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FTIR Study of Ion Solvation and Ion-Pair Formation in Alkaline and Alkaline Earth Metal Salt Solutions in Acetonitrile

J. Barthel[1] and R. Deser[1]

Received March 15, 1994; Revised August 2, 1994

The IR spectra of alkaline and alkaline earth metal perchlorate and of lithium bromide solutions in acetonitrile, obtained with the help of FTIR measurements in the region of the C-N stretching mode of the solvent, reveal bands produced by acetonitrile molecules in the solvation shells and bands of ClO_4^- ions in contact and solvent separated ion pairs. The shift and the attenuation of the C-N stretching band of acetonitrile at 2254 cm^{-1} is used for the calculation of cation solvation numbers for Li^+(4), Na^+(4), Mg^{2+}(6), Ca^{2+}(6) and Ba^{2+}(6). No solvation is assumed for the contact ion pairs of $LiClO_4$, LiBr, $NaClO_4$, $Mg(ClO_4)_2$, $Ca(ClO_4)_2$, and $Ba(ClO_4)_2$. The association constants of the symmetrical electrolytes are compared to those obtained from other methods.

Journal of Solution Chemistry 29 937 (2000)

FTIR Spectroscopy of Ion Solvation of $LiClO_4$ and LiSCN in Acetonitrile, Benzonitrile, and Propylene Carbonate†

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FTIR spectra of lithium perchlorate and lithium thiocyanate in acetonitrile, benzonitrile, and propylene carbonate were recorded in the temperature range from 5 to 45°C. New bands due to solvent molecules in the primary solvation shell of the lithium ions were detected in the region of the CN stretching mode of the nitriles and of the CO stretching mode of propylene carbonate. The band structures were studied in detail by deconvolution with band-fitting procedures and mean cation solvation numbers were deduced from the band area of the bulk solvent. For the systems acetonitrile–lithium perchlorate, benzonitrile–lithium perchlorate, and benzonitrile–lithium thiocyanate, solvation numbers of "free" and "bound" lithium ions were calculated with the help of the degree of association obtained from suitable anion vibrations.

KEY WORDS: FTIR spectroscopy; ion solvation; ion association; dipolar aprotic solvents.

Experiments

Nicolet 60 SX FT-IR (Ge/KBr beam splitter with DTGS detector)

Transmission geometry

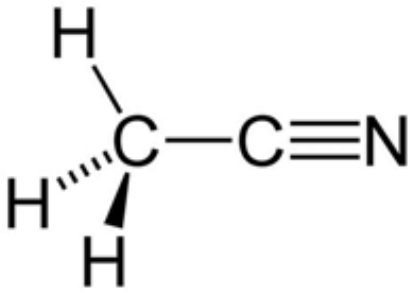
BaF_2 window
12.5 um Tin spacer (BN - Benzonitrile)
21.0 um Lead spacer (AN - Acetonitrile)

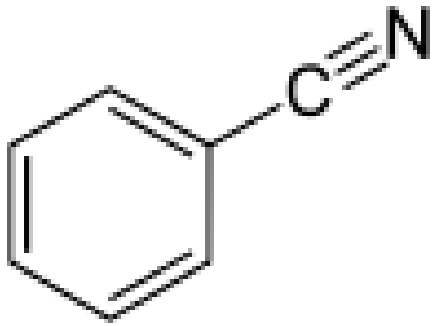
16.0 um (1994 salt dependence paper)

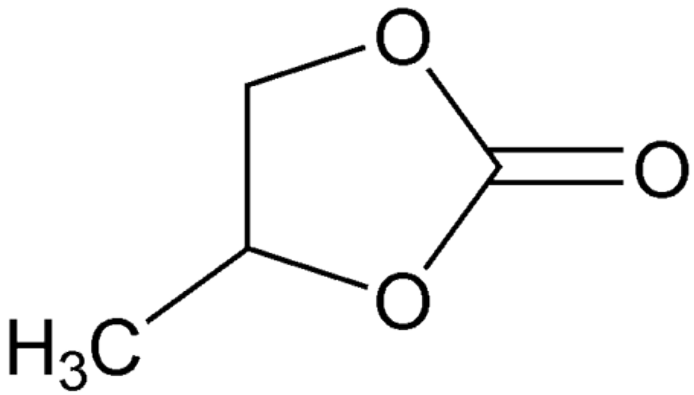
1 bounce ZnSe ATR (PC – Propylene Carbonate)

Single bounce ZnSe ATR

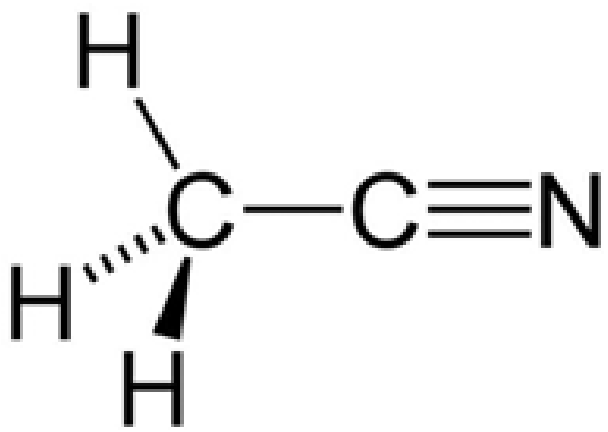
AN refluxed with CaH2 in dry N2
(water < 15 ppm, Organic impurities < 20 ppm)
BN stored with 0.4 nm molecular sieve
(water < 10 ppm, organic impurity < 500 ppm)

