexes (CTC) as the functional additives to electrolytes was also considered.⁵² It was found that for solutions containing CTC of metal lithium with hexamethylphosphoric triamide (HMPA) $\text{Li}^+[(\text{CH}_3)_2\text{N}]_3\text{PO}^-$ in γ -BL (lithium was added in excess, the ratio $[\text{HMPA}]:[\gamma\text{-BL}] = 1:2$), the conductivity increased by three orders of magnitude as compared with the initial solution without CTC and reached $4.2 \times 10^{-2}\text{ S cm}^{-1}$. The potential drop vs. current density dependence has shown that the transport properties of a complex electrolyte are better compared with the ordinary one. It was assumed that in the presence of CTC in solution the charge transfer can be realised by the chain mechanism, where the discharge of an ion is not preceded by its desolvation.



Most of the studies observed a correlation between the stability of complex lithium ions and the increase in the conductivity of the solution. Thus it was found⁵³ that the addition of crown ethers **7** and **9** to LiAsF_6 solutions in DME and **9** to LiClO_4 solutions in DME has practically no effect on the conductivity in the range of salt concentration from 10^{-4} to $5 \times 10^{-2}\text{ mol litre}^{-1}$. The result obtained can be explained by the weak interaction between lithium ions and ligands due to strong solvation of ions by the solvent molecules with the chelate structure. The addition of crown ethers to NaClO_4 solutions in DME resulted in formation of more stable complexes of sodium ions with ligands, thus decreasing the electrolyte association and increasing its conductivity. For more strongly associated electrolytes, the addition of macrocyclic ligands led to a greater increase in conductivity as compared with less associated electrolytes. For instance, the molar conductivity of a LiClO_4 solution in a cyclic ether, namely, 1,3-dioxolane, in the absence of macrocyclic compounds was lower as compared with its solutions in DME due to the stronger association of the salt in the former case. At the same time, the conductivities of 1,3-dioxolane solutions of LiClO_4 containing equimolar additions of **7–9** with $c_{\text{LiClO}_4} > 10^{-3}\text{ mol litre}^{-1}$ were substantially higher compared with DME solutions. The greatest increase in conductivity was observed upon addition of crown ether **8** (Fig. 1). It was concluded⁵⁴ that the extent of the complex-

**Figure 1.** Dependence of the molar conductivity of LiClO_4 and $\text{LiClO}_4 +$ crown-ether (1 : 1) solutions in 1,3-dioxolane on the salt concentration at 298 K:⁵⁴ (1) LiClO_4 , (2) $\text{LiClO}_4 + 7$, (3) $\text{LiClO}_4 + 9$, (4) $\text{LiClO}_4 + 8$.

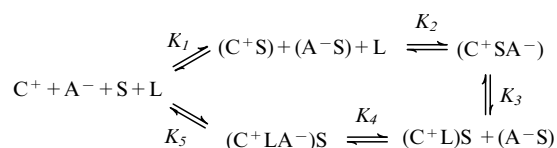
ing-induced increase in conductivity should be directly proportional to the increase in the solution dielectric constant (ϵ) observed in low-polar media due to the higher dipole moments of ion pairs comprising complex cations as compared with ordinary ion pairs.

Conductometric and spectroscopic studies of dissociation of salts $[\text{LiL}]^+[\text{ZPh}_3]^-$ and $[\text{LiL}]^+[\text{A}]^-$ ($Z = \text{C}, \text{Ge}$ and Sn , L is cryptand **12** and A is an anion of a CH-acid) in solvents of low polarity have shown that the introduction of a cryptand to solutions of organolithium compounds resulted in the formation of 'cryptand-separated' ion pairs with light absorption maxima independent of the solvent nature.^{55,56} In nonpolar solvents, the ion pairs comprising anions with strongly delocalised charges (Ph_3C^-) were less strongly associated. In more polar media, the inverse order of anion stability (with respect to ion pairs) due to the stronger ion-dipole interaction of localised charges with solvent molecules was found. Thus, in polar solvents, the electrolytes with charges localised on anions are associated to a lesser degree.

For lithium salts containing anions of CH-acids with strongly delocalised charges, the dissociation constants (K_d) remained virtually unchanged with the formation of cryptates. The degree of association changed only for salts containing anions with localised charges. On going from THF ($\epsilon = 7.6$, $K_d = 10^{-6}\text{ mol litre}^{-1}$) to cyclohexylamine ($\epsilon = 4.7$), and *N*-methylmorpholine, the dissociation constants of cryptate-containing ion pairs decreased by 3–4 orders of magnitude, whereas the transition to benzene ($\epsilon = 2.3$) resulted in their decrease by 9 orders of magnitude. Moreover, the constants depended linearly on the reciprocal dielectric constant of the medium.

A series of studies^{57–64} dealt with conductivity of lithium salts in media with similar dielectric constants, viz., acetonitrile (AN) and dimethylformamide (DMF), methanol and nitromethane (NM), with the aim of elucidating how the molecular structure of the solvent and the presence of macrocyclic ligands affect the transport properties of solvents. It was shown that the limiting

molar conductivity (Λ_0) of a complex electrolyte [LiL]Pi [L is diaza-18-crown-6 (**20**), Pi is picrate ion] in AN is smaller than Λ_0 of a simple LiPi salt. However, with an increase in the LiPi concentration (at the constant L concentration of 10.2×10^{-3} mol litre $^{-1}$), the molar conductivity of an electrolyte containing **20** became higher than without this additive. At a constant salt concentration, the molar conductivity increased with an increase in the L concentration. At the same time, the molar conductivity of KPi in AN with addition of **20** ($c_{20} = 5.2 \times 10^{-3}$ mol litre $^{-1}$) was lower and decreased with an increase in the ligand content.⁵⁷ The results obtained were analysed with account of the following equilibria:



where C is the solute, A is a counterion, S is a solvent molecule and L is a ligand.

Assuming that $K_2 > K_5$ and taking into account the strong association of LiPi in acetonitrile ($K_5 = 10^3$ kg mol $^{-1}$), the increase in conductivity can be explained by dissociation of nonconducting ion pairs, which is caused by complex formation (K_2). For KPi, it was concluded that equilibria 3, 4 and 5 weakly affect equilibria 1 and 2 due to insignificant association of the salt ($K_5 = 77$ kg mol $^{-1}$). It was also found that the addition of L to solutions of KPi and LiPi in MeOH did not affect the value of Λ due to the specific solvation of the ligand by solvent with the formation of H bonds. However, upon addition of an alkyl-substituted diazacrown ether RL (R = Alk), which can form complexes with cations, the conductivity of solutions decreased. The addition of crown ether **8** to LiPi and LiClO $_4$ solution in MeOH and DMF, in which these electrolytes are weakly associated, did not affect the value of Λ . For strongly associated LiPi and LiClO $_4$ in AN and NM (Fig. 2), the introduction of macro-

cyclic ligand **8** enhanced the conductivity, decreased the association constants, and made the decay in Λ which occurs with an increase in electrolyte concentration less pronounced.^{58,59} In an AN + NM mixed solvent, the association constants were practically independent of its composition (as might be expected for isodielectric systems); in the absence of **8**, the values of constants substantially differed from one another and depended nonlinearly on the mixed solvent composition.⁶⁰

Studies of the molar conductivity of solutions of lithium, sodium and potassium perchlorates in MeOH and AN containing crown ethers **7**, **8** and cryptands **13**, **14** have shown that the association constants, mobilities and Stokes radii of [ML] $^+$ complex ions are practically independent of the nature of the metal ion involved. As a rule, the association constants for complex ions were lower compared with 'free' ions; however, $\Lambda_0([ML]^+X^-) \leq \Lambda_0(MX)$ (Table 3).⁶¹⁻⁶⁴ It was assumed that the formation of complexes levels off the differences in the degrees of solvation, charge densities and sizes of complex ions, so that their mobilities depend solely on the size of the ligand attached. A deviation from this rule observed for large cryptate ions was attributed to the changes in their degrees of solvation, because for 'free' alkali ions Λ_0 increases as their solvation weakens

Table 3. Molar conductivity values at infinite dilution and association constants for lithium electrolytes at 298.15 K.

