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Electrochemical Properties of $LiAsF_6$ Solutions in Propylene Carbonate–Acetonitrile Binary Mixtures

E. Yu. Tyunina[a], * and **M. D. Chekunova**[b], **
[a]G.A. Krestov Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, 153045 Russia
[b]Ivanovo State Polytechnic University, Ivanovo, 153000 Russia
*e-mail: tey@isc-ras.ru
**e-mail: marchekunova@mail.ru

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Abstract—Conductivity of $LiAsF_6$ solutions in propylene carbonate–acetonitrile binary mixtures containing 0.2 to 1.4 mol/kg of ionophore is measured at temperatures of 283.15, 293.15, 303.15, and 313.15 K throughout the mixed solvent entire composition range. Concentration dependences of the system's conductivity can be described by the Casteel–Amis equation, except the lithium hexafluoroarsenate solution in acetonitrile. The activation energy of the charge transfer process in the studied solutions is determined; the $LiAsF_6$ solution in acetonitrile has the lowest activation energy. From conductometry measurements in dilute solutions, the electrolyte limiting molar conductivity is calculated using the Lee–Wheaton equation. The $LiAsF_6$ ionic association in the propylene carbonate–acetonitrile mixtures with the acetonitrile mole fraction from 0.2093 to 0.9006 is not observed; the salt is fully dissociated over this concentration range. The electrochemical stability range for 0.5 mol/kg $LiAsF_6$ in the propylene carbonate–acetonitrile mixture was determined by means of voltammetry at 298.15 K. The decomposition potentials in the cathodic region are due to lithium electrodeposition; they depend on ion–molecule and intermolecular interactions in the system; the anodic decomposition potentials are associated with the solvent oxidation.

Keywords: lithium hexafluoroarsenate, propylene carbonate, acetonitrile, conductivity, activation energy, electrochemical stability

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INTRODUCTION

One of basic research trends in the electrochemistry of solutions is the development of physico-chemical fundamentals of transfer processes based on the revelation of media effects on electrochemical characteristics of electrolyte systems under the changing conditions of temperature and the electrolyte composition. Electric conductivity and electrochemical stability are important performance features of nonaqueous electrolytes used in chemical devices for power accumulation [1–8]. Choice of electrolyte composition possessing optimal physico-chemical properties ensuring high electric conductivity and wide potential window is not an easy task. It used to be achieved nowadays mainly with empirical means [2] because so far a general theory of liquids is still absent. Search for optimal electrolyte for rechargeable lithium batteries is still not completed [9–16]. The process will continue in the course of the improving of the electrolyte components. It is known [1, 16, 17] that aprotic electrolytes that are in the current use comprise alkylcarbonates, ethers and esters, amides, sulfoxides, ionic liquids with dissolved complex salts ($LiPF_6$, $LiAsF_6$, $LiN(SO_2CF_3)_2$, $LiSO_3CF_3$, etc.). Our choice of $LiAsF_6$ solutions in the propylene carbonate–acetonitrile mixture as object of research is explained, firstly, by strong solvation ability, low viscosity, and high permittivity of the solvents, which affect the ionic charge transfer; secondly, these solvents are effective when used in primary power sources [18–24]. Additionally, $LiAsF_6$, even if somewhat toxic, is advantageous in comparison with other complex salts, in particular, it is inflammable, blast-proof, and thermostable.

Individual solvent, as a rule, do not ensure ionophore high conductivity; on this reason, solvent mixtures are widely used [2, 25–31]. It was shown earlier [18, 32] that the propylene carbonate–acetonitrile mixed solvent can be more advantageously used in chemical power sources as compared with $LiClO_4$/propylene carbonate and $LiAsF_6$/propylene carbonate electrolytes. It was also shown that the $LiAsF_6$/propylene carbonate–acetonitrile electrolyte is well chemically stable against lithium [32]. However, possible effects of the mixed solvent composition and the salt concentration on the charge transfer process and electrochemical stability of $LiAsF_6$ in the propylene carbonate–acetonitrile system were not revealed; and it is the features that are of interest for further development of the theory of concentrated electrolyte solutions. The understanding of processes and factors ensuring better electrochemical qualities of electrolyte solutions can foster creation of novel electrolytes.

