

Conductivity and stability towards lithium metal of lithium triflate (LiSO_3CF_3) and lithium bistrifluorosulfonylimide ($\text{Li}(\text{SO}_2\text{CF}_3)_2\text{N}$) in amines and their mixtures with ammonia

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Abstract

The solvates based on combinations of lithium salts with ammonia (called liquid ammoniates) form highly conductive and low cost electrolytes. The generalizing of this fact is possible with amines. Like ammoniates, their solvates possess properties which can widely vary with the composition, the nature of the amine and the anion. Mixtures of NH_3 , amine(s) and lithium salt(s) were also investigated. These properties include the glass-transition temperature, the conductivity, the vapour pressure and the corrosion rate of lithium. The conductivity can be as high as $1 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ at 60 °C. The lithium stability depends on the anion and on the nature of the amines: with *n*-propylamine and isopropylamine charged with lithium triflate (only 1.5 M) lithium metal is very stable even at +70 °C during several months.

Introduction

Alkali metals are soluble in liquid ammonia and in a lesser extent in amines yielding solvated electrons according to:



It is possible to shift this equilibrium to the left by adding large amounts of Li salts. This has been shown with liquid ammonia [1, 2]. Lithium metal becomes insoluble and can be used as anode in batteries using the solvates formed from Li salts and NH_3 , the liquid ammoniates, as electrolytes.

In this preliminary paper, we want to show that solvates of Li salts with amines can also be used to prepare Li battery electrolytes. As for ammonia, additions of Li salts in amine(s) shift the eqn. (1) to the left and the corresponding solvates, similar to ammoniates, are merely the generalizing of these last compounds since amines are derivatives of ammonia. New dimensions are given by the possibility of varying the nature of the amine and the possibility of using mixtures of amine(s) and ammonia.

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Among the amines some are very interesting for protecting Li, as we will see later.

So far, we considered concentrated solutions of Li or sodium salts (concentration >5 M) in liquid ammonia under an ammonia pressure lower than 1 bar (10^5 Pa) at room temperature (liquid ammoniates). For Li salts it was shown [3, 4] that nitrate and perchlorate ammoniates possess (i) a structure like fused salts with a transition temperature (liquid/gel or solid) close to 0–10 °C giving a good conductivity at room temperature and a poor one at low temperatures, and (ii) they can react with Li metal at high temperatures because ammonia is relatively free. For Li triflate or Li bistrifluorosulfonylimide ammoniates, a glass-like structure was found indicating the predominance of aggregates which trap NH_3 molecules leading to a very good stability of Li and a conductivity inferior to that of the ammoniates, but without transition temperature, which means an attractive conductivity at low temperatures. Notice that mixtures of LiNO_3 and Li triflate or Li bistrifluorosulfonylimide ammoniates can have a high conductivity without any transition temperature down to -40 °C or less.

The aim of this work was to study solutions of three Li salts – (LiSO_3CF_3 –Li triflate, $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ –LiTFSI, and LiNO_3 found interesting in combination with ammonia) –, in several amines selected for their dielectric constant ($\epsilon > 5$), physical properties (wide liquid temperature range towards low temperatures) and low cost: *n*-propylamine (melting point = -83 °C, boiling point = 48 °C), isopropylamine (m.p. = -101 °C, b.p. = 33 – 34 °C) and *n*-butylamine (m.p. = -49 °C, b.p. = -78 °C). Ethylenediamine (m.p. = 8.5 °C, b.p. = 118 °C) was also used for its potential use at high temperatures. Notice that mixtures of ethylenediamine with other amines or ammonia can lead to solvents of low freezing points.

Experimental

All the chemicals used were reagent grade or of highest available purity. Anhydrous Li triflate (Aldrich) and Li bistrifluorosulfonylimide (LiTFSI) (3 M) were dried under vacuum at 120 °C for 24 h, prior to use. All amines were obtained from Aldrich and NH_3 from Air Liquide (Electronic N45). The solutions were prepared by mixing adequate amounts of salts and amine(s) and/or ammonia. The solvates were stored and handled under an argon atmosphere to avoid contamination. The titration of water content, the conductivity or electrochemical cells have been described elsewhere [1, 3].