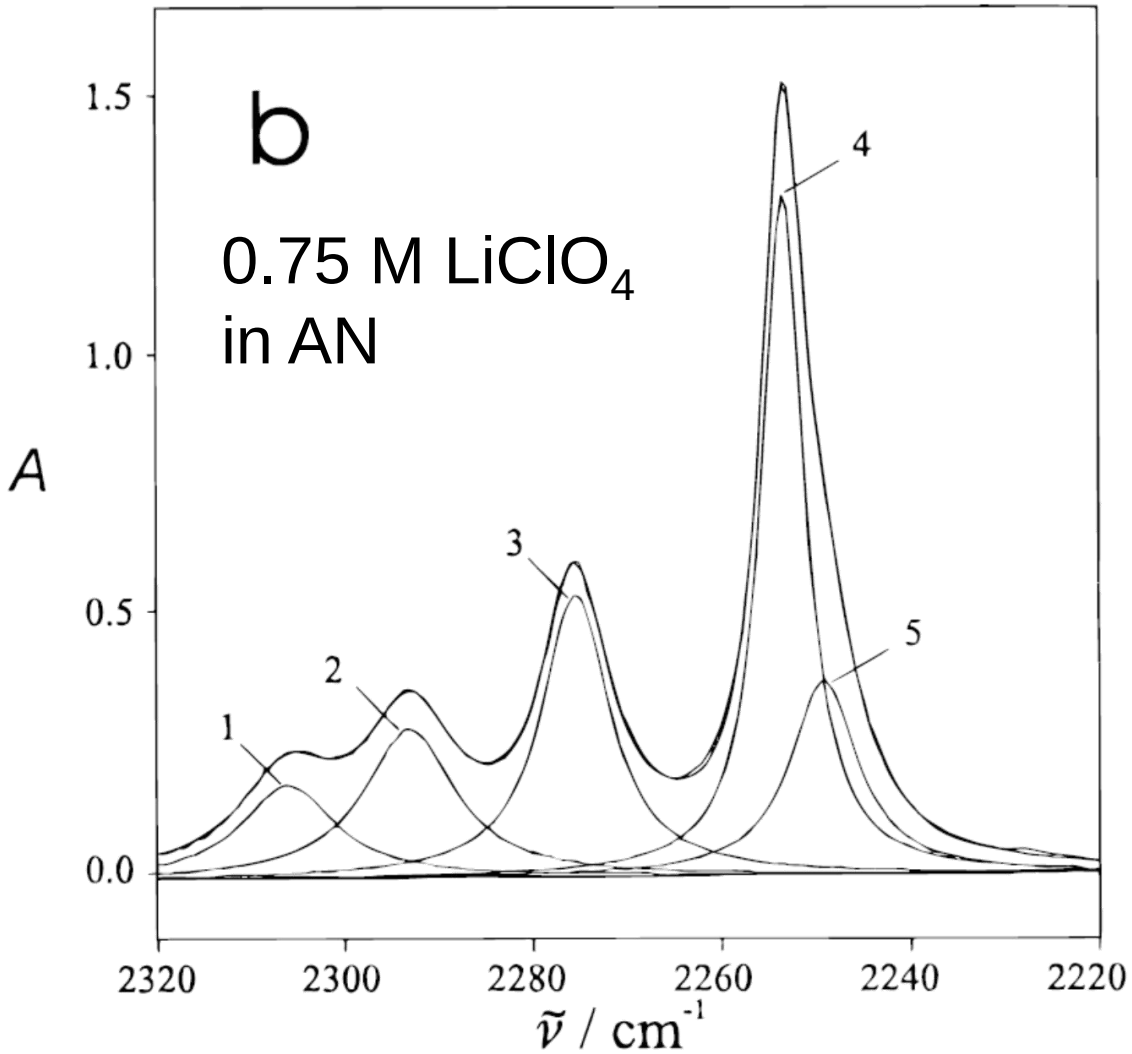






IR Spectra of Acetonitrile / $LiClO_4$



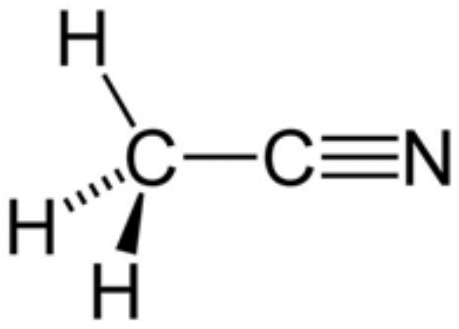


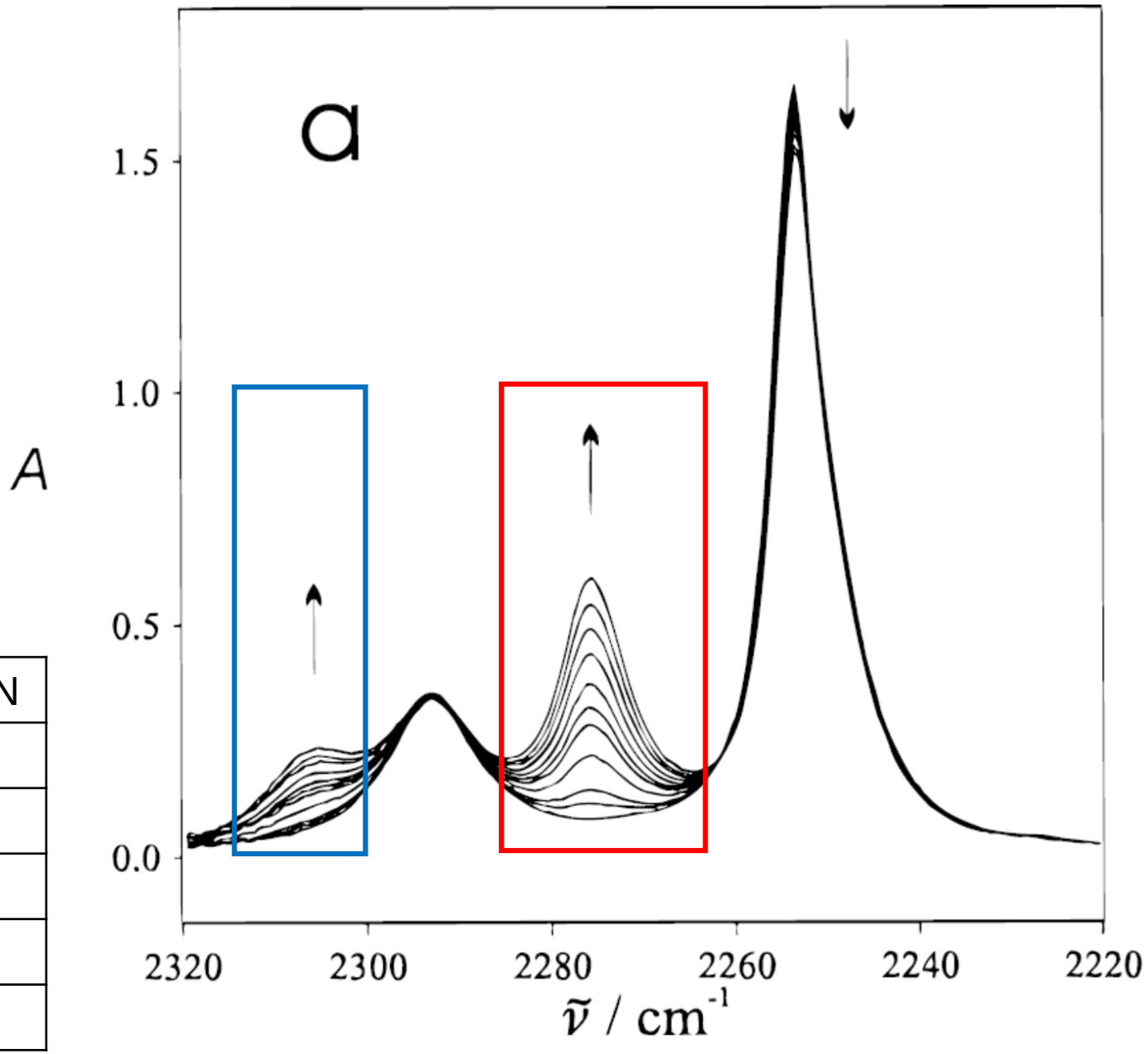
Band	Assignment	AN/LiClO4	AN/LiSCN
1 (ion)	$(\nu_3 + \nu_4)^{shift}$	2306.3	2304.9
2	$(\nu_3 + \nu_4)$	2293.1	2292.9
3 (ion)	ν_2^{shift}	2275.5	2274.0
4	ν_2	2253.5	2253.5
5	ν_2^{hot}	2249.1	2249.2

ν_2 : CN-stretch
ν_3 : CH_3 s-deform (1385 cm^{-1})
ν_4 : CC stretch (920 cm^{-1})