In this work we focused ourselves on the studying of the electric conductivity of $LiAsF_6$ solutions in propylene carbonate–acetonitrile mixtures with the ionophore concentration varying from 0.2 to 1.4 mol/kg measured at temperatures from 283.15 to 313.15 K. Also, the electrochemical stability region of 0.5 mol/kg $LiAsF_6$ solution in the propylene carbonate–acetonitrile mixed solvent at different acetonitrile mole fractions at 298.15 K was specified.

EXPERIMENTAL

In this work we used $LiAsF_6$ salt synthesized after the procedure described earlier [33]. Lithium hexafluoroarsenate was synthesized from metallic arsenic, hydrogen fluoride, and lithium hydroxide (all—chemically pure) [33]. The synthesis includes the orthoarsenic acid neutralization with lithium hydroxide and treatment of the obtained solution with hydrofluoric acid. To remove impurities from the obtained salt, the latter was recrystallized from acetonitrile (reagent grade) and dried in vacuum in two steps: first, with slowly (during 6–7 h) increasing temperature, starting from 303.15 and up to 363.15 K; second, it was filled in to glass ampoules with Teflon linings and exposed to a temperature of 368.15 K for 24–26 h. On the completing of the ampoule drying, the salt was analyzed: (a) the percentage of the main product was determined using an $[AsF_6]^-$-sensitive ion-selective electrode [34]; (b) the amount of hydroxoform-impurities $LiAsF_5OH$ was determined by titration with alkali (NaOH) solution usingh phenolphthalein as indicator: $LiAsF_5OH + 6NaOH \rightarrow Na_2HAsO_4 + 4NaF + LiF + 3H_2O$; and (c) the water content was determined using coulometric titration after Karl Fischer [35]. The base material content was no less than 99.5 wt %; the water content, less than 0.07 wt %. The $LiAsF_6$ salt was stored in sealed ampoules in a dry box. The salt quality was evaluated by conductometry (by comparing experimental $\Lambda°$ values with literature data [36–39]).

Acetonitrile (AN, reagent grade) was dried with phosphoric anhydride for two days, and then was distilled twice (the second distillation, above potassium carbonate [40]). Propylene carbonate (PC, reagent grade) was kept in argon atmosphere over molecular sieves (0.4 nm) for two days and then was distilled under reduced pressure [41]. Thus obtained solvents were analyzed for the water content by using the titration after K. Fischer [35]. The water content in the solvents under study was less than 0.005 wt %.

The solution preparation and measurements were carried out in inert atmosphere. The solutions were prepared by weight method, using a Sartorius-ME215S balance (Germany; precision of weighing: 1×10^{-5} g), subject to the bringing of weight to vacuum.

The electrolyte solution electric conductance was measured with a setup comprising automated ac digital bridge P-5083 (OOO Priborelektro, Russia). We used hermetic glass cells with two smooth platinum electrodes when working with concentrated solutions or with three smooth platinum electrodes when working with dilute solutions. The cells were calibrated using KCl aqueous solutions, after works [42] and [43] for dilute and concentrated solutions, respectively. The electrolyte solution conductivity was determined with due allowance for the solvent conductivity: the reciprocal of the solvent resistance was subtracted from the reciprocal of the studied solution resistance. The solution resistances were measured using five different frequencies over the 1-to-10 kHz range, with subsequent extrapolation to infinite frequency. To keep temperature constant accurate within 0.005 K, double temperature control was used. Relative error in the conductivity χ determination was 0.1%.

The electrolyte solution decomposition potentials were measured in a thermostatically controlled three-electrode cell deaerated with argon at 298.15 K. The working electrode (surface area 0.1 cm^2) and auxiliary electrode (thin wire, surface area 0.8 cm^2) were platinum ones, sealed in glass. The working electrode potential was measured against silver electrode in 0.01 M $AgNO_3$ + 0.5 M $LiAsF_6$ solution in acetonitrile ($E = 0.305$ V vs. silver/silver chloride reference electrode). Voltammograms were taken at a potential scan rate of 0.01 V/s using a PI-50-1 potentiostat (ZIP, Belarus). To determine the electrolyte solution decomposition potentials, logarithmic segments of the polarization curves were extrapolated to the current value of 10^{-5} A/cm^2 [44]. The accuracy of the potential measurements was ±2.5–5 mV.

