STUDY OF RHEOLOGICAL AND ELECTROLYTIC PROPERTIES OF DIMETHYLFORMAMIDE- γ-BUTYROLACTONE BASED ELECTROLYTES FOR LITHIUM BATTERIES

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Abstract

Studies on the behavior of ions in pure and mixed non-aqueous solvents are scarce in literature. An attempt has been made in this work to investigate the ion-solvent interactions of lithium perchlorate in the mixture of DMF- γ -butyrolactone (γ -BL). The density (ρ), viscosity (η), and equivalent conductivity (Λ) of LiClO₄ (0.01, 0.1,1.0 and 1.5 M solutions) in pure and mixed (80%-20%, 60%-40%, 50%-50%, 40%-60% and 20%-80%) solvents of DMF- γ -BL have been measured at different temperatures (25°C-65°C).

Introduction

Gel polymer electrolytes are promising separators for Li batteries and received much attention these last years [1-3]. The solvents widely used as plasticizers to enhance conductivity include propylene carbonate (PC), ethylene carbonate (EC), g-butyrolactone (g-BL), tetraglyme (TG) and N,N-dimethylformamide (DMF) [4-7].

According to the basic principle to obtain high electrical conductivity it is necessary to associate high dielectrical constant that enables the plasticizer to dissociate the salt into ions more easily and low viscosity which leads to high ionic mobility [8-10].

In this paper DMF and g-BL mixtures at different volume percentage of DMF.and LiClO₄ salt concentrations in the temperature range 298.15 – 338.15 K were studied. Transport properties of these electrolyte mixtures were determined.

g-BL and DMF have relatively high permitivity which means good dissociative ability toward Li-salt. g-BL has higher viscosity than DMF and their mixture will have lower one so the ionic mobility would be enhanced.

Experimental

DMF and γ -BL prior to use are dried with molecular sieves (48h) and stored in a dessicator under argon.

Lithium salt (Aldrich) were also stored at 110°C under vacuum for 24h and then stored in a dessicator. The solvent mixtures DMF- γ -BL were prepared by volume and mixtures of LiClO₄ (c = 0.01, 0.1, 1.0, 1.5 mol.l⁻¹) were prepared in dry atmosphere.

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The values of viscosities in the temperature range 25°C-65°C were obtained using thermostated ubbelhode capillary tube and a Schott-Generate AUS 310 viscosimeter. The volumetric weights of the solutions of pure and mixed solvents were determined by the pycnometric method. Conductivity measurements have been carried out using a Philips PM6303 impedance analyzer which operates at 1000 Hz and a platinum electrodes conductivity cell.

Results and discussion

From experimental values of equivalent conductivities Λ and using the quasi-lattice theory of electrolyte solutions $\Lambda = \Lambda_0 - SC^{1/3}$ we have obtained the values of Λ_0 for each pair of concentration and temperature:

Using the experimental values of viscosities the Jones-Dole equation constants *A* and *B* are determined.

$$\eta/\eta_0 = 1 + A C^{1/2} + B C$$
 (1)

A and B coefficients of Jones-Dole equation are the measure of, for A (Falkenhagen coefficient) the ion-ion interaction and B (Jones-Dole Equation) the measure of ion-solvent interaction.

The viscosity data were also examined and the free energies of activation of solute and solvent are determined.

Viscosity

The variation of viscosity for studied electrolyte solvent mixtures with temperature and concentration in solution are shown in Fig. 1. The curves are fitted to Guzman-Andrade law [1]. With the increase of the temperature and the decrease of the salt concentration, the curves show a continuous decrease of the viscosity. The viscosity goes through a minimum when the volume percentage of DMF in the γ -BL-DMF electrolyte mixtures is going from 80% to 20% via 50% (Fig. 2).



Fig. 1 Viscosity dependence of the DMF-g-BL (1:1) system with the salt concentration 0.1 - 1.5M LiClO₄ (temperature range 298-238 K)



Fig. 2 Conductivity variations of the DMF-g-BL (1:1) system with the salt concentration 0.1 - 1.5M LiClO₄ (temperature range 298-238 K)

From 80% to 50 % DMF, the viscosity energy of activation $E_{a,\eta}$ (see Table 1) decreases smoothly (3.731 kJ.K⁻¹.mol⁻¹ to 3.453 kJ.K⁻¹.mol⁻¹) and from 50% DMF to 20% it decreases sharply (64%); It means that the necessary energy for a molecule to be displaced to a vacancy is less and we could expect a change in the structure of the electrolyte solvent mixture.

Table 1 Viscosity activation energy $E_{a, \eta}$ (kJ.K⁻¹.mol⁻¹) Conductivity activation energy $E_{a,\Lambda}$ (kJ.K⁻¹.mol⁻¹) as a function of DMF percentage (by volume) in the γ -BL-DMF 1M LiClO₄.

w DMF (%)	20	50	80
$E_{a,\eta}(kJ.K^{-1}.mol^{-1})$	2.204	3.453	3.731
$E_{a,\Lambda}(kJ.K^{-1}.mol^{-1})$	13.867	14.130	16.916

Conductivity

The conductivity is an important characteristic of the electrolyte and it has to be the highest possible because it is of the prime importance for the Li-batteries improvement life. The curves showing the variation of the conductivity of the electrolyte solvent mixtures γ -BL-DMF-LiClO₄ (XM) are displayed in figures 2, as a function of temperature and the molarity of the salt LiClO₄. The higher conductivity is obtained for 1M LiClO₄ and 50% DMF at T = 298.15 K (σ_{25} = 5 mS.cm⁻¹). The activation energy of equivalent conductivity $E_{a, \Lambda}$ is determined by using an Arrhenius type relation for the conductivity variations at different temperatures

 $\Lambda = k \exp\left(-E_{a,\Lambda}/RT\right)$ (2)

k is a fitting parameter $E_{a,\Lambda}$ is the activation energy of the conductivity.

The activation energy of conductivity is almost constant and does not vary with the volume percentage of DMF in the electrolyte solvent mixture (see Table 1).

Conclusion

The effects of salt concentration, solvent mixture composition and temperature on the viscosity and conductivity of DMF-g-BL-LiClO₄ are studied.

In the temperature range determined transport properties obey to the Arrhenius law. According to the results we could expect a change in the structure of the electrolyte solvent mixture.

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