Electrolyte	Λ_0/S cm 2 mol $^{-1}$	K_a /litre mol $^{-1}$	Ref.
Solvent — AN			
LiClO $_4$	173.22±0.02	23±0.3	59
[Li(7)]ClO $_4$	172.30±0.01	7.97±0.01	61
[Li(8)]ClO $_4$	166.2±0.2	15±1	61
[Li(13)]ClO $_4$	167.01±0.01	8.81±0.04	64
[Li(14)]ClO $_4$	163.66±0.01	5.2±0.1	64
[Li(15)]ClO $_4$	149.41	15.90±0.06	64
[Li(16)]ClO $_4$	148.89	13.77±0.07	64
[Li(17)]ClO $_4$	127.67	16.98	52
Solvent — nitromethane			
LiClO $_4$	110.6±0.2	205±2	60
[Li(8)]ClO $_4$	97.03±0.2	13.1±0.3	60
LiPi	86.4	1.6×10^6	60
[Li(8)]Pi	73.31±0.06	84.7±0.5	60
Solvent — DMF			
LiClO $_4$	73.34±0.04	9±1	59
[Li(8)]ClO $_4$	70.32±0.2	10±1	59
LiPi	58.33±0.05	12	59
[Li(8)]Pi	57.9±0.2	16±1	59
Solvent — methanol			
LiClO $_4$	110.52±0.03	25±1	59
[Li(7)]ClO $_4$	108.50±0.03	7.967±0.001	61
[Li(8)]ClO $_4$	109.17±0.02	2.4±0.004	61
[Li(14)]ClO $_4$	109.55±0.05	15±2	63
[Li(17)]ClO $_4$	97.18	13.97	62
Solvent — PC			
LiClO $_4$	26.75	1.2	50
[Li(7)]ClO $_4$	28.91	—	46
[Li(9)]ClO $_4$	27.30	—	50
[Li(17)]ClO $_4$	23.52	0.48	62
LiBF $_4$	28.57	0.29	46
[Li(8)]BF $_4$	31.06	—	46
[Li(10)]BF $_4$	30.83	—	46
[Li(11)]BF $_4$	32.70	—	46
LiCF $_3$ SO $_3$	24.27	1.91	46
[Li(8)]CF $_3$ SO $_3$	27.14	—	46
[Li(10)]CF $_3$ SO $_3$	26.73	—	46

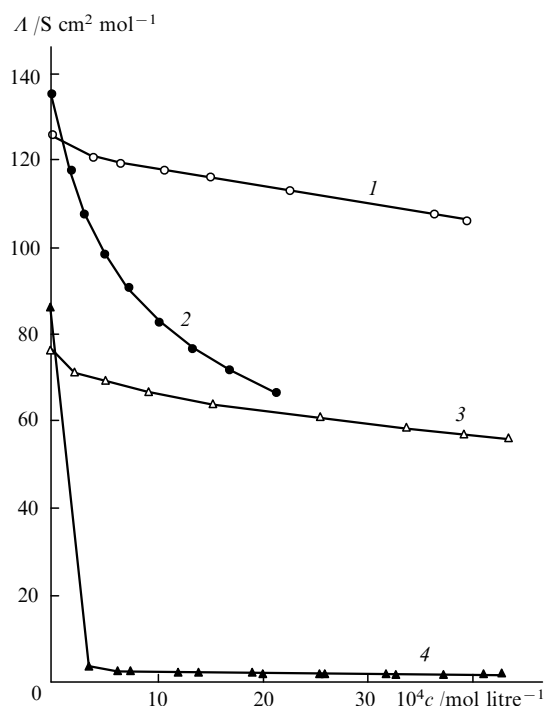


Figure 2. Dependence of the molar conductivity of lithium picrate LiPi solutions in (1, 2) acetonitrile and (3, 4) nitromethane on the salt concentration at 298.15 K.^{58,59} Concentration of additive **8**: (1) 46.43×10^{-4} (3) 89.05×10^{-4} mol litre $^{-1}$, (2, 4) in the absence of **8**.

($\text{Li}^+ < \text{Na}^+ < \text{K}^+$) and Stokes radii increase. Similar results were reported in Ref. 65. The addition of dicyclohexyl-18-crown-6 to ethanol solutions of NaCl, KCl and RbCl ($c = 10^{-4}$ – 10^{-3} mol litre $^{-1}$) resulted in complete dissociation of the electrolytes. At the same time, the values of A_0 decreased. For the system KI + crown ethers in AN, the A_0 values were lower than in solutions without ligands, decreasing with a decrease in the r_1/r_2 ratio, where r_1 is the ionic radius and r_2 is the cavity radius. It is of note that electrolytes based on [K(12-crown-4)]I and [K(15-crown-5)]I ($r_1/r_2 > 1$) in AN exhibited association constants of 28 ± 4 and 23 ± 5 litre mol $^{-1}$, respectively, whereas the original electrolyte KI was completely dissociated. The explanation of this effect invokes the fact that the effective radii of complex ions are smaller than those of solvated ('free') ions. It is known that an increase in association constants due to complex formation is most pronounced for multicharged strongly solvated ions, e.g., halides of rare-earth elements with the cations strongly bound with organic ligands partially substituting their solvate shells.⁶⁶

The effect of the addition of crown ethers **9** and **19** and cryptand **14** on the thermodynamics of electrolytic dissociation and the conduction of KSCN in such solvents as AN, DMSO, PC and their binary mixtures with chlorobenzene was also studied.^{67,68} It was found that throughout the range of mixed solvent concentrations ($\epsilon = 5$ – 66), the association constants are smaller for electrolytes with complex cations than for simple salts. However, the conductivity in the systems studied ($c_{\text{KSCN}} = 10^{-3}$ – 10^{-4} mol litre $^{-1}$) increased with the addition of macrocyclic compounds as a result of a decrease in the degree of electrolyte association only for mixed solvents enriched with the nonpolar component. In individual solvents with relatively high dielectric constants (AN, DMSO and PC) and binary mixtures with high contents of these solvents, the degree of electrolytic dissociation of potassium thiocyanate was high; however, the conduction decreased upon addition of crown ethers and cryptands. This effect was attributed to the increase in the cation size with the formation of complexes comprising macrocyclic ligands, which reduced the cation mobility. In addition to the change in the ion size, the nature of the ligand attached also plays a certain role. It was shown⁶⁹ that, as compared with A_0 of free ions in AN, a decrease in $A_0(\text{ML}^+)$ ($\text{M}^+ = \text{Na}^+, \text{K}^+$) is more pronounced for complex ions containing macrocyclic ligand **9** with two *tert*-butyl substituents than for complex ions with similar but larger ligands with four *tert*-butyl substituents. The explanation of these results invoked the fact that in the latter case complex cations $[\text{ML}]^+$ were less stable and retained their association with anions.