RESULTS AND DISCUSSION

Electric Conductivity at Strong Dilution

The data on the molar conductivity of $LiAsF_6$ solutions in the PC–AN binary solvent over the concentration range from 3.8×10^{-4} to 70×10^{-4} mol/kg were analyzed using the Lee–Wheaton model [45–47] modified by Pethybridze [48], in order to allow for the solvent dielectric saturation caused by its interaction with the electrolyte. The molar conductivity ($\Lambda°$) limiting values and the association constants (K_A) were determined by the solving of the following set of nonlinear equations:

(1) the concentration dependence of the molar conductivity

$$\Lambda_i^{\text{theor}} = \alpha\left\{\Lambda^0\left[1 + C_1\beta k + C_2(\beta k)^2 + C_3(\beta k)^3\right] - \frac{\rho k}{1+t}\times\left[1 + C_4\beta k + C_5(\beta k)^2 + \frac{t}{12}\right]\right\}, \tag{1}$$

(2) the law of mass action (to calculate the association constants)

$$K_{\text{A}} = \frac{(1-\alpha)\gamma_{\text{a}}}{\alpha^2 C\gamma_{\pm}^2}, \tag{2}$$

(3) expression for the calculations of the mean ionic activity coefficients

$$\gamma_{\pm} = \exp\left(-\frac{qk}{1+kR}\right), \tag{3}$$

where α is the dissociation degree, q is the Bierrum length (the Bierrum's parameter), γ is the activity coefficient, R is the ions' closest approach parameter, and C is the molar concentration (M). The parameters of equation (1) are given in works [46, 49]. To process the experimental data, we used the nonlinear least squares method that allowed the minimizing of the FX function:

$$\text{FX} = \sum_{i=1}^{n}\left(\Lambda_i^{\text{exp}} - \Lambda_i^{\text{theor}}\right)^2\Big/(n-m), \tag{4}$$

where n is the number of experimental points, m is the number of optimized parameters. The optimization was carried out with respect to two parameters ($\Lambda°$, K_{A}) at a fixed value of the ions' closest approach parameter R equal to the Bierrum length $q = e^2/8\pi\varepsilon\varepsilon_0 kT$ [50]. In these calculations we used experimental conductometry data for the concentrations not exceeding, according to Fuoss, the quantity $C = 2\varepsilon^3 \times 10^{-7}$ M [51], as well as data [52] on the density, viscosity, and permittivity of the mixed solvent.

The results of the calculations are given in Table 1. With the increasing of temperature, the molar conductivity at infinite dilution grows. The limiting values of the LiAsF_6 molar conductivity ($\Lambda°$) in AN and PC measured separately differ by about one order of magnitude. The electrolyte dilute solution conductivity is mainly determined by changes in such properties as the system's viscosity and permittivity ε. The molar conductivity value is a compromise of the concurring effects of the two factors. The studied systems containing solvents with high ε value are shown to have practically no ionic association because the calculated values of the association constants appeared being nearly zero within the limits of error over the entire composition of the mixed solvent. Thus, the charge transfer process and the system's transport properties at low concentrations are determined by the solvent viscosity and its temperature dependence.

Electric Conductivity of Concentrated Solutions

In Table 2 we give values of the conductivity of LiAsF_6 solutions in the AN–PC mixed solvent at temperatures 283.15, 293.15, 303.15, and 313.15 K. The character of LiAsF_6 concentration effects on the conductivity for the LiAsF_6 solutions in the individual solvent is different. For the LiAsF_6 solutions in PC we have a well pronounced maximum in the concentration dependence of conductivity, whereas for the LiAsF_6 solutions in AN we observed monotonous conductivity growth with the increasing of the concentration up to the forming of saturated solution. The conductivity isotherms that are characterized by the conductivity maximum can be described by the Casteel–Amis empirical equation [53]:

$$\chi/\chi_{\max} = \left(m/m_{\max}\right)^a \times \exp\left[b\left(m - m_{\max}\right)^2 - a m_{\max}^{-1}\left(m - m_{\max}\right)\right], \tag{5}$$

