Raman study of ion pairing in solutions of lithium salts in dimethyl sulfoxide, propylene carbonate and dimethyl carbonate

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ABSTRACT

Raman study of ion pairing in dimethyl sulfoxide (DMSO), propylene carbonate (PC) and dimethyl carbonate (DMC) solutions of five lithium salts has been performed in the concentration range from 0.05 to 0.25 molar fraction of a salt and the dependences of the amount of the free anions, solvent separated ion pairs (SSIPs) and contact ion pairs (CIPs) on salt concentrations have been determined, which significantly differ from salt to salt and from one solvent to another. In DMSO solutions, at 0.075 mole fraction of a salt, when the conductivity maximum is showing up, the order for increasing concentration of anions is $BF_4^- < ClO_4^- < N(SO_3CF_3)_2^- \leq B(C_2O_4)_2^- < CF_3SO_3^-$, and the order for decreasing concentration of SSIPs is $BF_4^- > ClO_4^- > B(C_2O_4)_2^- \geq N(SO_3CF_3)_2^- > CF_3SO_3^-$. These do not coincide with the order for increasing conductivity, probably signifying the influence of other factors, like the mass and radius of charge carriers, on conductivity. In the $LiClO_4$–DMSO, $LiClO_4$–PC and $LiClO_4$–DMC systems, the order of solvents for increasing concentration of free anions as PC = DMC($= 0$) $<<$ DMSO and that for decreasing concentration of SSIPs as DMC $>$ PC $>$ DMSO at $c_{LiClO_4} = 0.075$ mole fraction perfectly coincide with the order of solvents for increasing conductivity as DMC $<$ PC $<<$ DMSO. This means that no free ions exist in the PC and DMC solutions at $c_{LiClO_4} = 0.075$ mole fraction, and their conductance is solely ensured by SSIPs.

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1. Introduction

In our previous paper, phase diagrams of lithium salt systems in dimethyl sulfoxide, $(CH_3)_2SO$ (DMSO), propylene carbonate $C_4H_6O_3$ (PC), and dimethyl carbonate $C_3H_6O_3$ (DMC) have been obtained and conductivity measurements have been performed [1]. The shape of the phase diagrams has been compared and the following order of anions for decreasing association of LiX salts with one and the same solvent, DMSO at $c_{LiX} = 0.2$ suggested, $ClO_4^- > CF_3SO_3^- > BF_4^- > NO_3^-$. The eutectic-type phase diagrams of the $LiClO_4$–PC and $LiClO_4$–DMC systems correspond to ideal, non-interacting solutions. The conductivity isotherms for the DMSO solutions at $c_{LiX} = 0.2$ are arranged in the order for increasing conductivity as $CF_3SO_3^- < ClO_4^- < B(C_2O_4)_2^- < BF_4^- < NO_3^-$, $N(SO_3CF_3)_2^-$. This order looks very similar to that for decreasing association of salts with DMSO signifying that both phase diagrams and conductivity are sensitive to all types of association equilibriums and account for both solvation and ion pairing phenomena. For the solutions of $LiClO_4$ in DMSO, PC and DMC at $c_{LiClO_4} = 0.5$–1 mole fraction of the salt the order of solvents for increasing conductivity is DMC $<$ PC $<<$ DMSO.

In the Raman study of cation and anion solvation [2], it has been found that in all solutions studied, notwithstanding the differences in the physical properties (polarity, dielectric constant, dimerization, hydrogen bonding, conformation equilibria) of the solvent and in the structure and properties of the anion, both the lithium cation and the anion solvation equilibria are quantitatively similar. In all cases, solvation numbers of cations are close to two and do not vary with the growth of concentration, and solvation numbers of anions decrease in a quite similar manner if the salt content is growing and are close to four in concentrated solutions. Therefore a conclusion has been drawn that solvation phenomena have no decisive importance in determining the properties of salt systems. Due to this fact, one can expect that differences in the properties of salt solutions may be determined by ion pairing phenomena.

To monitor the formation of various ion pairs, viz., solvent-separated (2SSIP), solvent-shared (SSIP), and contact (CIP) ones, numerous methods are used including X-ray and neutron diffraction techniques, molecular dynamics simulations, sound absorption, and dielectric spectroscopy [3–5]. The latter method is now of special attention in speciation studies due to adding a temporal coordinate to structural and thermodynamic data and especially because of an ability to see 2SSIPs indiscernible by other methods [6].

Vibrational spectroscopy also offers valuable opportunities in understanding the speciation problem [7,8] enabling one to detect signatures of ion pairing in solutions. On the first place, such phenomena are showing up as extra lines appearing in the vicinity of intense lines

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corresponding to non-degenerated vibrations of anions. Another, less definitely tractable evidence of ion pairing is splitting of weak lines corresponding to degenerated vibrations.

Upon adding LiClO$_4$ and LiNO$_3$ to DMSO, extra lines appear on the high-frequency side of the lines corresponding to the totally symmetric ν_1 (A$_1$) Cl−O and ν_1 (A'$_1$) N−O vibrations of anions. For perchlorates, the line at 933 cm^{-1} is assigned to free, unperturbed ClO$_4$ anions, the line at 938–939 cm^{-1} belongs to anions in SSIPs [9], and that at 944–946 cm^{-1} reflects the presence of CIPs where perturbations of the anion are the strongest [10,11]. Line shifts for nitrates are similar [12–14]: 1042 cm^{-1} for free, unperturbed anions, 1044–1047 cm^{-1} for SSIPs, and 1052 cm^{-1} for more complex aggregates (CIPs or triplets). Ion pairing of BF$_4^-$ ions has been studied in LiBF$_4$–acrylonitryle

solutions where the lines corresponding to the totally symmetric ν_1 (A$_1$) B−F vibrations of free anions manifest themselves at 766 cm^{-1}, certain ion pairs give lines at 773 cm^{-1}, and more complex aggregates at 783 cm^{-1} [15,16].