The molar conductivity of potassium chloride solutions with additions of cryptand **14** was calculated for different interaction potentials using the Monte-Carlo method.⁷⁰ For KCl solutions with concentrations of 0.10 and 0.15 mol litre $^{-1}$ at 298 K, the values of A were found to be 128.82 and 126.52 S cm 2 mol $^{-1}$, respectively, whereas for the same solutions with additions of cryptand **14** the A values turned out to be substantially smaller, *viz.*, 71.5 and 65.9 S cm 2 mol $^{-1}$, respectively. For a constant cryptand-to-salt concentration ratio, the molar conductivity decreased as the concentration increased in the range from 0.03 to 0.15 mol litre $^{-1}$. If the overall interaction potential took into account the hydrodynamic component in addition to the Coulomb attraction and repulsion forces, an adequate agreement of calculated and experimental A values was observed. However, the authors failed to derive a generalised interaction potential which would allow one to adequately simulate both the structural (neutron diffraction spectra) and dynamic (conduction) properties of the system studied.

2. Lithium electrolytes with molecularly encapsulated anions

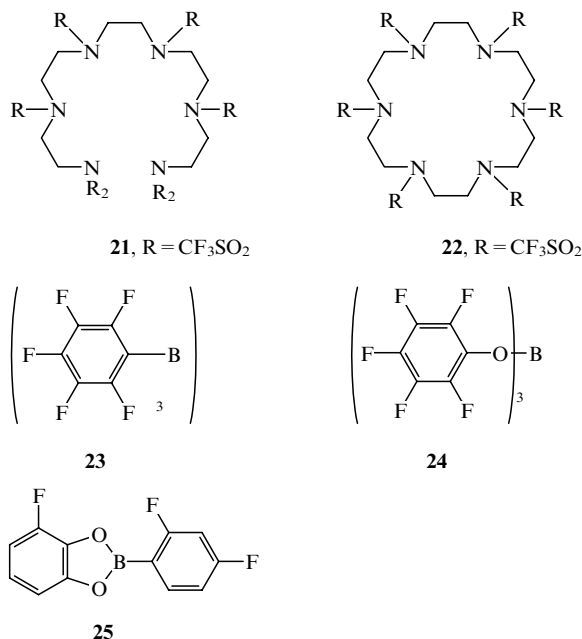
By binding anions of lithium salts into complexes, it is possible to reduce not only the conductivity of a solution (due to a decrease in the degree of ion association), but also the transport number of lithium. Most of the known ligands capable of forming anionic

complexes cannot be used in lithium CPS, because they either coordinate anions by forming hydrogen bonds or comprise positively charged fragments (or metal atoms) acting as Lewis acids. Recently, new neutral ligands, *viz.*, cyclic and linear azacompounds, in which the electron-acceptor groups CF_3SO_2 were substituted for hydrogen atoms in NH groups [octakis(trifluoromethylsulfonyl)pentaethylene hexamine (**21**), hexakis(trifluoromethylsulfonyl)hexacyclene (**22**), *etc.*] were studied.^{71–73} Nitrogen atoms of nonsubstituted polyamines display electron-donor properties, which favour the formation of complexes with cations. Upon introduction of electron-acceptor groups, these ligands become the receptors of anions due to the local positive charge that appears on the nitrogen atoms as the electronic density shifts to the substituent. The formation of complexes by linear ligands and anions was confirmed by the NEXAFS method (X-ray absorption spectra in solution). For complexes with cyclic ligands isolated in the solid state, this was confirmed by X-ray diffraction technique. It was shown that, for an equimolar concentration ratio of ligands and lithium halides (LiCl, LiBr, LiI, $c = 0.1$ or 0.2 mol litre $^{-1}$), the conductivity of THF solutions increased by 1–3 orders of magnitude (Table 4). The conductivity also increased with an increase in the number of sulfonamide groups NSO_2CF_3 for both cyclic and linear ligands. For LiBr and LiCl solutions in THF, the conductivity increased with an increase in the ligand concentration, however, to a lesser extent; the conductivity of a THF solution of lithium iodide remained virtually unchanged as the ligand-to-salt concentration ratio changed from 1:1 to 1:2. The greatest increase in conductivity with the introduction of macrocyclic ligands was observed for solutions of the most strongly associated salt, *viz.*, lithium chloride, which exhibited the lowest conductivity. It was noticed that, upon introduction of macrocyclic ligands comprising six and seven sulfonamide groups in a ring, the conductivity of lithium halide solutions in THF increased to practically the same value ($\sim 1.6 \times 10^{-3}$ S cm $^{-1}$), although their solutions without additives exhibited quite different conductivities.

Yet another group of anionic receptors comprises boron-containing ligands with fluorinated aryl and alkyl groups: boranes [(C_6F_5) $_3\text{B}$ (**23**), *etc.*], borates [($\text{C}_6\text{F}_5\text{O}$) $_3\text{B}$ (**24**), *etc.*], boronates [($\text{C}_6\text{H}_3\text{F}$) $_2\text{O}_2\text{B}(\text{C}_6\text{H}_3\text{F}_2)$ (**25**), *etc.*].^{74–77} As compared with borane (**23**), borate (**24**) has a higher solubility in solvents of low polarity

Table 4. The effect of the addition of equimolar amounts of boron- and nitrogen-containing anionic receptors on the conductivity of lithium electrolytes at 298.15 K.^{71–77}

Electrolyte	σ / S cm $^{-1}$
Solvent — DME	
0.2 M LiCl	5.0×10^{-6}
0.2 M LiCl + 0.2 M (24)	3.0×10^{-3}
0.2 M LiCl + 0.2 M (23)	2.6×10^{-3}
0.2 M LiI	7.3×10^{-4}
0.2 M LiI + 0.2 M (24)	3.2×10^{-3}
0.2 M LiI + 0.2 M (23)	2.2×10^{-3}
0.2 M LiCF $_3$ COO	3.3×10^{-5}
0.2 M LiCF $_3$ COO + 0.2 M (24)	3.3×10^{-3}
0.2 M LiCF $_3$ COO + 0.2 M (23)	3.2×10^{-3}
0.2 M LiCF $_3$ COO + 0.2 M (25)	1.2×10^{-3}
0.8 M LiF + 0.8 M (24)	6.4×10^{-3}
0.8 M LiF + 0.8 M (23)	6.6×10^{-3}
Solvent — THF	
0.1 M LiCl	7.5×10^{-6}
0.1 M LiCl + 0.1 M (21)	1.6×10^{-3}
0.2 M LiCl	1.6×10^{-6}
0.2 M LiCl + 0.2 M (22)	1.4×10^{-3}
0.1 M LiBr	2.9×10^{-5}
0.1 M LiBr + 0.1 M (21)	1.8×10^{-3}