where a, b are the constants, $m_{\max}$ is the solution concentration corresponding to the conductivity maximum ($\chi_{\max}$). In Table 3 we give thus obtained coefficients of Equation (5), which are characteristic of the extreme dependence of the LiAsF_6 solution conductivity in AN–PC mixtures at the AN mole fraction values from 0 to 0.7438. These coefficients are required in the determination of the optimal composition of electrolyte solutions at different temperatures. The conductivity was shown to increase with the increasing of temperature because of decrease in the solution viscosity. At that, in the studied compositions of the mixed solvent the position of maximum does not change. Decrease in the AN content in the binary solvent results in a shift of the maximum in the $\chi = f(m)$ dependence to the left, that is, toward lower electrolyte concentrations. Similar shift of the conductivity maximum ($\chi_{\max}$) with the decreasing of temperature is observed for LiAsF_6 solutions in pure PC. This behavior of electrolytes was reported for other solvents and solvent mixtures [50, 54–56]; it may evidence existence of energy barrier that depends first and foremost on the solvent composition and temperature. These results confirm the fact [1–3, 57] that combination of a solvent possessing high permittivity (ensuring ionic dissociation of electrolyte) with one possessing low viscosity (facilitating ion migration in the solution) favors an increase in conductivity.

In conformity with the transition-state theory [57, 58], the temperature dependence of the conductivity of the studied solutions at temperatures from 283.15 to 313.15 K can be described by exponential equation:

$$\chi = A_{\chi}\exp\left(-E^{\neq}/RT\right), \tag{6}$$

where $E^{\neq}$ is the activation energy for the charge transfer process in electrolyte solution, R is the universal gas constant, A_{χ} is the preexponential factor. The

Table 1. Results of processing of conductometry data for $LiAsF_6$ solutions in the propylene carbonate–acetonitrile mixed solvent (x_2 is the acetonitrile mole fraction, $\sigma(\Lambda)$ is the molar conductivity standard deviation)

x_2	T, K	$\Lambda°$, S cm mol^{-1}	R, Å	$\sigma(\Lambda)^a$, S cm mol^{-1}
0.0000	253.15	7.634 ± 0.079	4.24	0.005
	273.15	14.26 ± 0.18	4.27	0.028
	293.15	22.87 ± 0.21	4.31	0.036
	313.15	33.11 ± 0.15	4.38	0.022
0.2093	253.15	12.63 ± 0.05	4.52	0.010
	273.15	22.13 ± 0.12	4.55	0.018
	293.15	33.31 ± 0.08	4.61	0.025
	313.15	46.15 ± 0.21	4.68	0.041
0.5070	253.15	27.34 ± 0.02	5.11	0.006
	273.15	41.58 ± 0.15	5.17	0.027
	293.15	57.62 ± 0.02	5.25	0.004
	313.15	75.61 ± 0.16	5.34	0.023
0.6956	253.15	44.49 ± 0.12	5.66	0.019
	273.15	62.90 ± 0.12	5.71	0.020
	293.15	83.34 ± 0.06	5.86	0.010
	313.15	105.45 ± 0.05	6.00	0.027
0.8023	253.15	58.63 ± 0.23	6.07	0.040
	273.15	79.56 ± 0.07	6.09	0.005
	293.15	104.12 ± 0.12	6.26	0.016
	313.15	128.99 ± 0.18	6.48	0.022
0.9006	253.15	76.86 ± 0.60	6.69	0.062
	273.15	102.10 ± 0.13	6.80	0.021
	293.15	129.07 ± 0.43	6.93	0.270
	313.15	157.82 ± 0.17	7.08	0.028
1.0000	253.15	102.62 ± 0.26	7.50	0.090
	273.15	132.09 ± 0.19	7.55	0.043
	293.15	163.28 ± 0.09	7.63	0.012
	313.15	195.84 ± 0.14	7.71	0.026

[a] $\sigma(y) = \left(\sum\left(y_i^{\text{exp}} - y_i^{\text{calc}}\right)^2 \Big/ n\right)^{0.5}$, where y_i^{exp}, y_i^{calc} are the experimental and calculated values of the measured quantity, n is the number of experimental points.