Results and discussion

The amines like ammonia do not dissolve in a large extent LiAsF_6 , LiPF_6 and LiBF_4 . Only Li triflate, LiTFSI and LiNO_3 give interesting ammoniates and were therefore considered. Their solutions in pure amines, in mixtures of amines or in mixtures of amine(s) and ammonia were studied in order to get thermodynamical data and informations especially on their structure. Here, we only give the most typical results dealing with:

(i) *n*-propylamine (or isopropylamine)–Li triflate mixtures: their conductivity isotherms are presented in Fig. 1 (together with *n*-butylamine–Li triflate curves). The maxima of κ are for the composition: Li triflate–*n*-propylamine (almost the same composition as for the *n*-butylamine adduct). The interest in using propylamine rather than butylamine is obvious and may be caused by a higher dielectric constant of the

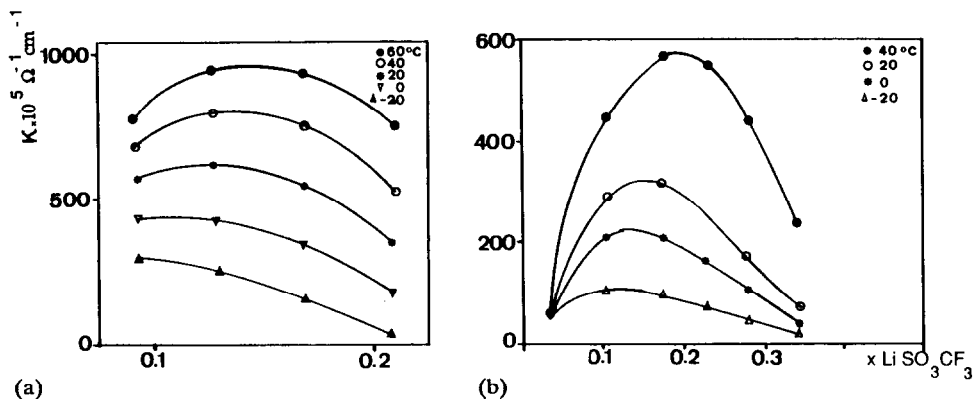


Fig. 1. Conductivity isotherms ($^{\circ}\text{C}$) of (a) LiSO_3CF_3 -*n*-propylamine and (b) LiSO_3CF_3 -*n*-butylamine systems as a function of lithium salt mole fraction.

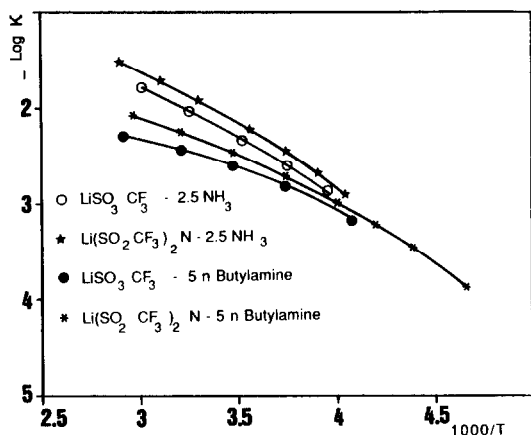


Fig. 2. Conductivity of LiSO_3CF_3 - and $\text{Li}(\text{SO}_2\text{CF}_3)_2\text{N}$ -based electrolytes vs. reciprocal temperature.

smaller amine. For this composition (the concentration is only roughly 1.5 M) no reaction of Li with the electrolyte occurred at $+70^{\circ}\text{C}$, within several months.

(ii) *n*-butylamine-Li triflate or LiTFSI mixtures, compared with NH_3 mixtures with the same salts: the conductivity ($\log \kappa = f(1/T)$) enhancement, observed when the salts are added, is shown Fig. 2. LiTFSI gives solutions which are nearly 1.5 times more conductive than solutions prepared with Li triflate at $+25^{\circ}\text{C}$. This conductivity advantage is reduced at lower temperatures. The nonlinear plot $\log \kappa$ versus $(1/T)$ can be interpreted in terms of a 'three-parameter equation' of a VTF type [5]:

$$\ln \kappa = K_{\kappa} / (T - T_0) + 1/2 \ln T + \ln A_{\kappa} \quad (2)$$

where K_{κ} , T_0 and A_{κ} are constants, with $K_{\kappa}R = \text{Arrhenius activation energy } E_a$.

Table 1 gives the values of the activation energies (obtained by least square analysis) for some compositions.

The value for E_a are similar for these solvates which suggests an analogous mechanism for the electrical conductance. The higher conductivity obtained with imide

TABLE 1

The activation energy of the VTF equation for conductivity κ and the glass-transition temperature T_g of lithium salt-amine systems

System	E_a (eV)	T_g (°C)
LiSO_3CF_3 -5.5 <i>n</i> -butylamine	7.8×10^{-2}	-111
$\text{Li}(\text{SO}_2\text{CF}_3)_2\text{N}$ -5.5 <i>n</i> -butylamine	8.8×10^{-2}	-177
LiSO_3CF_3 -2.5 NH_3	12.6×10^{-2}	-122
$\text{Li}(\text{SO}_2\text{CF}_3)_2\text{N}$ -2.5 NH_3	8.5×10^{-2}	-133