(*e.g.*, their solubilities in dimethyl carbonate at room temperature were > 1 and $0.3 \text{ mol litre}^{-1}$, respectively). The complexing of these ligands with halide ions was also confirmed by X-ray absorption spectra of solutions (NEXAFS). The addition of boron-containing ligands to lithium halide solutions in DME substantially increased the conductivity and solubility (see Table 4). For example, lithium fluoride was practically insoluble in solvents with low dielectric constants; however, the addition of a compound **23** or **24** (1 : 1) to its 1 M solution in DME yielded solutions with conductivities of $(6.2\text{--}6.8) \times 10^{-3} \text{ S cm}^{-1}$. The conductivity was shown to increase with an increase in the number of fluorine atoms in the ligand molecules. Boron-containing ligands, especially boranes, are electrochemically stable and compatible with the lithium anode. Thus for the 1 M LiF + 1 M **23** solution in a mixed PC-ethylene carbonate-dimethyl carbonate (1 : 1 : 3) solution, the range of working potentials reached 5.0 V. Compared with such electrolytes as LiPF₆ and LiAsF₆, lithium halides are cheaper and less toxic. Taking into account that the starting reagents for the synthesis of boron-containing anionic receptors are also inexpensive and of a low toxicity, electrolytes with complex anions have the prospects of gaining a wide use in future.

III. Polymeric electrolytes

Currently, keen attention is drawn to the safety of application and utilisation of waste power sources. In this respect, metallic lithium is an environmentally clean material as compared with lead and cadmium. The safety of lithium CPS for the environment and human beings is ensured by the correct choice of nonaqueous electrolyte solutions.

Numerous studies in the field of polymeric lithium electrolytes were largely aimed at solving the problems of enhancing the stability of the electrolytic system with respect to the lithium anode and increasing the safety and reliability of the performance of lithium batteries used for energising domestic devices.⁷⁸

The main drawback of polymeric electrolytes is their low conductivities at room temperature. Under the conditions mentioned, these electrolytes are mostly in a quasicrystalline state ($\sigma = 10^{-6}\text{--}10^{-7} \text{ S cm}^{-1}$). The conductivity increases only with the transition to the amorphous state (as the temperature rises). To improve the characteristics of polymeric electrolytic systems, different additives were extensively used, along with the procedures of modifying the polymer structure itself (which allows, *e.g.*, the reduction of the glass transition temperature). The addition of

plasticisers that, as a rule, represent electrolyte solutions in low-molecular aprotic solvents led to formation of hybrid biphasic gel-electrolytes with acceptable conductivities. However, they were highly active with respect to lithium electrodes. Additions of macrocyclic compounds weaken the association of ions in non-polar polymeric matrices, thus increasing the conductivity.

The effect of cryptand **14** additives on the conductivity of sodium salt of an oxysiloxane polymer was studied.⁷⁹ It was found that with addition of the cryptand, the conductivity increased by a factor of 15 irrespective of temperature and concentration and was $1.7 \times 10^{-5} \text{ S cm}^{-1}$. It was concluded that, in the general case, the conductivity should increase with an increase in the equilibrium constant of the formation of cation-cryptand complexes and an increase in the association constant of the polymeric electrolyte. This agrees with the conclusions made in the studies of solutions of liquid-phase lithium electrolytes. Cations are free charge carriers despite their sufficiently strong solvation by the polymer, and a cryptand additive should not cause any substantial conductivity rise. This was confirmed in several studies.⁸⁰⁻⁸⁴ Additions of cryptand **14** or crown ether **8** to polymeric electrolytes based on NaSO₃CF₃, NaBF₄, NaI and NaSCN solutions in amorphous polyethylene oxide were shown to reduce their solubilities and conductivities.^{80,81} Using spectroscopic methods, it was shown that association of these salts is insignificant and all polymer-salt complexes studied were amorphous. At the same time, the solubility and conductivity of NaSO₃CH₃ which is poorly soluble in the polymer increased with the addition of the crown ether and cryptand but did not reach the values observed for the other electrolytes of this system. An analysis of parameters of the Vogel-Tamman-Fulcher (VTF) equation which describes the temperature dependence of conductivity showed that the addition of the cryptand decreases the number of charge carriers for electrolytes with weakly associated NaSO₃CF₃, NaBF₄, NaI and NaSCN salts, increasing it only for electrolytes containing the more strongly associated salt NaSO₃CH₃.

Solid electrolytes based on Li[CF₃SO₂N(CH₂)₃OCH₃] complexes with cryptands **12-14** and crown ethers **7-9** and Li[(CF₃SO₂)₂N] complexes with **9** were also studied (Fig. 3).^{83,84} It was assumed that amorphous phases are formed due to the difference in the radii of the macrocycle cavity and the cation. The method of differential scanning calorimetry has shown that the most stable macrocycle-salt complexes [ML]⁺X⁻ (M is an alkali metal, L is a crown ether or cryptand), in which the sizes of the cation and the ligand's (**7**, **12**) cavity match most closely one another, form only crystalline phases. A series of amorphous complexes of macrocyclic compounds and lithium salts were

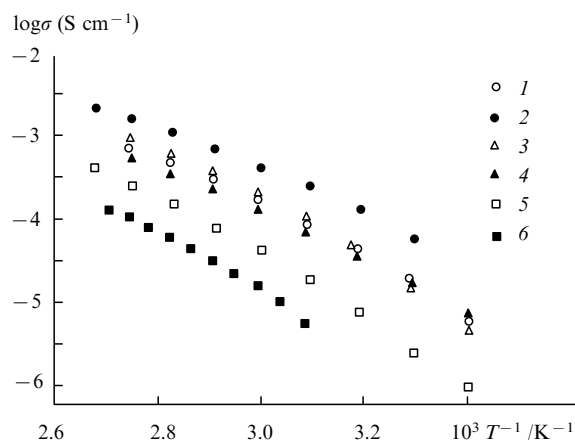


Figure 3. Temperature dependence of the specific conductivity (σ) of amorphous complexes: (1) [Li(**14**)]CF₃SO₂N(CH₂)₃OCH₃, (2) [Li(**13**)]CF₃SO₂N(CH₂)₃OCH₃, (3) [Li(**12**)]CF₃SO₂N(CH₂)₃OCH₃, (4) [Li(**9**)]CF₃SO₂N(CH₂)₃OCH₃, (5) [Li(**8**)]CF₃SO₂N(CH₂)₃OCH₃ and (6) [Li(**7**)]CF₃SO₂N(CH₂)₃OCH₃.⁸¹

synthesised where the size ratio mentioned was violated. Complexes with cryptands passed into the amorphous state at lower temperatures as compared with complexes with crown ethers. The presence of asymmetric anions favoured the glass transition.⁸⁴ Amorphous samples with the lowest glass transition temperature exhibited the greatest conductivity ($10^{-4.5}$ S cm⁻¹). An analysis of IR and Raman spectra has shown that cryptands most effectively screen lithium cations. The parameters of the VTF equation have shown that cryptate complexes exhibit higher concentrations of charge carriers as compared with complexes with crown ethers (see Fig. 3).