dependences $\ln\chi = f(1/T)$ at different $LiAsF_6$ concentrations in the AN–PC mixtures were shown to be linear over entire composition range of the mixed solvent (the mean correlation coefficient is $r_{\text{corr}} = 0.989$). And this allowed determining the charge transfer activation energy ($E^{\neq}$) in the studied solutions from their slope. In Fig. 1 we give concentration dependences $E^{\neq} = f(m)$ for the $LiAsF_6$ solutions in the AN–PC mixed solvent. Our analysis of the obtained results showed the charge transfer activation energy for the $LiAsF_6$ solutions in the aprotic solvent mixtures to increase when passing from AN to PC. The lowest $E^{\neq}$ values were obtained for $LiAsF_6$ solutions in pure acetonitrile, which is in good agreement with the conductivity data. We showed the absence of ion association in the studied solutions; also, the conductivity values over the mixed solvent entire composition obey Eqs. (5) and (6). The results obtained evidence the realization of ion–migration charge transfer mechanism in the $LiAsF_6$–mixed solvent (AN–PC) system.

The electrolyte-concentration dependence of the charge-transfer process activation energy can be described by the following equation [59]:

$$E^{\neq} = E^{\neq 0} + x_2 E^{\neq \text{el}}, \tag{7}$$

where $E^{\neq 0}$ is the solvent contribution to the charge-transfer process activation energy, $E^{\neq \text{el}}$ is that of iono-

Table 2. The conductivity ($\chi \times 10^3$, S cm^{-1}) of $LiAsF_6$ solutions in the propylene carbonate–acetonitrile binary system (x_2 is the acetonitrile mole fraction)

x_2	m, mol kg^{-1}	T, K			
		283.15	293.15	303.15	313.15
0.0000	0.1912	2.572	3.237	3.946	4.709
	0.4006	3.886	4.993	6.183	7.474
	0.6085	4.296	5.652	7.136	8.766
	0.8123	4.146	5.603	7.223	9.030
	1.0974	3.442	4.875	6.519	8.404
	1.3901	2.499	3.765	5.288	7.032
0.3081	0.3053	6.083	7.320	8.613	9.954
	0.5867	8.242	10.11	12.08	14.16
	0.9694	8.496	10.74	13.17	15.80
	1.4610	6.475	8.727	11.27	14.06
	1.6000	5.588	7.749	10.17	12.91
0.5089	0.2561	8.017	9.337	10.67	12.04
	0.3633	10.05	11.77	13.52	15.29
	0.5307	12.15	14.36	16.48	18.95
	0.7129	13.36	15.97	18.62	21.42
	1.0810	13.53	16.62	19.81	23.19
	1.3970	12.61	15.81	19.18	22.74
0.7438	0.3294	13.52	15.28	17.03	18.81
	0.5322	17.94	20.42	22.90	25.41
	0.6898	20.09	23.03	25.97	28.94
	1.1527	21.77	25.53	29.39	33.29
	1.4441	20.63	24.63	28.79	33.01
1.0000	0.1153	9.730	10.60	11.45	12.30
	0.2255	18.12	19.78	21.38	22.97
	0.2933	22.22	24.48	26.47	28.45
	0.3835	27.09	29.64	32.11	34.52
	0.4912	32.00	35.09	38.09	40.98
	0.7257	39.72	43.73	47.67	51.48
	1.2021	–	–	57.93	63.23

fore, x_2 is the solute mole fraction. To find the parameters of Equation (7), we plotted linear dependence $E^{\neq} = f(x_2)$, whose slope is $E^{\neq el}$, and the intercept is $E^{\neq 0}$. In Table 4 we give the parameters of Eq. (7) for $LiAsF_6$ solutions under study in the acetonitrile and propylene carbonate, as well as in other aprotic solvents with high permittivity, for which the ion–migration charge transfer mechanism is valid. Our analysis of the data in Table 4 showed that the $LiAsF_6$ solutions in AN give the least solvent and ionophore contributions to the charge-transfer process activation energy. This is due to the AN small viscosity that is several times less than that of PC and other aprotic solvents. According to the ion–migration charge transfer mechanism, the charge transfer is realized by the ions hopping from one equilibrium state to another under the action of electric field [57, 58]. The transfer is controlled by energy barrier that depends on the solvent and electrolyte properties. An important factor of the ion mobility is the solvent viscosity; less viscous medium enhances the ions' faster motion. This is confirmed by the symbasis of the changes in the solvent viscosity and $E^{\neq el}$ value: they both decrease in the series acetonitrile < N-methyl-2-pyrrholidon < γ-butyrolactone < propylene carbonate (Table 4). The $E^{\neq el}$ parameter in Eq. (7) characterizes the solute ion motion in electric field with due allowance for the ion–solvent interaction.

