Journal of Molecular Liquids 187 (2013) 332–336

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Electrochemical properties of lithium hexafluoroarsenate in methyl acetate at various temperatures

Elena Yu. Tyunina [a,*], Marina D. Chekunova [b,c]

[a] G. A. Krestov Institute of Solution Chemistry, Russian Academy of Science, 1, Akademicheskaya St., Ivanovo 153045, Russia
[b] Department of Chemical and Environmental Engineering, Ivanovo State University of Civil Engineering and Architecture, 20, 8 March St., Ivanovo 153037, Russia
[c] Department of Chemistry and Chemical Engineering in Energetics, Ivanovo State Power University, 34, Rabfakovskaya St., Ivanovo 153003, Russia

ARTICLE INFO

Article history:
Received 25 March 2013
Received in revised form 6 June 2013
Accepted 31 August 2013
Available online 13 September 2013

Keywords:
Lithium hexafluoroarsenate
Methyl acetate
Specific electroconductivity
Activation energy
Electrochemical window

ABSTRACT

Electrical conductivities of $LiAsF_6$ in methyl acetate were measured in concentration range of 0.4269–2.2672 $mol \cdot kg^{-1}$ at 253.15, 263.15, 273.15, 283.15, 293.15, 303.15, 313.15, and 323.15 K. Data were treated by using the semi-empirical Casteel–Amis equation at high concentrations. The dependence of conductivities on the temperature was described by the Arrhenius relationship. It was shown that activation energies for conductivity linearly increased with the mole fraction of $LiAsF_6$. The variation tendency of the energies of activation for the conductivities of $LiAsF_6$ in the order of aprotic solvents (propylene carbonate, γ-butyrolactone, methyl acetate, tetrahydrofuran) has been discussed on the basis of the hypothesis that various conduction mechanisms occur at high concentration in the solvents of low permittivity. The anodic and cathodic stabilities of the $LiAsF_6$ in methyl acetate were measured on a Pt electrode, a wide enough electrochemical stability window being observed.

1. Introduction

Progress in battery technology, using lithium electrolytes in nonaqueous solutions, has occurred largely in the past decade [1–5]. The requirements for effective nonaqueous battery electrolytes are high specific conductivities of the solution over a large temperature range, sufficiently high solubility of the salt ($>0.5\ mol \cdot dm^{-3}$), high energy density and stability over a sufficiently large voltage range (~3.0 V). It is well known that the conductivity of the electrolyte solution is an important factor in the performance of batteries [6] and consequently capacitors. The investigations of electrolyte solutions in acetonitrile [7], γ-butyrolactone [8,9], N,N-dimethylformamide [10], propylene carbonate [11] and other solvents have been recently made. Solutions of $LiAsF_6$ in methyl acetate (MA) are unusual electrolyte systems. Methyl acetate has low viscosity ($\eta = 0.368\ mPa \cdot s$), low melting point (175 K), low dielectric constant ($\varepsilon = 6.67$) and high solubility for lithium salts [12,13]. Methyl acetate exhibits surprisingly high conductance [4,14–16]. $LiAsF_6$ is favorably regarded as an electrolyte salt because of its high conductivity and apparent stability toward lithium [17].

Electrolyte solutions in MA exhibit complex behavior. Ion solvation and association of $LiAsF_6$ in MA were studied using infrared and Raman spectroscopy [15,18]. It was found that depending upon the total concentration (from 10^{-5} to 0.5 $mol \cdot dm^{-3}$) various complexes existed such as triple ions, solvent separated and contact dimeric species. At higher concentrations ($>0.5\ mol \cdot dm^{-3}$) the measurement of the electrical conductance of $LiAsF_6$ in MA was not reported. The relatively high conductivity observed in systems containing a solvent of low permittivity suggested that at high concentrations different mechanisms of charge transfer could be involved [19–21]. The study of $LiAsF_6$ in MA was chosen as no systematic investigation of the temperature dependence on transport properties in this system is available. High concentration studies were undertaken since concentrated solutions are generally used in organic electrolyte batteries, wet electrolyte capacitors and electroorganic synthesis [22]. In addition to high conductivity, an electrolyte electrochemical stability during the operation of the battery is another requirement for the electrolyte to meet. Electrolyte stability is well known to be quantified within its oxidative and reductive decomposition limits [1,3,4,16] in volts, which is known as the "electrochemical window" that should be wide. The degradation of an electrolyte would not occur within the range of the working potentials of both the cathode and the anode. The investigation results of the electrochemical stability of $LiAsF_6$ in methyl acetate at 293.15 K are reported here. This work continues the series of investigations on electrochemical and transport properties of lithium hexafluoroarsenate in nonaqueous solvents [9,23–26].