Hot :
Hot band (transition between excited state)
$N/N_o \sim e^{-E/kT}$

IR Spectra of Acetonitrile / $LiClO_4$





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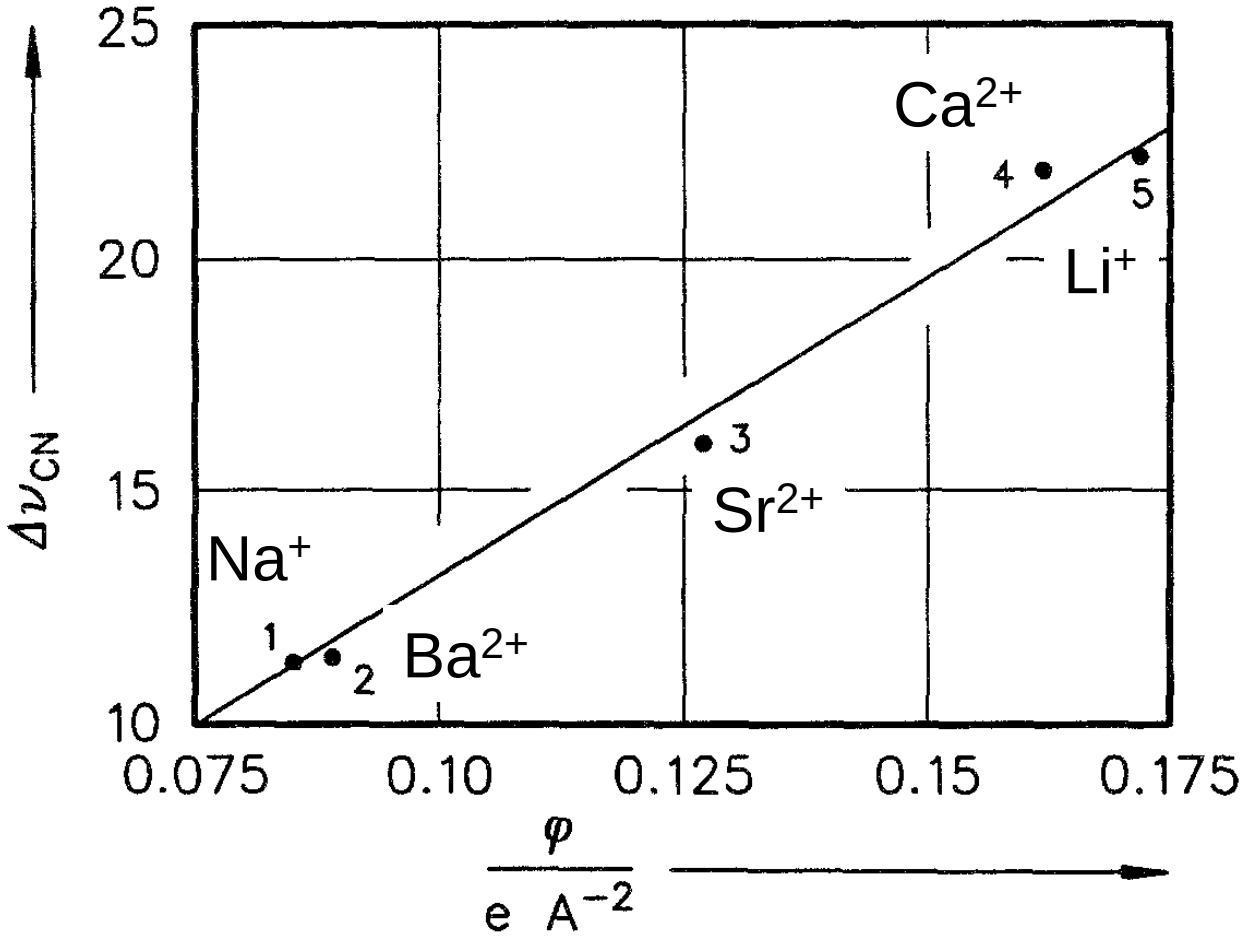
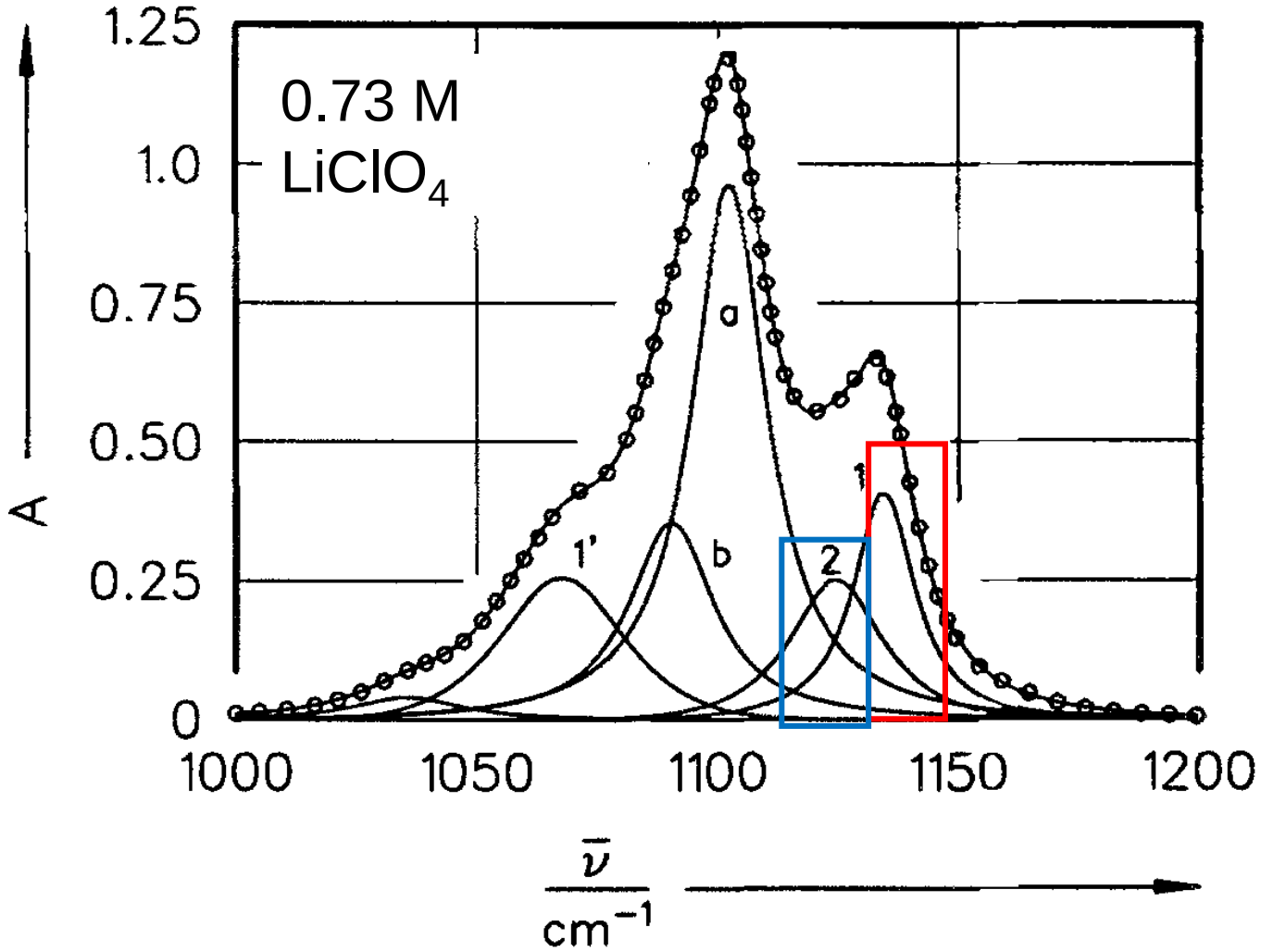
5	ν_2^{hot}	2249.1	2249.2