Table 3. The parameters of Casteel–Amis equation for $LiAsF_6$ concentrated solutions in the propylene carbonate–acetonitrile mixed solvent at different temperatures (x_2 is the acetonitrile mole fraction, $\sigma(\chi)$ is the molar conductivity standard deviation)

x_2	T, K	$\chi_{max} \times 10^3$, S cm^{-1}	m_{max}, mol kg^{-1}	a	b	$\sigma(\chi) \times 10^3$ [a], S cm^{-1}
0.0000	283.15	4.24 ± 0.05	0.668 ± 0.023	0.027 ± 0.032	−1.024 ± 0.119	0.005
	293.15	5.64 ± 0.07	0.732 ± 0.023	0.028 ± 0.034	−0.946 ± 0.123	0.001
	303.15	7.22 ± 0.01	0.791 ± 0.022	0.029 ± 0.037	−0.883 ± 0.128	0.002
	313.15	9.02 ± 0.01	0.846 ± 0.020	0.028 ± 0.038	−0.839 ± 0.130	0.003
0.3081	283.15	8.68 ± 0.04	0.818 ± 0.013	0.714 ± 0.101	−0.376 ± 0.084	0.003
	293.15	10.86 ± 0.04	0.866 ± 0.013	0.769 ± 0.088	−0.282 ± 0.084	0.004
	303.15	13.24 ± 0.05	0.919 ± 0.015	0.778 ± 0.105	−0.242 ± 0.085	0.008
	313.15	15.85 ± 0.08	0.969 ± 0.013	0.793 ± 0.090	−0.205 ± 0.072	0.008
0.5089	283.15	13.71 ± 0.03	0.922 ± 0.005	1.023 ± 0.030	0.078 ± 0.030	0.001
	293.15	16.68 ± 0.04	0.996 ± 0.003	0.999 ± 0.019	0.062 ± 0.019	0.001
	303.15	19.83 ± 0.07	1.072 ± 0.010	0.945 ± 0.053	0.023 ± 0.052	0.005
	313.15	23.21 ± 0.09	1.128 ± 0.001	0.972 ± 0.007	0.043 ± 0.006	0.001
0.7438	283.15	21.85 ± 0.02	1.063 ± 0.002	0.921 ± 0.013	−0.068 ± 0.011	0.002
	293.15	25.54 ± 0.03	1.125 ± 0.003	0.923 ± 0.020	−0.052 ± 0.017	0.001
	303.15	29.90 ± 0.01	1.163 ± 0.009	0.712 ± 0.071	−0.250 ± 0.058	0.001
	313.15	33.40 ± 0.02	1.246 ± 0.005	0.914 ± 0.016	−0.036 ± 0.013	0.001

[a] $\sigma(y) = \left(\sum\left(y_i^{exp} - y_i^{calc}\right)^2 \Big/ n\right)^{0.5}$, where y_i^{exp}, y_i^{calc} are the experimental and calculated values of the measured quantity, n is the number of experimental points.

The Electrochemical Stability

In addition to the conductivity, the electrochemical stability is one of the most important characteristics of novel electrolytic compositions destined to the combinations with cathodic materials of the high-voltage lithium-ion batteries. It is known [2, 3, 5, 16, 62] that electrolyte systems can be used with no visible deterioration of their functionality only within some restricted ranges of electrode potential. These “potential windows” must be sufficiently wide to ensure practical applications. Their upper and lower potential limits are determined by numerous factors, such as the solute and solvent nature, surface reactions between the electric conductor and the electrolyte, impurities in the electrolyte, etc. [2, 3, 5, 16, 62]. Nonaqueous electrolytes are stable in wider potential limits as compared with aqueous ones [13, 57, 63]. We studied the electrochemical resistance against oxidation of electrolyte system comprised 0.5 mol/kg of $LiAsF_6$ in AN–PC mixtures by using voltammetry. The decomposition potentials for the studied solutions at different ratios of the co-solvent in the mixtures are given in Table 5 and Fig. 2.