An increase in conductivity at room temperature by 2 orders of magnitude (up to 10^{-4} – 10^{-3} S cm⁻¹) for polymeric electrolytes based on LiClO₄ and polyethylene oxide observed upon introduction of crown ether **8** was explained⁸⁵ by the formation of stable complexes of crown ethers with lithium ions. However, the addition of 1,4,7,10,13-pentaoxa(13)orthocyclophane (benzo-15-crown-5) had practically no effect on the conductivity in the system mentioned, because the formation of complexes with lithium ions was complicated. The solid polymeric electrolytes synthesised were well compatible with the lithium anode and stable during long-term storage.

New synthetic methods for polymeric and liquid electrolytes of the series of nitrogen-containing compounds, *viz.*, aromatic amines, diarylamines and organosilicon compounds with ammonium groups and their practical applications as the additives have been reported.⁸⁶ Organosilicon derivatives of 4,4'-bipyridyl were referred to as most promising. The additives mentioned almost double the conductivity of polymeric electrolytes and prevent the capacity fade during cycling.

The mobility of ions in polymeric electrolytes is directly associated with the mobility of polymeric chain fragments, which is the main factor limiting the conductivity. An approach to enhancement of the conductivity and simultaneous increase in the transport number of lithium ion is the use of compounds which act as Lewis acids and can interact with anions. For example, good results were obtained where cyclic boron-containing compounds **26** ($n = 1-3, 7.2$), particularly, 2,4,6-tris(2-methoxyethoxy)boroxine were introduced into polymeric electrolytes based on LiSO₃CF₃ and poly(methyl methacrylate).⁸⁷ This was explained by the effective interaction of oligoether oxygen-containing fragments with lithium ions and the anion-acceptor nature of boroxine rings. Introduction of 11-acryloyloxy-3,6,9-trioxaundecyl biphenyl-2,2'-diyl borate (**27**) into solutions of strongly associated electrolytes of LiCl and CF₃CO₂Li in both polar and low-polar media, as well as of electrolytes formed by LiBF₄ and **1** in DME and dimethyl carbonate (DMC) increased the conductivity.⁸⁸ In contrast, introduction of the same additive to solutions of well dissociated salts, namely, LiBF₄ and **1** in polar solvents resulted in a decrease in the ionic conduction, which was explained by a decrease in viscosity (Table 5). It is of note that the conductivity increased for all gel-polymeric electrolytes, because the additive introduced was built-in into the polymer structure in such a way that the microviscosity of the solution surrounding the ions remained unchanged.

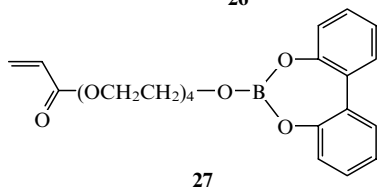
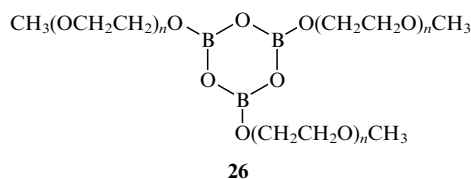
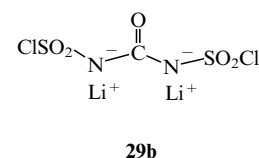
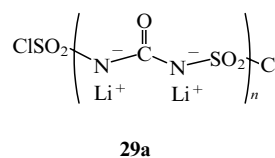
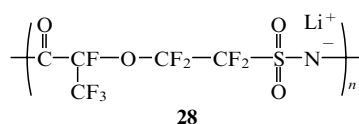


Table 5. The effect of the addition of equimolar amounts of **27** on the conductivity of lithium electrolyte solutions ($c_m = 0.2$ mol kg⁻¹) at 298.15 K.⁸⁸

Salt	Electrolyte	Conductivity (mS cm ⁻¹) in a medium of			
		PC	γ-BL	DME	DMC
LiCF ₃ COO	without addition	0.33	5.2	0.024	$< 5 \times 10^{-4}$
	with addition	0.82	1.2	0.19	2.8
LiBF ₄	without addition	2.7	4.3	0.19	1.5×10^{-3}
	with addition	2.2	3.1	2.5	0.027
Li(CF ₃ SO ₂) ₂ N	without addition	3.0	4.3	3.0	0.25
	with addition	2.4	3.3	6.9	0.42

In a number of studies, it was suggested to use lithium salts with polymeric anions. Thus for electrolytes based on acrylates of a co-polymer of ethylene oxide and propylene oxide and containing a lithium salt with a polyimide anion, *viz.*, lithium poly(5-oxo-3-oxa-4-trifluoromethyl-1,1,2,2,4-pentafluoropentamethylene-sulfonimide) (**28**), the conductivity was of an order of magnitude of 10^{-5} S cm² and the transport number of lithium > 0.7 substantially exceeded the value obtained for polymeric electrolytes with a 'monomeric' lithium salt **1**.⁸⁹ Polyanionic electrolytes prepared by introducing Lewis bases (imidazole) into the polymeric structure (the 'base in chain' method) were studied.⁹⁰ Plasticisation of the corresponding lithium polyimide salts (**29a, b**) by chloroaluminates (1 : 1) and AlCl₃ made it possible to substantially decrease the glass transition temperature (< -20 °C) and obtain liquid-phase systems with the electrolyte conductivity values currently best for polyanionic electrolytes. Thus the conductivity of lithium poly(carbamine sulfonylimide) (**29a**) reached the maximum value upon addition of 20% LiAlCl₄ ($10^{-2.9}$ S cm⁻¹ at 25 °C) (Fig. 4), whereas, for a similar complex with the 1,3-dichlorosulfonyl-1,3-dilithiocarbamide (**29b**), the maximum conductivity value obtained upon introduction of 40% LiAlCl₄ did not exceed $10^{-3.3}$ S cm⁻¹. However, the presence of Lewis acids (AlCl₃, BF₃) in the system can initiate corrosion of the power source materials and other undesirable electrochemical processes. In this connection, it was proposed to 'fix' a Lewis acid directly in the polymer chain. For this purpose, the $-\text{O}-\text{B}-(\text{Ph})-\text{O}-([\text{CH}_2]_2\text{O})_n$ ($n = 2-23$) polymers synthesised by the 'acid in chain' method were transformed into polymeric anions by complexation with lithium salt anions representing Lewis acids (*e.g.*, Ph⁻, CN⁻).⁹¹ The largest conductivity values were obtained for short polyether chains $([\text{CH}_2]_2\text{O})_n$ which separated the anionic centres in the polymer. The polymers thus synthesised were reported to exhibit lower chemical activities and better compatibility with cathodic and anodic materials as compared with their analogues obtained by the 'base in chain' method. It is expected that higher values of ionic conduction can be reached by using lithium compounds with anions of a higher basicity, such as methoxide and formate ions, as well as with the methyl anion (CH₃⁻).