Salt dependence of $\Delta\nu_{CN} = \Delta\nu_{CN}^{shift} - \Delta\nu_{CN}$



1 $NaClO_4$
2 $Ba(ClO_4)_2$
3 $Sr(ClO_4)_2$
4 $Ca(ClO_4)_2$
5 $LiClO_4$

IR Spectra of $LiClO_4$ anion



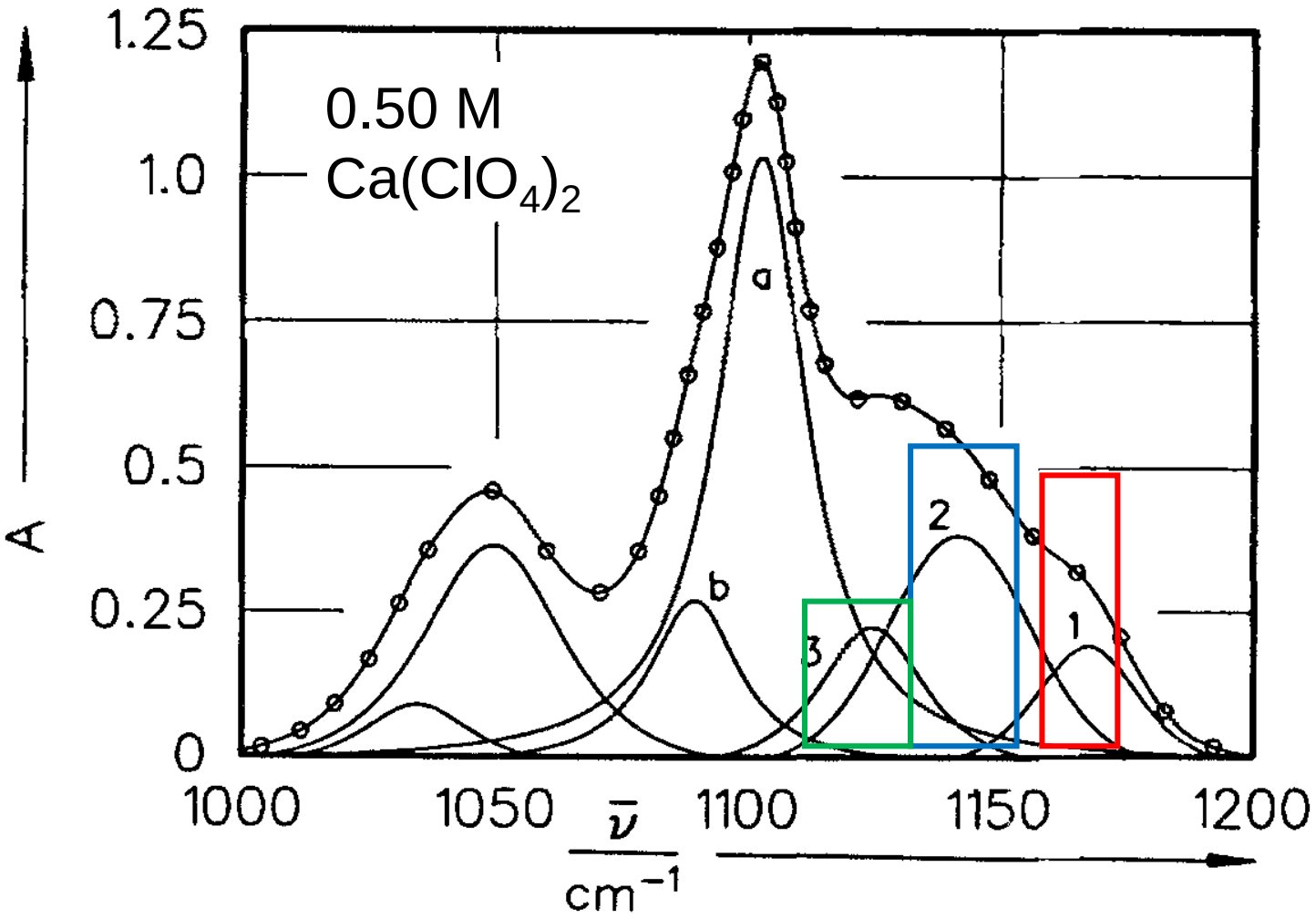
Free ClO_4^- : 1102 cm^{-1}
(tetrahedral T_D symmetry)

(b) Combination of $\nu_2 + \nu_4$

Antisymmetric Cl-O deformation
(C_{3v} symmetry)
(1) 1134 cm^{-1} : Contact Ion Pair
(2) 1124 cm^{-1} : Solvent Separated IP

(1') 1068 cm^{-1} : CIP
(It might be ν_1 stretch)

IR Spectra of $Ca(ClO_4)_2$ anion



Antisymmetric Cl-O deformation (C_{3v} symmetry)

(1) 1166 cm^{-1} : Contact Ion Pair

(2) 1141 cm^{-1} : Solvent Separated IP

(3) 1124 cm^{-1} : Solvent Separated IP

$Ca_2^+ \cdots AN \cdots ClO_4^-$

Band (3) is shown for $Ca(ClO_4)_2$ and $Ba(ClO_4)_2$

Cation Solvation Number

$$c_0 = c_{solv} + c_{SIP1}$$
$$c_{solv} = c_{free} + c_{SSIP} + c_{SIP2}$$

c_0 : Concentration of ion

Species	Symbol	Solvated
$C^+ \cdots ClO_4^-$	CIP_1	No
$C^+ \cdots AN \cdots ClO_4^-$	SSIP	Yes
C^+	Free	Yes
$ClO_4^- \cdots C^{2+} \cdots ClO_4^-$	CIP_1	No
$C^{2+} \cdots ClO_4^-$	CIP_2	Yes
$C^{2+} \cdots AN \cdots ClO_4^-$	SSIP	Yes
C^{2+}	Free	Yes

Cation Solvation Number

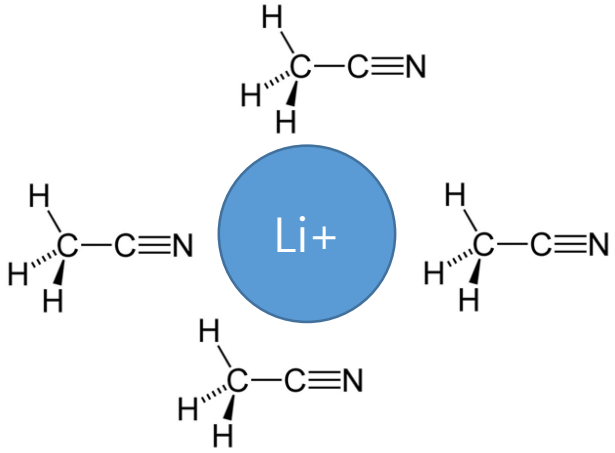
$$c_0 = c_{solv} + c_{SIP1}$$
$$c_{solv} = c_{free} + c_{SSIP} + c_{SIP2}$$