2. Experimental

2.1. Chemicals

Lithium hexafluoroarsenate was prepared as described previously by synthesizing from metallic arsenic (Russia, "pure" grade), hydrofluoric acid (Russia, "pure" grade) and lithium hydroxide (Russia, "pure" grade) [26–28]. The product was recrystallized from acetonitrile (Russia, best

---

* Corresponding author.
E-mail address: tey@isc-ras.ru (E.Y. Tyunina).

0167-7322/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molliq.2013.08.019

purity ≥ 99%) and dried under vacuum at temperatures slowly increasing (for 6–7 h) from 303.15 to about 363.15 K. Then the salt was dried in vacuum at 368.15 K for 24–26 h. Lithium hexafluoroarsenate was tested for the presence of $LiAsF_5OH$ impurities by the titration of its solution with a 0.01 M NaOH in the presence of phenolphthalein as an indicator according to the reaction: $LiAsF_5OH + 6NaOH \rightarrow Na_2HAsO_4 + 4NaF + 3H_2O$. The salt contained no less than 99.5% of a component that was checked using ion-selected electrode [26]. The water content in the salt was determined with Karl Fischer coulometric titration [29] and did not exceed 0.07%. The salt was kept in the shut glass ampoules in the dry box.

Methyl acetate (Russia, "pure" grade) was dried with 4 Å molecular sieves for 24 h and boiled with $LiAlH_4$; then distilled in an argon atmosphere [13,14]. The residual water content in MA found by the Karl Fischer method was less than 0.005%. The content of peroxides in MA was less than 0.005%. Solutions were prepared by mass (with an accuracy of 1×10^{-5} g) using Sartorius-ME215S balance and taking into account weight reduction to vacuum. The salt was slowly added to the solvent in a dry box, the solvent and solutions also being stored in a dry box. All experiments were run without contacts with the laboratory atmosphere.

2.2. Apparatus and procedure

Conductance measurements were made with R-5083 automatic digital bridge (Russia) as a conductivity meter using a conductance cell with two electrodes made of smooth platinum, the measuring procedure being described [30]. The hermetic glass (Pyrex) cell was mounted in a lid for immersion in a temperature bath. This thermostatic bath was equipped with a cooling coil connected to the cryostat (model MK-70, Russia) by tubing. The double thermostatic control allowed maintaining the bath temperature with accuracy better than 0.005 K. The calibration of the conductance cell was based on the conductance of aqueous potassium chloride solutions [31]. To eliminate electrode polarization effects, resistances were measured at five different frequencies in the range of 1–10 kHz and extrapolated to infinite frequency. All data were corrected by the specific conductance of the solvent. Taking into account the sources of error (calibration, measurements, purity of materials, temperature, molality), the experimental uncertainty of specific conductance was within $\pm 0.00003\ S\cdot cm^{-1}$. The overall relative uncertainty of the electrical conductivity was estimated to be 0.2%.

The measurements of $LiAsF_6$ decomposition potentials in methyl acetate were carried out in a three-electrode cell at 293.15 K, the electrolyte being degassed with argon. The working (5.0 mm diameter) and the counter electrodes were made from platinum and sealed in glass. The potentials of the working electrode were measured versus the reference Ag electrode in solution of $0.01\ mol\cdot dm^{-3}$ $AgNO_3$ and $0.5\ mol\cdot dm^{-3}$ $LiAsF_6$ in acetonitrile. Current–voltage curves of the solutions investigated were obtained on Potentiostat PI-50-1 (Russia) with a scan rate of $10\ mV\cdot s^{-1}$. The overall uncertainty of the measurements was estimated to be $\pm 2.5 \div 5$ mV.

3. Results and discussion

3.1. Variation of specific conductivity with concentration

The investigations of $LiAsF_6$ conductance in MA at low concentration were reported [14,15]. The minimum in the dependence of molar conductivity on concentration was found to lie in the region of large dilutions ($C \ll 0.01\ mol\cdot dm^{-3}$). This region is defined by weak temperature dependent specific conductance in the solutions studied. The addition of the electrolyte to MA resulted in permittivity increasing; then conductivity began to increase that can be interpreted in terms of new charge species formation (triple ions) in the solvent of low permittivity (MA). The average association constant $K_p = 0.972 \cdot 10^6\ dm^3\cdot mol^{-1}$ and the average constant of the triple ion formation $K_t = 69.162\ dm^3\cdot mol^{-1}$ for $LiAsF_6$ in MA were determined on the basis of Fuoss–Hsia conductance equations with the expansion of Fernandez-Prini [32], and Salomon et al. [14]. For low permittivity solvents ion association with ion pairs and even higher ion aggregates might occur [28]. The dielectric constant of solvent began to increase from that of the pure solvent for salt concentrations > approximately $0.01\ mol\cdot dm^{-3}$, which is roughly the same concentration where conductivity begins to increase with increasing salt concentration [14,33].