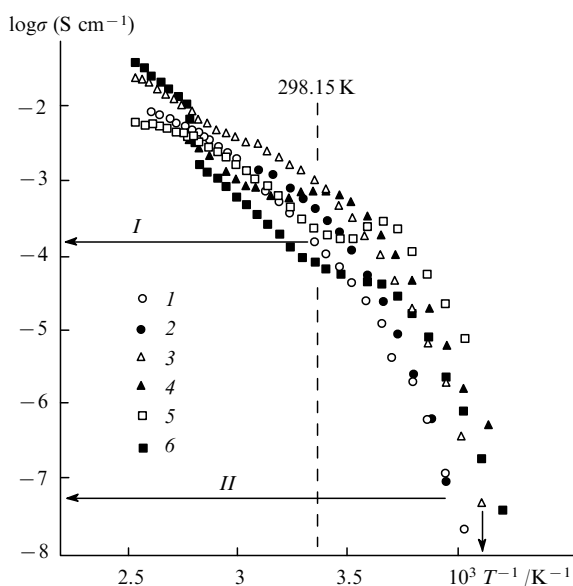
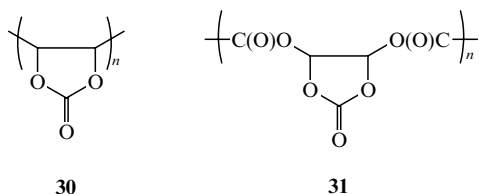


Figure 4. Temperature dependence of the specific conductivity of polymeric electrolytes based on lithium complexes with polyanions, *viz.*, $(1-x)\mathbf{29a}-\text{AlCl}_3$ (1:1)– $x\text{LiAlCl}_4$ (see Ref. 90). Arrows designate the conductivity of (I) an electrolyte without LiAlCl_4 at 298.15 K and (II) an electrolyte containing 20 mol.% LiAlCl_4 at the glass transition temperature; x : (1) 0, (2) 0.1, (3) 0.2, (4) 0.3, (5) 0.4, (6) 0.5.

Polymeric electrolytes with relatively high conductivities can be obtained not only in the amorphous state but also in the crystalline state. The following ‘rigid’ polymers were synthesised: poly(vinylene carbonate) (**30**) and poly(2-oxo-1,3-dioxolane-4,5-diyl oxalate) (**31**).⁹² In contrast to most polymeric electrolytes known, the addition of a lithium salt (LiCF_3SO_3) to these polymers decreased the glass transition temperature and the maximum conductivity was reached at a higher salt concentration (the molar concentration ratio of the salt to the monomeric units of polymers was 1:1). The crystalline structure of these polymers did not prevent the ionic transport, because the mobility of ions in the polymer is independent of the segmental mobility of polymeric chains.



In a number of cases, solid polymeric electrolytes based on amorphous co-polymers of acrylonitrile with the maximum concentration of lithium salt were found⁹³ to exhibit unusually high conductivity, *viz.*, $\sim 10^{-3} \text{ S cm}^{-1}$. Moreover, the conductivity of systems studied was shown to be either virtually independent of the temperature or have a weakly pronounced inverse temperature dependence as compared with the Arrhenius-type dependence. Measurements of charge transfer numbers showed that it is mainly cations that are involved in the ionic transport. An analysis of IR spectra of electrolytes confirmed the presence of substantial amounts of ion pairs, triplets and more complex associates of lithium salts. Based on these results, the authors proposed that highly concentrated macromolecular polymeric solutions have a special structure which involves ionic clusters interacting with one another. The ionic transport in such solutions proceeds by an unusual, low-energy mechanism. The use of extremely high (close to the solubility limit) concentrations of lithium salts in polymeric matrices was assumed to be promising for the development of highly conductive solid polymeric electrolytes.

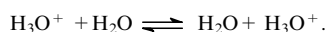
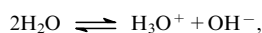
Recently, great success was achieved in studying the so-called ionic liquids, *viz.*, salts with unusually low melting points, which remain in the liquid state even at room temperature. Such systems are of great interest as the electrolytes for lithium CPS. Based on lithium salts and Lewis acids (AlCl_3), the following liquid electrolyte systems with conductivities of $> 10^{-3} \text{ S cm}^{-1}$ at room temperature were synthesised: $0.33 \text{ LiCF}_3\text{SO}_3-0.67 \text{ AlCl}_3$,⁹⁴ $0.4 \text{ LiSCN}-0.6 \text{ AlCl}_3$.⁹⁵ It was assumed that, due to ion–molecule interactions, the following complex anions are formed in these systems: $[\text{Al}_n\text{Cl}_{3n+1}]^-$, $[\text{Al}_n\text{Cl}_{3n-m+1}(\text{SCN})_m]^-$, *etc.*, and the melt structure changes, which makes crystallisation difficult and is favourable for the system to retain its liquid or glassy state. Moreover, the charge transfer mechanism is virtually independent of the structural relaxation of the medium (the charge is transferred preferentially by cations).

The above methods for modifying chemically the electrolytic systems are different; however, they have a common theoretical basis determined by the ion-migration (Stokes) mechanism of charge transfer. These methods were largely applied to dilute solutions of lithium electrolytes in aprotic solvents and polymers. Concentrated electrolyte solutions in aprotic solvents, which are used in lithium CPS, still remain insufficiently studied. The results obtained to date^{9,53,54} suggested that, in low-polar solvents, the greatest increase in conductivity upon addition of macrocyclic compounds takes place at concentrations below the molar conductivity minimum point, *i.e.*, where ion pairs prevail in solution. For higher concentrations (in the ‘anomalous’ range), the conductivity increased to a lesser extent, apparently, due to the changes in the nature and composition of ions.

For strongly associated electrolytes in solvents with low and moderate dielectric constants and polymers, the conductivity increases mainly due to the weakened association and increased solubility. The most pronounced weakening in the ion association was observed with the formation of lithium–cryptand complexes as compared with lithium–crown ether complexes. As a rule, an increase in conductivity in these media is proportional to the increase in the stability constant of the complex ions formed. With an increase in ligand concentration, conductivity increases and reaches a maximum at the equimolar Li:L ratio. In more polar solvents, where the electrolyte is sufficiently soluble and weakly associated, and the size of the ligand attached exceeds that of the solvating shell, the mobility of ions can decrease due to an increase in their Stokes radii. For electrolytes in polar media, in which the ions are strongly solvated (*e.g.*, for lithium salt solutions in propylene carbonate, $K_a \approx 0$), the conductivity can increase as a result of weakening in solvation, and, correspondingly, a decrease in the ‘free’ (solvated) ion radius with the formation of a complex with a macrocyclic ligand. At the same time, in certain cases, a substantial weakening in the lithium ion solvation upon its complexing can increase the association constants for the electrolytes involving complex cations as compared with ordinary electrolytes.