Cation Solvation Number

$$c_0 = c_{solv} + c_{SIP1}$$
$$c_{solv} = c_{free} + c_{SSIP} + c_{SIP2}$$

$$A_{CN}^{shift} = nd\varepsilon_{CN}^{shift}c^{solv}$$
$$A_{ClO4}^{CIP1} = nd\varepsilon_{ClO4}^{CIP1}c^{CIP1}$$

$$A_{CN} = n\varepsilon_{CN}c_{AN}$$
$$A_{CN}^{*} = n\varepsilon_{CN}^{*}c_{AN}^{*}$$



n : cation solvation number
n = 4

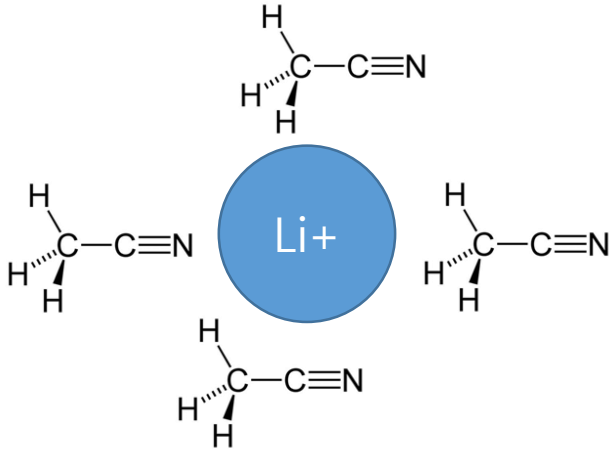
AN* : CN stretching mode of AN in a sample of pure AN
AN : AN which does not participating in solvation shell

Cation Solvation Number

$$A_{CN}^{shift} = nd\varepsilon_{CN}^{shift}c^{solv}$$

$$A_{CN} = n\varepsilon_{CN}c_{AN}$$

$$A_{CN}^{*} = n\varepsilon_{CN}^{*}c_{AN}^{*}$$



n : cation solvation number

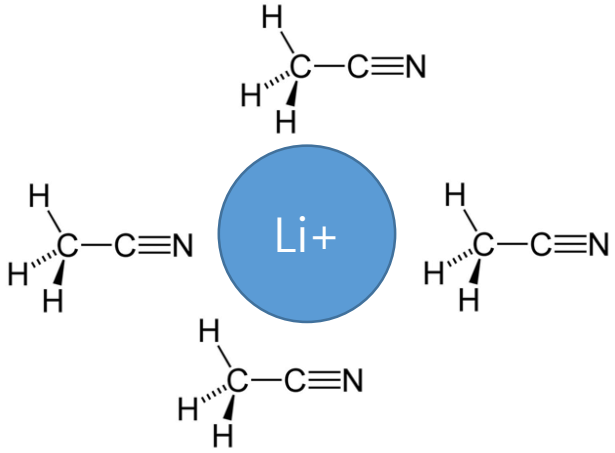
n = 4

$$\varepsilon_{CN}^{shift} = \frac{A_{CN}^{shift}}{A_{CN^*} - A_{CN}} \cdot \varepsilon_{CN}$$

Cation Solvation Number

$$c_0 = c_{solv} + c_{SIP1}$$

$$A_{CN}^{shift} = nd\varepsilon_{CN}^{shift}c^{solv}$$
$$A_{ClO4}^{CIP1} = nd\varepsilon_{ClO4}^{CIP1}c^{CIP1}$$



n : cation solvation number
n = 4

$$c^{o} = \frac{A_{CN}^{shift}}{nd\varepsilon_{CN}^{shift}} + \frac{A_{ClO_4}^{CIP_1}}{d\varepsilon_{ClO_4}^{CIP_1}}$$

$$\varepsilon_{CN}^{shift} = \frac{A_{CN}^{shift}}{A_{CN*} - A_{CN}} \cdot \varepsilon_{CN}$$

Cation Solvation Number

$$c_0 = c_{solv} + c_{SIP1}$$

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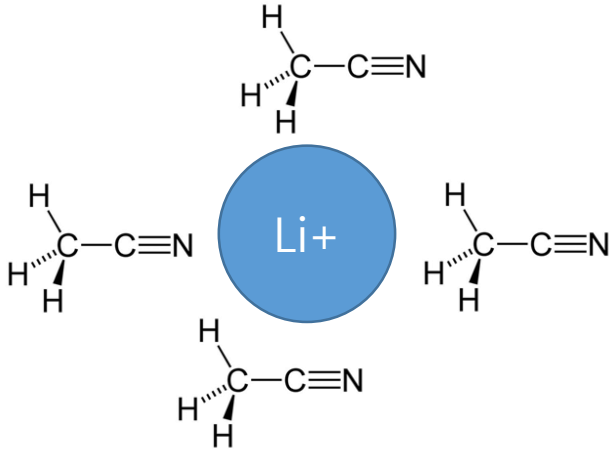

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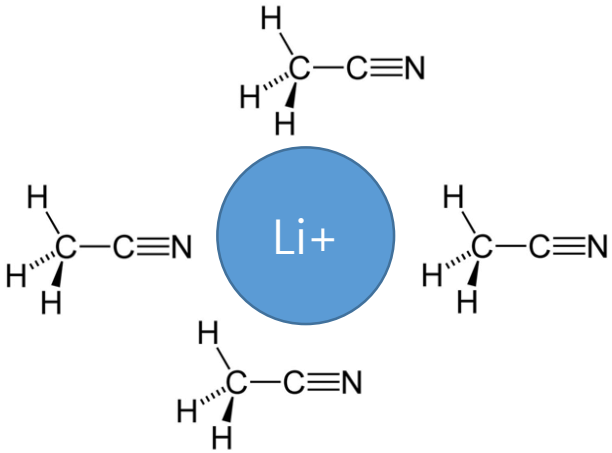
$$\varepsilon_{CN}^{shift} = \frac{A_{CN}^{shift}}{A_{CN*} - A_{CN}} \cdot \varepsilon_{CN}$$

n determined by measurements at two different concentrations

Cation Solvation Number

n = 4 (Li+, Na+)

n = 6 (Mg^{2+}, Ca^{2+}, Ba^{2+})