Analogous properties are characteristic of trifluoromethylsulfonate solutions. For LiCF$_3$SO$_3$ dissolved in DMSO, the lines corresponding to the symmetric bending δ_s (A$_1$) CF$_3$ vibrations are split into two components assigned to free anions (754 cm^{-1}) and certain ion pairs (758 cm^{-1}) [17]. In acetone solutions, an additional line at 762 cm^{-1} presumably reflects the presence of CIPs or more complex aggregates [17,18]. Bis (trifluoromethylsulfonyl) imide anion N(SO$_3$CF$_3$)$_2^-$ in solutions exists in the form of cis- and trans-conformers, the latter being more stable [19,20]. The most intense Raman line at 740 cm^{-1}
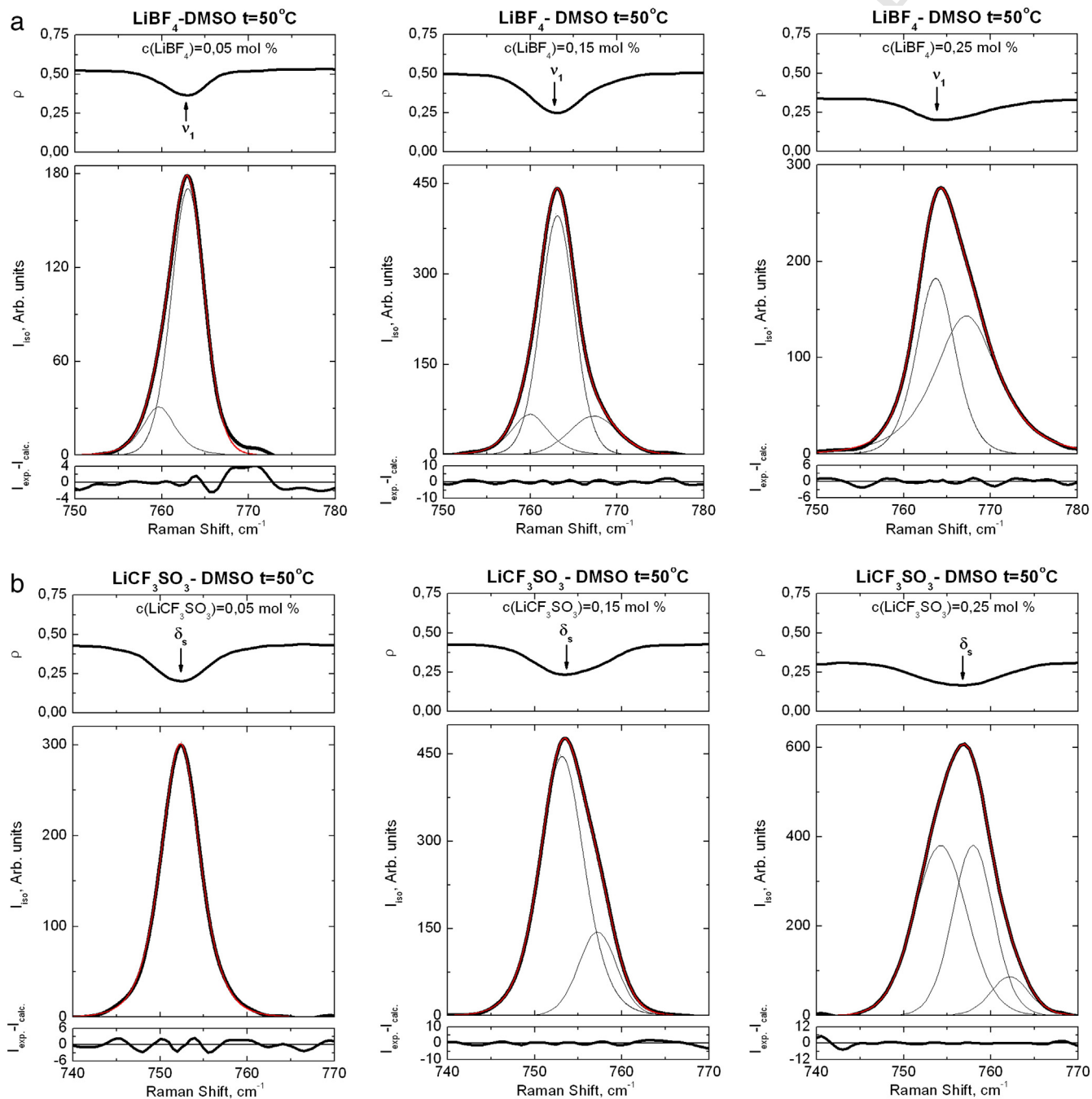

Fig. 1. Evolution of isotropic Raman spectra of anion vibrations upon adding the salt to DMSO, PC and DMC. Upper panels—depolarization ratios. Middle panels—experimental spectra (thick black lines) and overall data fits (thin red lines); components of the lines corresponding to anion vibrations are given in thin black lines. Lower panels—residuals. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)