The anodic limit of solution decomposition in the system under study is determined by the solvent oxidation reactions. The propylene carbonate oxidation leads to the formation of intermediates resulting from the opening of the ring in the solvent molecule [64]. What happens as a result of the acetonitrile anodic polarization is still an open question [62].

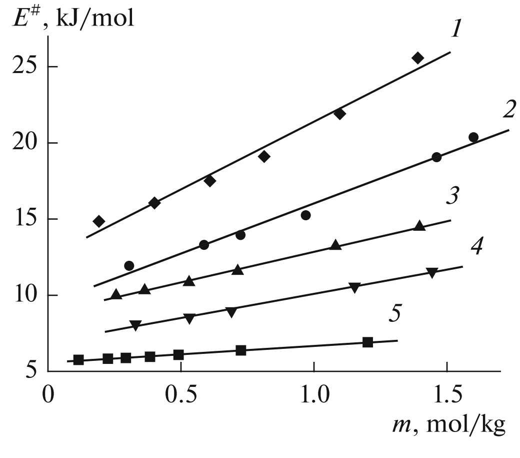

Fig. 1. Concentration dependence of the charge transfer activation energy for $LiAsF_6$ solutions in the propylene carbonate–acetonitrile mixed solvent at different mole fractions of acetonitrile (x_2): (*1*) 0; (*2*) 0.308; (*3*) 0.509; (*4*) 0.744; (*5*) 1.

Table 4. Parameters of Equation (7) for $LiAsF_6$ solutions in aprotic solvents

Solvent	$\eta \times 10^3$, Pa s (298.15 K) [3]	ε (298.15 K) [3]	$E^{\neq 0}$	$E^{\neq \mathrm{el}}$	r_{corr}
Acetonitrile	0.341 (303.15 K)	35.9	5.55 ± 0.03	28.16 ± 1.12	0.996
N-methyl-2-pyrrholidon	1.67	32.2	11.34 ± 0.29 [60]	41.79 ± 2.27 [60]	0.989
γ-butyrolacton	1.73	39.1	9.27 ± 1.01 [61]	95.01 ± 9.72 [61]	0.979
Propylene carbonate	2.53	64.92	12.13 ± 0.71	100.89 ± 8.93	0.984

Table 5. Decomposition potentials for $LiAsF_6$ solutions ($m = 0.5$ mol kg^{-1}) in the propylene carbonate–acetonitrile binary system at 298.15 K (x_2 is the acetonitrile mole fraction)

x_2	E_c, V	E_a, V	Electrochemical window, V
0	−3.3	1.3	4.6
0.2	−3.3	0.9	4.2
0.4	−3.1	1.0	4.1
0.6	−3.2	1.2	4.4
0.8	−3.4	1.2	4.6
1	−3.5	1.3	4.8

From the cathodic side, the electrolyte stability region in aprotic solvents is restricted by the cation reduction potential, according to the following reaction: $Li^{+} + 1\bar{e} \rightarrow Li$. The $LiAsF_6$–PC and $LiAsF_6$–AN systems are characterized by rather negative cathodic decomposition potential, which is ascribed to lithium ion discharge (and the lithium metal is the most strong reducing agent). For the $LiAsF_6$–PC and $LiAsF_6$–AN systems, the cathodic decomposition limit is −3.3 and −3.5 V, respectively.

It should be noted that the value of the $LiAsF_6$–AN-system cathodic decomposition potential is more negative than that of the $LiAsF_6$–PC one. This fact may be due to different solvation of the electroactive lithium ions, which is one of the factors determining electrochemical processes. Large-sized AsF_6^- ions are practically not solvated which is due to lower electric field strength around the AsF_6^- ion as compared with the lithium ion [63]. The lithium ions retain part of the solvent molecules. The lithium ion coordination number in AN (n = 4–9 [3, 65–67]) somewhat exceeds that of the lithium ions in PC (n = 4–5 [3, 65, 66, 68]). As a result, additional expenditure of energy is required in the desolvation stage that precedes the lithium ion electrochemical reduction. In solutions containing AN at a mole fraction from 0.4 to 0.6 the lithium ion reduction occurs at more positive potentials. In our preceding paper [52] we found, by the calculating of molar volumes, molar viscosities, and molar capacities, that in the AN–PC mixed solvent containing 0.5 mole fraction of AN the AN- and PC-molecules form a complex at a ratio of 1 : 1. Correspondingly, the "positive" shift of the lithium ion reduction potential in the mixed solvent containing 0.4 to 0.6 mole fraction of AN can be associated with the concurrency of two processes: the lithium ion solvation and the complex formation between the AN- and PC-molecules.