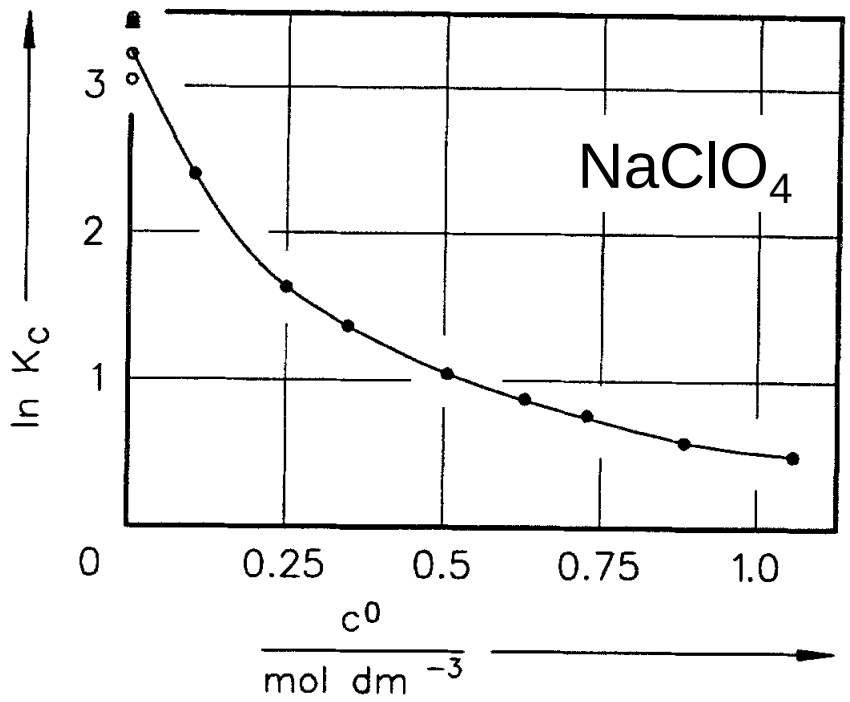


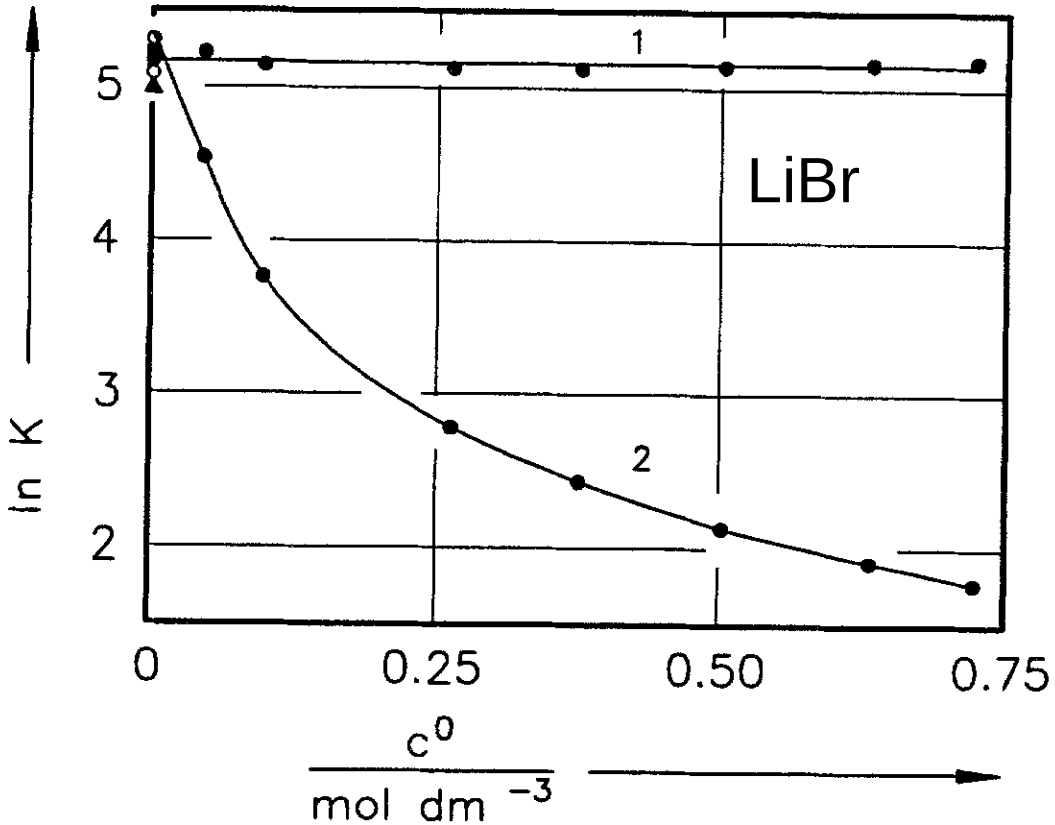
n : cation solvation number
n = 4

Association Constants

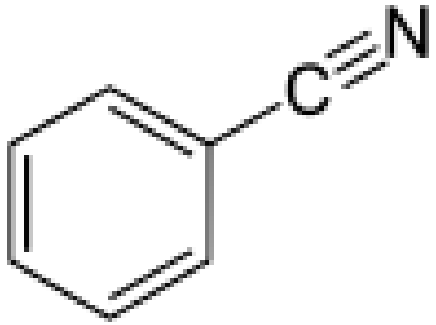
$$C^+ + A^- \rightleftarrows [C^+A^-]^o$$