The measurement of the electrical conductance of $LiAsF_6$ in MA at higher concentrations ($>0.5\ mol\cdot dm^{-3}$) was not reported. In this study the specific conductivity in concentrated range from $0.42\ mol\cdot kg^{-1}$ up to $2.26\ mol\cdot kg^{-1}$ was measured since concentrated solutions are generally used in organic electrolyte batteries. The specific conductivity values of $LiAsF_6$ in MA are given as functions of molality, *m*, (0.42 to 2.26) $mol\cdot kg^{-1}$ and temperature (253.15 to 323.15) K (Table 1). Isotherms of dependence $\chi = f(m)$ for the $LiAsF_6$ in MA are typical. The conductivity rises at first, passes through a maximum and then decreases. In low permittivity solvents such as MA, the maximum conductivity was observed to be shifted to the region of higher concentrations than those of highly polar solvents [1,13]. As the concentration of salt increased, the concentration of ion pair also increased. Moreover, earlier measurements of Raman spectra of $LiAsF_6$ in MA [18] showed that solvation of the lithium cation occurred through the carbonyl group of methyl acetate molecules. The variations of χ with *m* can be explained by the competition between an increase in the number of charged carriers (ions, ion pairs, etc.) and an increase in viscosity, η. It caused the maximum on χ isotherms when the viscosity contribution became predominant to hinder particle mobility [34]. The most concentrated electrolyte solution is likely to be characterized by both a large number of ion aggregates and a high viscosity [8,33].

The concentration dependence on specific conductivity may be described by empirical relationship of Casteel and Amis [35]:

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

where a and b are some constants and $m_{\max}$ is a salt concentration corresponding to the maximum in specific conductivity, $\chi_{\max}$. The fitted parameters of Eq. (1) are presented (Table 2), the fitted curves being solid lines (Fig. 1). Using Eq. (1), the optimum composition of electrolyte solutions can be determined at different temperatures. The values of $\chi_{\max}$ and $m_{\max}$ were mainly estimated by the viscosity, the dielectric constant of solvent and the ionic size as well as by temperature [1,4]. Thus, $\chi_{\max}$ and $m_{\max}$ shifted to higher values as temperature increased. The linear correlation $\chi_{\max}$ vs. $m_{\max}$ was observed for the system studied (correlation coefficient $r_{corr} = 0.989$). It can be noted that the electrolyte in the solvent with low ε shows conductance comparable to that of solutions with high permittivity solvents. The conductivity

Table 1
Specific electroconductivities, χ, of $LiAsF_6$ in methyl acetate as a function of molality, *m*, and temperature, *T*.

T (K)	253.15	263.15	273.15	283.15	293.15	303.15	313.15	323.15
m ($mol\cdot kg^{-1}$)	$10^3\cdot\chi$ ($S\cdot cm^{-1}$)[a]							
0.42690	4.968	5.538	6.032	6.485	6.803	7.024	7.196	7.264
0.82380	9.877	11.33	12.73	13.96	14.95	15.86	16.60	17.32
1.05700	11.77	13.74	15.48	17.70	19.36	20.82	22.10	22.30
1.26183	12.90	15.27	18.26	20.75	22.45	24.39	26.15	27.66
1.54460	13.73	16.53	19.56	22.46	25.31	27.88	30.25	32.38
1.91980	12.99	16.21	19.58	22.93	26.29	29.38	32.37	35.10
2.17980	12.38	15.57	19.15	22.62	26.25	29.60	32.81	35.68
2.26728	–	–	–	–	25.63	28.98	32.21	35.05

[a] Standard uncertainties $u(\chi(x))$ are $u(\chi(T)) = 0.00001\ S\cdot cm^{-1}$, $u(\chi(m)) = 0.000004\ S\cdot cm^{-1}$, $u(\chi(cell)) = 0.00002\ S\cdot cm^{-1}$, and the combined expanded uncertainty $U_c(\chi) = 0.00003\ S\cdot cm^{-1}$ (level of confidence 0.95).