IV. Electrolytic solvosystems for lithium batteries and mechanisms of charge transfer in solutions

To understand the reasons for the electrochemical behaviour of electrolytic systems of different nature in wide ranges of electrolyte concentrations and temperatures, it is necessary to gain an insight into the nature of charge carriers and the mechanism of charge transfer. It is known that the high conductivity typical of concentrated aqueous solutions of bases and acids used as the electrolytes in conventional CPS is caused by the chain mechanism of conduction.^{13,96,97} This mechanism is distinguished by the exchange interaction between the electrolyte ions which correspond to the lyonium and lyate ions of the solvent and the solvent molecules (H_2O , H_2SO_4 , H_2SeO_4 , H_3PO_4 , HF). Thus in an aqueous solution, hydroxonium ions (hydrated protons) and water molecules exchange protons



Several approaches were proposed for estimating different contributions to the charge-transfer mechanism in solutions.^{13, 66, 98–103} However, to date, no sufficiently reliable criteria and methods were proposed for elucidation of the nature of charge carriers, which makes the studies of the conduction mechanism in nonaqueous media quite difficult.¹⁰⁴ The greater complications arise for concentrated electrolyte solutions for which the concepts of the Debye–Hückel–Onsager theory and the law of independence of ions' motions (the Kohlrausch law) are not fulfilled. One of the approaches to assessing the conduction mechanism in electrolyte solutions consists in comparing the activation energies of the conduction and viscous flow processes. For example, within the framework of this approach, it was assumed that the charge transfer in the LiCl–AlCl₃–CH₃NO₂–SOCl₂ system (see Refs 27, 28) with the electrolyte concentration > 1 mol litre⁻¹ occurs by both the ion-migration and chain mechanisms. The latter mechanism provided high conductivity values during the lithium battery discharge irrespective of the observed increase in the solution concentration and viscosity.

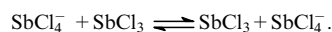
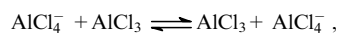
The conduction mechanism may be characterised by the transport number of ions (*t_i*), which however is insufficient to confirm the chain mechanism of conduction. Transport numbers of ions for most binary aqueous solutions of salts insignificantly deviate from the average value of 0.5; in aqueous solutions of acids and bases, *t_{H+}* and *t_{OH-}* are substantially higher, *viz.*, from 0.75 to 0.85. In nonaqueous solvents, transport numbers strongly depend on the differences in the degrees of solvation for cations and anions. For example, the greatest part of solvation energy for lithium salts in PC (up to 80%) falls to cations.¹⁷ Hence, as a rule, *t_{Li+}* is smaller than the transport number of the corresponding anion and is equal to 0.3–0.5. The known attempts to analyse the experimental results on conductivities and the solution structure ambiguously assessed these data and often led to unorthodox conclusions. Thus it was suggested^{105, 106} that electrolyte solutions be considered as impurity conductors in which the charge is transferred by electrons and holes rather than by ions. Based on high-frequency studies, electrolyte solutions were concluded to have ionic lattices like those in crystals and the presence of a long-range order was assumed to be a key condition for enhancing the mobility of charge transfer in condensed media.

The possibility of realising the chain mechanism of conduction in solutions is largely determined by the structure and the degree of self-ionisation of the solvent, which depends (in protic solvents) on the strength of bridging hydrogen bonds between molecules.^{96, 97} For instance, in liquid ammonium the constant of self-ionisation (at –50 °C) was found to be ~ 10⁻²³ due to a weak N···H···N bond and a low ε, and the mobility of ions formed upon autoprotolysis was not anomalously high.^{107, 108} Such an order of magnitude is typical of self-ionisation constants of most nonassociated aprotic solvents. Nonetheless, the charge transfer by the chain mechanism can also occur in aprotic media. In this case, anomalous mobility values were observed for lyonium and/or lyate ions formed upon self-ionisation of solute associates.

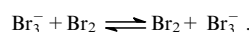
In binary liquid systems formed by protic (H₂SO₄, H₃PO₄) acids and proton-containing organic bases (RH) (such as acetamide, *N*-methylacetamide, *N,N*-dimethylacetamide, *etc.*), in the range of high acid concentrations, the charge was shown to be transferred by the chain mechanism as in individual acids.^{109–113} Bearing in mind that, for binary systems of organic bases with strong aprotic acids (MX_{*n*}) (SbCl₃, FeCl₃, SnCl₄, SbCl₅), the conductivity isotherm has a maximum, it may be assumed that the charge transfer in these systems also occurs by the chain mechanism in the range of high acid concentrations. The components of these systems are prone to autoionisation; hence, the acid–base interaction occurs between the lyonium ion MX_{*n-m*}⁺ of the acid and the lyate ion R⁻ of the base to give a nonelectrolyte MX_{*n-m*}R_{*m*}. This results in the increase in the concentration of the

lyate ions of the acid MX_{*n+1*}^{p-} and the lyonium ions of the base RH₂⁺ in the solution. It is the mobility of these ions that determines the conduction of solutions.

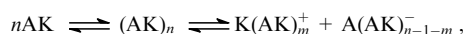
For chlorides (solvated chloride-containing ions, *e.g.*, SbCl₄⁻ or AlCl₄⁻) in ultra-concentrated solutions based on antimony trichloride and aluminium chloride, the following halogenotropic mechanism of conduction was postulated:^{109–111, 114, 115}



For bromides and iodides (polyiodides, I₃⁻, Br₃⁻), PCl₅ and PBr₅ in liquid bromine and iodine, the same mechanism was suggested.^{116–118}



It was shown¹¹⁹ that the conduction of salt solutions in low-polar solvents in a wide range of concentration (from 0.1 mol litre⁻¹ to fused salts) is largely determined by self-ionisation (autosolvation) of the electrolyte



where K(AK)_{*m*}⁺ and A(AK)_{*n-1-m*}⁻ are the autosolvated cation and anion, respectively.

According to concepts put forward,^{116–118} ions in concentrated solutions form aggregates which are involved in the charge transfer. Moreover, with an increase in electrolyte concentration, upon passing its minimum at 0.01–0.1 mol litre⁻¹, the molar conductivity of low-polar solutions was shown to increase due to the increased number of such aggregates, irrespective of the simultaneous increase in the solution viscosity. A hypothesis that an electrolyte in a concentrated solution passes into a state similar to that of a melt, which was put forward in the studies under discussion, was confirmed by the results of studying the molten ZnBr₂–AlBr₃ and SbBr₃–AlBr₃ systems. With an increase in salt concentration, the molar conductivity values of these melts (with a correction made for viscosity) increased up to a point where the conductivity of the individual liquid electrolyte is reached. According to this hypothesis, for any concentration of an electrolyte solution, its molar conductivity (with a correction made for its viscosity) cannot exceed the corresponding value of a hypothetical molten individual electrolyte under equal conditions. The anomalous conductivity can be observed not only for solvents with low dielectric constants but also in polar solvents at sufficiently high electrolyte concentrations. For both cases, a similar type of the dependence of the molar conductivity on the concentration was suggested.