$$K_c = \frac{c^{CIP}}{(c^o - c^{CIP})^2}$$

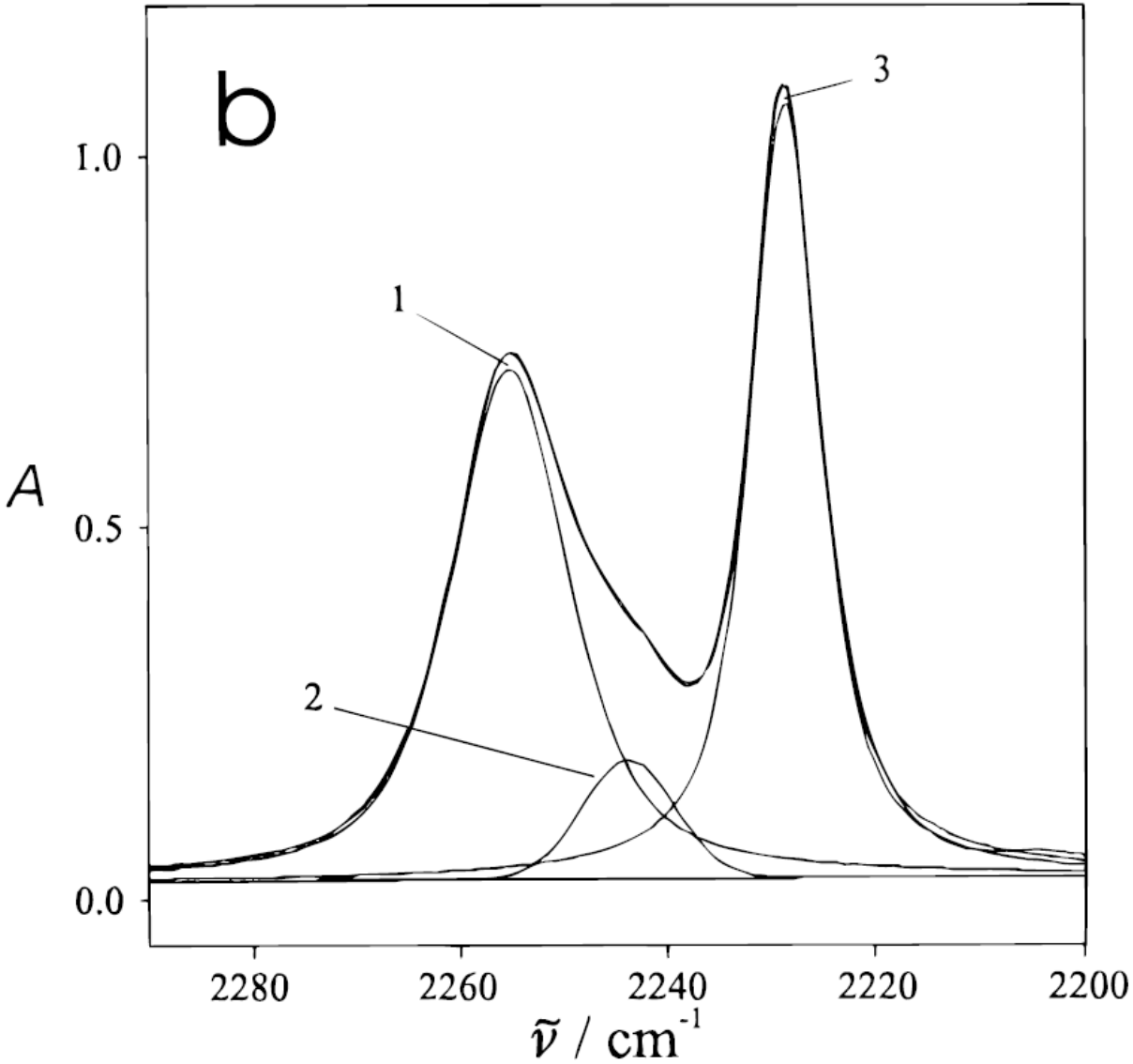




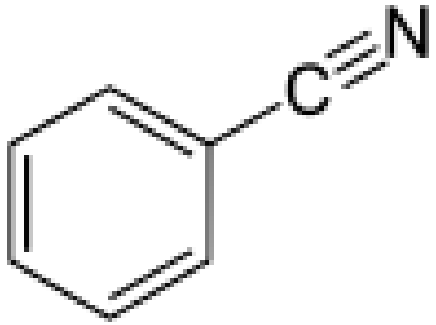
IR Spectra of Benzonitrile/ $LiClO_4$



Band	Assignment	BN/LiClO4	BN/LiSCN
1 (ion)	ν_4CN^{shift}	2254.9	2253.3
2	$\nu_4CN^{monomer}$	2242.6	2242.0
3 (ion)	ν_4CN^{dimer}	2228.8	2228.8



IR Spectra of Benzonitrile/ $LiClO_4$



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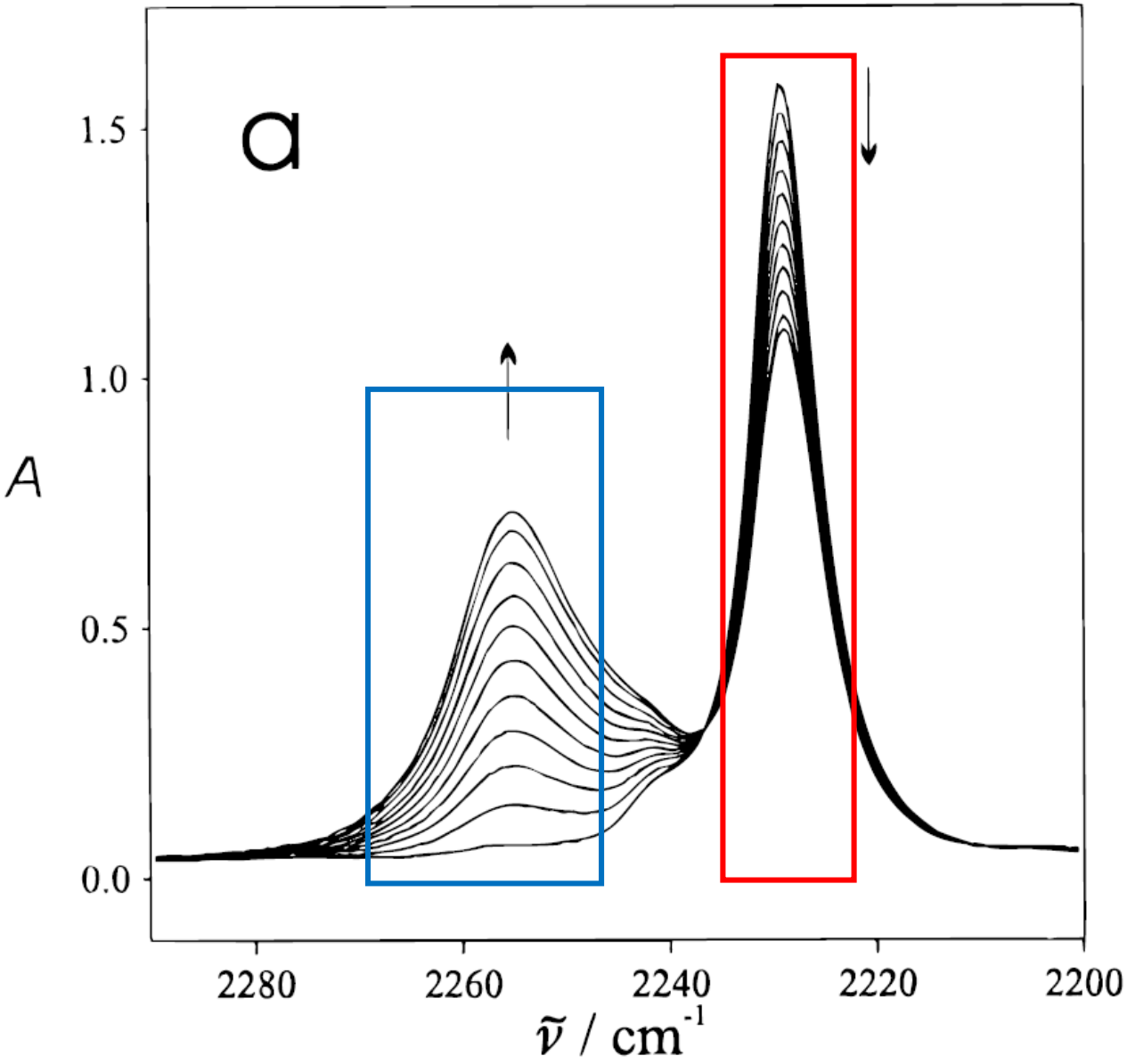
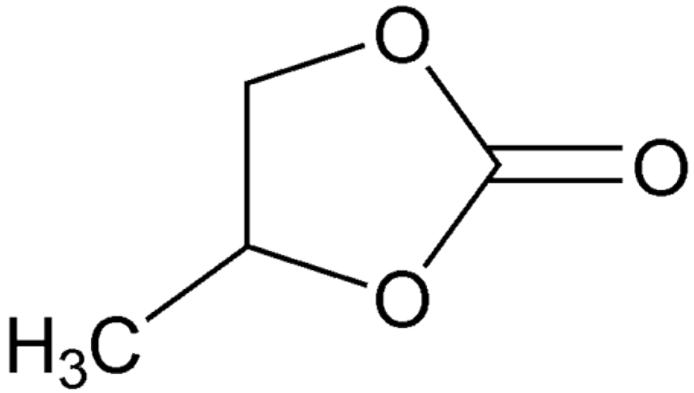
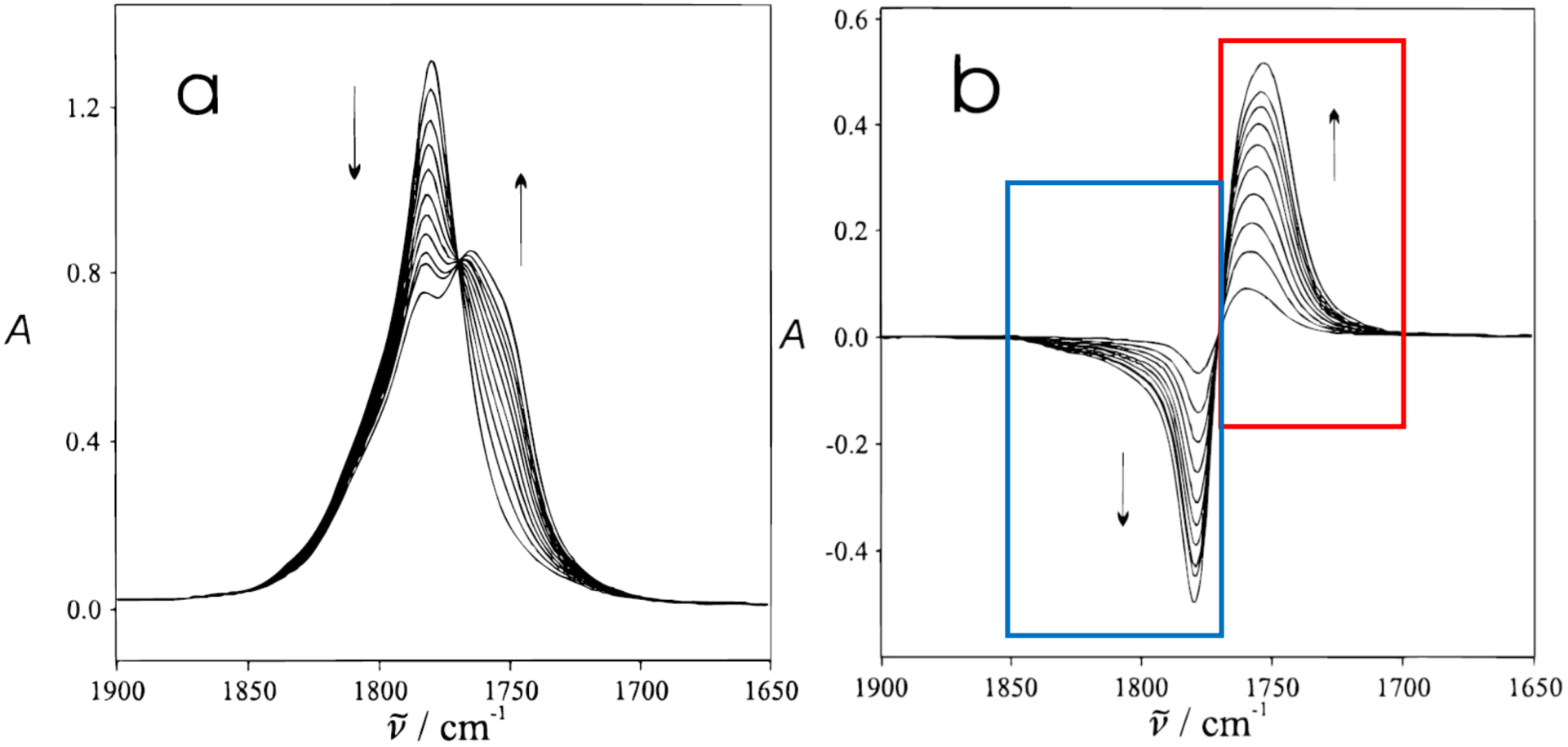
3	ν_4CN^{dimer}	2228.8	2228.8