The data on the conductivity of the studied system (Table 2) may be thought of as being in contradiction with the data on the decomposition potentials; and

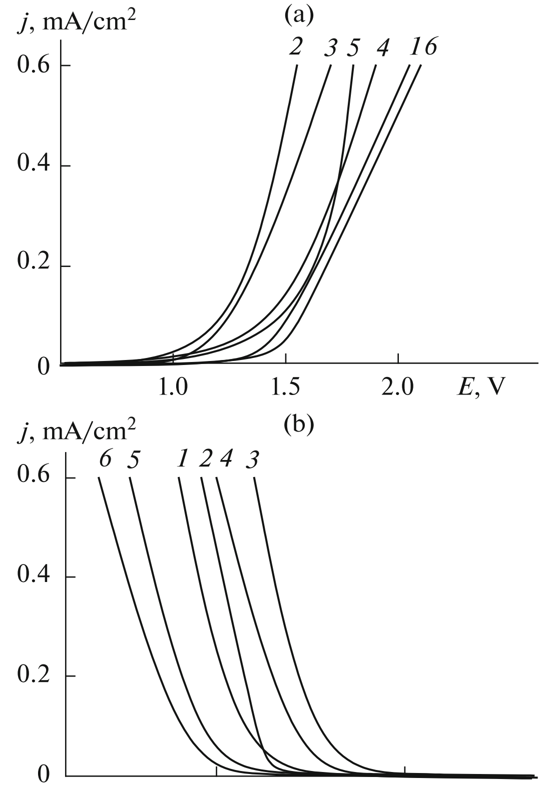

Fig. 2. Anodic (a) and cathodic (b) voltammograms in 0.5 M $LiAsF_6$ solutions in the propylene carbonate–acetonitrile mixed solvent at different mole fractions of acetonitrile (x_2): (*1*) 0; (*2*) 0.2; (*3*) 0.4; (*4*) 0.6; (*5*) 0.8; (*6*) 1.0.

yet, they complement each other. According to the ion–migration charge transfer mechanism, the conductivity must be larger in the solutions of less strongly solvated ions because such ions can easier realize the hopping from one equilibrium state to another under the action of electric field, in accord with the Eyring theory [58]. However, very important is the value of viscosity of the medium the ions move in. The lithium ion is stronger solvated in AN than in PC, judging from the cathodic decomposition potentials; yet, AN is much less viscous than PC (by a number of 7, see Table 4), And this leads to the significant rise in the conductivity of the $LiAsF_6$ solutions in acetonitrile as compared with those in propylene carbonate (Table 2).

CONCLUSIONS

Conductivity and decomposition potentials of electrolyte systems containing lithium hexafluoroarsenate in the propylene carbonate–acetonitrile mixed solvent are measured at different temperatures. The studied $LiAsF_6$/PC–AN system is shown to have practically no ionic association in the dilute solutions region; at higher concentration, the charge-transfer process occurs by ion-migration mechanism. Increase in temperature results in the increasing of conductivity over the studied range of the ionophore concentrations, as well as of the molar conductivity at infinite dilution over the entire composition of the PC–AN mixed solvent. The charge-transfer process activation energy for $LiAsF_6$ solution in a mixture of the two aprotic solvents increased with the decreasing of the AN content in the mixture. The ionophore solutions in acetonitrile have the maximal conductivity values because the solvent has very small dynamic viscosity. Adding of AN enhanced the $LiAsF_6$–PC traditional conductivity; the $LiAsF_6$–PC–AN electrolyte demonstrated high chemical stability when contacting the lithium metal. The studied solutions have rather wide region of electrochemical stability; at that, the widest potential window (4.8 V) was observed for $LiAsF_6$ solution in acetonitrile. Thus, by and large, the $LiAsF_6$–PC–AN electrolyte possesses advantageous characteristics and is suitable for applications in electrochemical devices for power accumulation.

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