Similar conclusions were drawn in Refs 32–34. Based on the results of studying thermodynamic and transport properties of lithium electrolytes in a wide range of concentrations in solvents of different types (glymes, sulfamides, AN, γ-BL, PC and their mixtures), it was concluded that at least two conduction mechanisms should be taken into account, *viz.*, the ion-migration mechanism, which occurs at low electrolyte concentrations, and the chain mechanism (charge transfer accompanied by rotation of complexes-associates), which occurs at high concentrations. It was assumed that the state of a highly concentrated electrolyte solution is similar to that of a fused salt. The chain mechanism of conduction can occur in both low-polar and polar aprotic solvents with sufficiently high electrolyte concentrations. In highly concentrated solutions, as the distance between ions decreases, the chain mechanism prevails and the difference in the conductivity values for solvents with low and high ε values decreases. A low viscosity of the medium and a high solvation power of the solvent, which weaken the ion association and facilitate reorientation of dipoles in the electric field, favour the charge transfer to occur by the chain mechanism.

However, for the chain mechanism (in contrast to the ion-migration mechanism), many properties of electrolytic systems (viscosity, solvation, association) can exert the opposite effects on the conduction. For example, despite the high viscosity of anhydrous sulfuric acid, the mobilities of the lyonium H_3SO_4^+ and the lyate HSO_3^- ions are comparable with the mobilities of H^+ and OH^- ions in water; in aqueous solutions, the mobility of protons substantially exceeds those of other ions, even if the hydration energy of H^+ is the highest; among the large number of electrolytes completely dissociated in aqueous solutions, only acid and base solutions, *i.e.*, electrolytes that comprise the ions formed by the self-ionisation (autoprotolysis) of the solvent have anomalously high conductivity values. The prototropic conduction decreases with an introduction of both electrolytes and non-electrolytes into these solutions,⁹⁷ which is usually attributed to the hydration of ions and molecules accompanied by the changes in the water structure built by hydrogen bonds. Such a structure is best suited for the chain transfer of protons. At the same time, it was found¹²⁰ that the additivity of the molar conductivity is typical of the whole composition range of an isomolar $\text{HCl} + \text{KCl}$ mixture in methanol. A similar λ vs. composition dependence was also observed for an aqueous $\text{HCl} + \text{LiCl}$ system ($c_{\text{Li}} \leq 8 \text{ mol litre}^{-1}$). Taking into account these results, it was concluded that the prototropic mechanism of proton transfer is retained even for high concentrations of aprotic electrolytes.

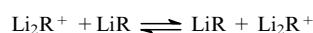
It should be also noted that, in contrast to other ions, the mobilities of H^+ and OH^- increase with an increase in the pressure.⁹⁶ The temperature coefficient of conduction is positive for both aqueous solutions of acids and bases and other electrolytes with the usual ion-migration mechanism of conduction. The effect of the temperature on the structure of hydrogen bonds in water is apparently less significant compared with the effects of pressure and chemical factors (solvation). A comparison of different physicochemical parameters of water and other liquids in a wide temperature range have shown that water retains a sufficiently distinguishable structure up to the critical point.¹²¹

An analysis of the conduction data for different kinds of aqueous and nonaqueous electrolyte solutions have shown that the chain mechanism of conduction is realised in aprotic media if, first, the chemical nature of the electrolyte is similar to that of the solvent (solutes comprise lyonium or lyate ions of the solvent) and, second, at high concentrations, the solvent and/or the electrolyte form a polymeric structure with intermolecular bonds.

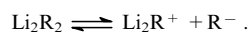
The presence of a certain solution structure is often characterised by high viscosity values (*e.g.*, H_2SO_4 , H_3PO_4 , H_2SeO_4 , concentrated electrolyte solutions). On the other hand, such associated liquids as water, $(\text{HF})_n$, SbCl_3 , *etc.*, in which the charge is transferred by the corresponding ions by the chain mechanism, exhibit relatively low viscosities. Evidently, under conditions necessary for the chain mechanism to occur, an additional decrease in the viscosity should facilitate the charge transfer.

To develop nonaqueous electrolytic solvosystems with the chain mechanism of conduction, it is necessary to carry out a quest for new-in-principle lithium electrolytes and nonaqueous media which will match the requirements described above. One of the approaches in such a research is to develop electrolytic solvosystems based on organolithium compounds. Organolithium compounds pertain to the group of the so-called electron-deficient structures, like organoelement compounds of the Groups II and III on the Periodic System (R_2Be , R_3B , R_3Al).^{122, 123} At the same time, organolithium compounds behave in reactions as the reagents with a deficit of electrons and react in the same manner as carbanions. The deficit of electrons manifests itself in a strong association of molecules $n\text{RLi} \rightleftharpoons (\text{RLi})_n$ ($n = 2-6$) by means of bridge bonds formed by the electrons of the $\text{C}-\text{Li}$ bond and free $2p$ orbitals of the lithium atoms. It was assumed¹²⁴ that the nature of $\cdots\text{Li}-\text{C}\cdots\text{Li}-\text{C}\cdots$ 'lithium' bonds in the associates of organolithium compounds is similar to that of hydrogen bonds.

A possibility that lithium ions of an electrolyte Li^+X^- and a solvent LiR are transferred by a mechanism similar to that of proton transfer in water, *i.e.*,



should be attributed to dissociation (self-ionisation) of the associate $(\text{RLi})_n$ (a dimer, in the simplest case)



The compound LiR should preferentially be of the nucleophilic nature, *i.e.*, have the affinity to lithium ions, and the lithium salt should contain a weakly basic anion (X^-) for these processes to be realised.

It is known that the complexes formed by aliphatic and aromatic organolithium compounds with lithium halides, which are less reactive than the original organolithium compounds, are stable in air and more handy in applications. The ability to form complexes depends on the nature of the radical (R), the lithium salt anion and the solvent. It is also of note that polyacetylene films ($\sigma = 10^{-12}-10^{-9} \text{ S cm}^{-1}$) doped with organolithium compounds had an anomalously high conductivity ($20-160 \text{ S cm}^{-1}$)¹²⁵ typical of electron-conducting polymers and charge-transfer complexes.¹²⁶ In this connection, it seems interesting to explore the possibility of using organolithium compounds as one of the components of the medium (solvent) for electrolytes in lithium CPS.

* * *

In the past decade, the main research on electrolytic systems for lithium power sources was directed to modifying chemically the electrolytes and solvents traditional for this field. A key problem for these studies is the enhancement of conductivity of lithium salt solutions in aprotic solvents and polymers in order to optimise the electrochemical processes and improve the performance of lithium CPS. The advances in the field of physics and chemistry of solutions, chemistry of polymers and coordination chemistry allow one to understand and explain the specific features of charge transfer in condensed media and serve as the theoretical basis for the development of new electrolytic systems.

The most promising research directions involve the studies of highly concentrated solutions (including ionic liquids), the use of principles of molecular encapsulation of ions by macrocyclic ligands, and the quest for systems with nontraditional mechanisms of ionic transport. However, it is clear that the possibility of enhancing the conductivity within the framework of the approaches based on the ion-migration charge-transfer mechanism, *e.g.*, by reducing the solvent viscosity and the degree of ionic solvation (increasing their mobility), or decreasing the degree of association of the electrolyte (increasing the number of charge carriers) are limited.

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