IR Spectra of Propylene Carbonate / $LiClO_4$

Band	Assignment	PC/LiClO4	PC/LiSCN
1 (ion)	$\nu_1 CO^{shift}$	1779.5	1779.4
2	$\nu_1 CO^{monomer}$	1753.1	1755.9





Mean Solvation Number

$$1 - \frac{E_S}{E_S^*} = \frac{c_S^* - c_S + \bar{n}\, c}{c_S^*}$$

E_s^* : Absorbance of AN*
AN* : CN stretching mode of AN in a sample of pure AN
AN : AN which does not participating in solvation shell

$$\frac{c_S}{c_S^*} - \frac{E_S}{E_S^*} = n\frac{c}{c_S^*}$$

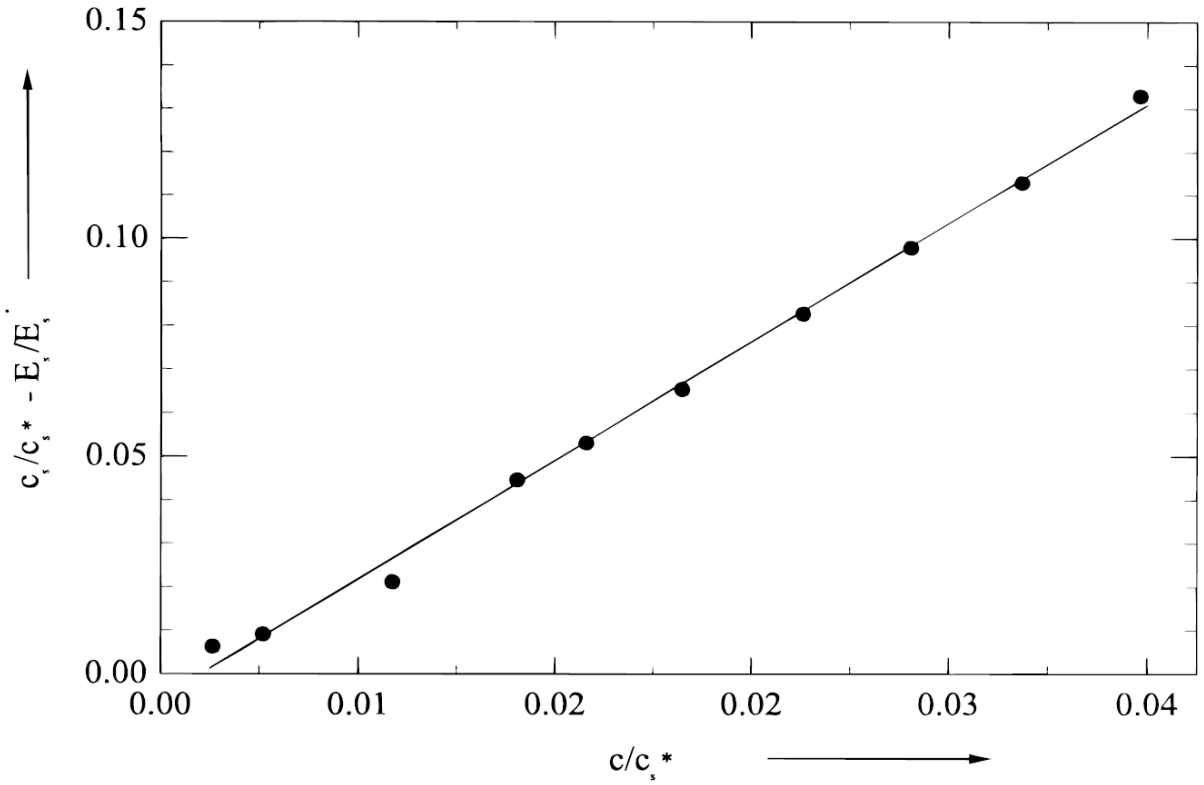


Fig. 5. Determination of the mean solvation number, $\bar{n}$, of $LiClO_4$ in AN at 25°C by linear regression of Eq. (3).

Mean Solvation Number

Table VI. Mean Solvation Numbers, $\bar{n}$, of the Studied Electrolytes at 25°C in the Concentration Range $c_{min}-c_{max}$[a]

System	$\bar{n}$	$c_{min} - c_{max}$	K_A	Ref.
AN/$LiClO_4$	3.4	0.05–0.73	22.0	10
AN/LiSCN	2.7	0.07–0.68	1775	10
BN/$LiClO_4$	2.0–1.7	0.11–1.00	224	10
BN/LiSCN	2.0–1.6	0.11–1.02	2690	30
PC/$LiClO_4$	2.3–1.7	0.12–1.29	5.20	11
PC/LiSCN	2.0–1.6	0.13–1.19	180	30

Anion spctra