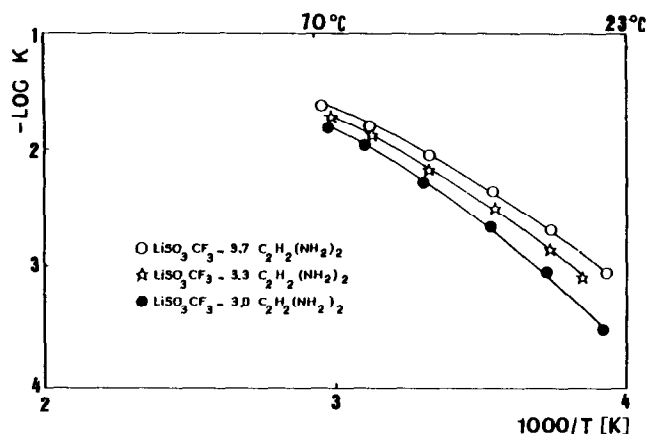


Fig. 3. Conductivity of LiSO_3CF_3 -ethylenediamine electrolytes vs. reciprocal temperature.

salt at high temperatures is probably due to the high level of charge delocalization in $(\text{SO}_2\text{CF}_3)_2\text{N}^-$ anions reducing ion pairing in these electrolytes. The glass-transition temperatures (T_g) somewhat below can provide from the higher viscosity of imide systems [6].

In addition to the conductivity advantage afforded by the imide salt, the electrolyte based on $\text{Li}(\text{SO}_2\text{CF}_3)_2\text{N}$ remains in liquid state at temperatures as low as -40°C for NH_3 solvates and -70°C for amine solvates.

Studies of the Li stability show that Li seems to be more stable in presence of LiTFSI than in presence of Li triflate, but, with time, Li precipitates from LiTFSI solutions. Its composition is not yet known.

(iii) ethylenediamine-Li triflate mixtures: in Fig. 3, the curves $-\log \kappa = f(1/T)$ are represented for three Li compositions and there is no well-defined transition temperature, although there is no liquid state at low temperatures. First, the interest in such mixtures comes from the good conductivity at high temperatures and under a very low pressure, and second more particularly, from the very good behaviour of Li metal which is not attacked, even at $+70^\circ\text{C}$ within several months.

(iv) ammonia-*n*-butylamine-LiNO₃-Li triflate mixtures: these mixtures showed that it is possible to modify the conductivity and the pressure of the electrolytes, at will. Figure 4 shows the curves $-\log \kappa = f(P_{\text{NH}_3})$ for a given composition of the mixture.

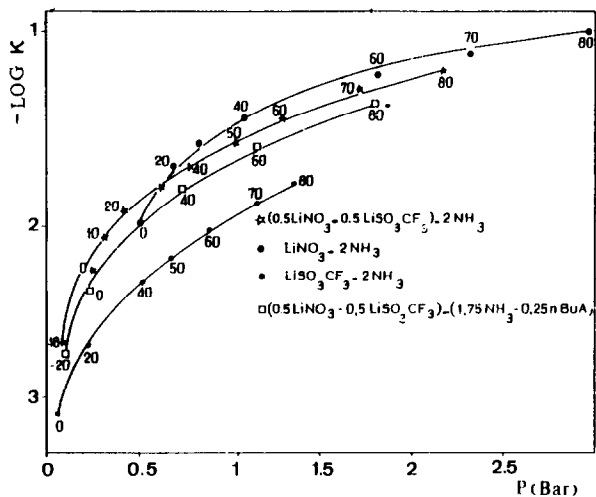


Fig. 4. Conductivity isotherms ($^{\circ}\text{C}$) of $(\text{LiNO}_3\text{-LiSO}_3\text{CF}_3 \text{ salts})\text{-NH}_3\text{-}n\text{-butylamine}$ solvents mixtures as a function of solvent vapour pressure.

Conclusions

Amines are interesting solvents to prepare battery electrolytes. Although they generally possess a lower dielectric constant than ammonia (except ethylenediamine) which means stronger ion-pairing and lower conductivity for the same salt concentrations, in presence of Li triflate they are less reactive towards Li metal. This property allows the use of less-concentrated solutions than with pure ammonia and therefore leads to interesting conductivities, because of the low viscosity.

The use of mixtures of ammonia and amine(s) is also of interest. Although this paper does not contain many data on these mixtures, the possibilities they offer are important and well illustrated by our examples. The combination of the use of Li triflate and amines which protect Li metal in mixtures with ammonia and possesses a high dielectric constant, can lead to enhanced conductivities, low vapour pressure and wide operating temperature ranges.

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