

Spectroscopic Studies of Ion Solvation in 3-Substituted Liquid 2-Oxazolidones

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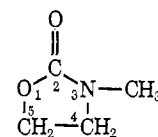
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Abstract: A comprehensive study of ion solvation in 3-methyl-, 3-ethyl-, 3-isopropyl-, and 3-*tert*-butyloxazolidones has been undertaken involving alkali metal chlorides, bromides, iodides, thiocyanates, perchlorates, and tetraphenylborates. Ammonium salts of several of these anions also were studied. The techniques employed included far-infrared spectroscopy, infrared spectroscopy, proton nuclear magnetic resonance, and sodium nuclear magnetic resonance. The far-infrared studies show the spectral bands to be cation dependent and anion independent indicating contact ion pairs are not likely within the lifetime of $\leq 10^{-7}$ sec for the cation structural entity. The infrared studies reinforce the far-infrared observations for the NH_4^+ ion. The proton nuclear magnetic resonance studies indicate that the tetraphenylborate anion exhibits a pronounced interaction with the solvent as the proton shifts are positive for tetraphenylborate while negative for all other anions. An increased electron density around solvent protons attributable to anionic interaction would result in a positive shift. The sodium-23 nuclear magnetic resonance shows that salts of thiocyanate and iodide anions probably produce ion pairs. Also this technique provides evidence that the tetraphenylborate salts may be completely dissociated or involve solvent-separated ion pairs.

Spectroscopic techniques are being applied to the study of ion solvation with increasing frequency. The most commonly used techniques are far-infrared spectroscopy,²⁻¹⁰ infrared spectroscopy,^{8,11-14} proton nuclear magnetic resonance spectroscopy (pmr),^{5,7,8,15-19} and sodium nuclear magnetic resonance spectroscopy.²⁰⁻²⁵ Although these techniques individually provide considerable information about the state of ions in solution, a comprehensive study of a system using all of the above techniques may yield a more complete model of ion solvation.

The liquid 3-substituted 2-oxazolidones have not been widely investigated as solvents. Huffman and Sears have studied a series of eight liquid 2-oxazolidones

as possible electrolytic solvents.²⁶ They found the dielectric constants at 1 MHz ranged from 39.9 to 84.0 and also completed a study of electrolytes in 3-methyl-2-oxazolidone.²⁷



3-methyl-2-oxazolidone

Because of their high dielectric constants it was decided to undertake a comprehensive spectroscopic study of electrolytes with a series of four 3-substituted 2-oxazolidones: 3-methyl-2-oxazolidone (3Me2Ox; *d* 77.5), 3-ethyl-2-oxazolidone (3Et2Ox; *d* 66.8), 3-isopropyl-2-oxazolidone (3-*i*-Pr)2Ox; *d* 51.0), and 3-*t*-butyl-2-oxazolidone (3-*t*-Bu)2Ox; *d* 57.6). By undertaking a comprehensive spectroscopic study using all four of the techniques mentioned above, models for ion solvation in these solvents may be obtained.

Experimental Section

Chemicals. All four 3-substituted 2-oxazolidones were prepared by the Homeyer method.^{26,28,29} They were purified by fractional freezing or vacuum distillation²⁶ with the exception of 3-ethyl-2-oxazolidone for which the contents of the reaction vessel were first extracted with pentane before vacuum distillation. The solvents were stored under nitrogen. The freezing and/or boiling points were within a few tenths of a degree Centigrade of literature values.²⁶ Karl Fischer titrations showed water content for 3Me2Ox < 0.034%, 3Et2Ox < 0.072%, 3(*i*-Pr)2Ox < 0.045%, and 3(*t*-Bu)2Ox < 0.046%.

Potassium, rubidium, and ammonium tetraphenylborates and ammonium perchlorate were prepared as previously described.^{30,31} All other salts were the purest commercially available grades and were used without further purification except for drying.

Measurements. Far-infrared measurements from 40 to 400

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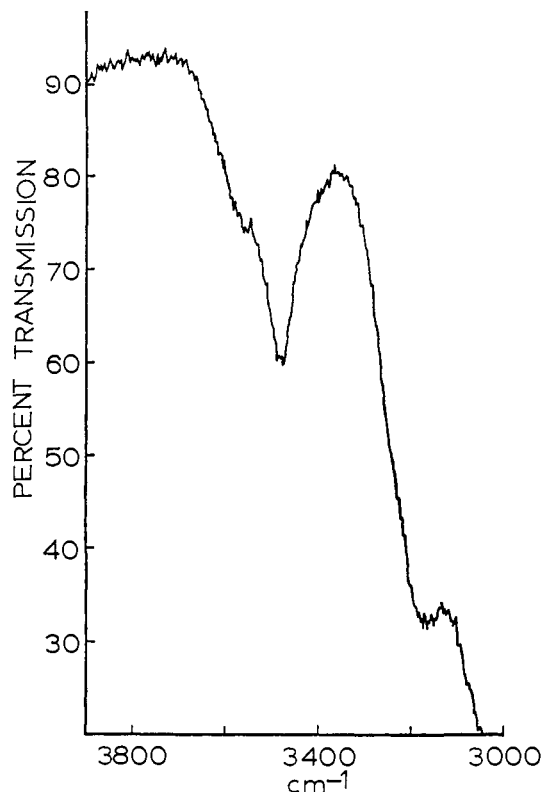


Figure 1. Formation of a new band due to NH_4^+ stretching; 0.5 M NH_4I in 3-methyl-2-oxazolidone.

cm^{-1} were obtained on a Beckman R.I.I.C. FS-720 interferometer equipped with F.T.C. 300 Fourier transform electronics using R.I.I.C. FS-03 vacuum-tight cells with polyethylene windows and 0.075-mm Teflon spacers. In addition, measurements between 200 and 4000 cm^{-1} were taken on a Beckman Model IR-12 infrared spectrometer. For the region between 200 and 400 cm^{-1} the cell was equipped with polyethylene windows and from 400 to 4000 cm^{-1} KBr windows were used.

The pmr measurements were made on a Varian A-60 nuclear magnetic resonance spectrometer using tetramethylsilane as an internal standard. The reproducibility was ± 0.3 Hz.

The sodium-23 nuclear magnetic resonance spectra were run on a Bruker HFX-10, 90 MHz instrument equipped with a General Radio Corp. voltage divider. By means of the voltage divider the normal field strength of 21,140 G was reduced to 20,118 G allowing the sodium-23 spectra to be observed using the 22.62-MHz probe designed for ^{13}C applications. The spectra were run with the instrument in the field sweep configuration and the magnet in the unlocked mode. The samples were placed in nonspinning 10-mm nmr tubes with a reference solution of saturated sodium chloride in water inserted coaxially in a 1-mm nmr tube. When the shift observed for any solution was too close to the aqueous sodium chloride shift, an alternate standard, saturated sodium tetraphenylborate (NaBPh_4) in nitromethane, was used.

Results and Discussion

Far-Infrared Region. Table I gives the data obtained from the far-infrared spectra of the salt solutions studied. As has been reported previously for other solvents with moderate to high dielectric constants,^{5-10,31} a single new band was found in the far-infrared region with the frequency independent of the salt concentration. Furthermore, the band frequency is dependent on the cation, but the anion has no effect on the band location. In solvents with low dielectric constants this new band is anion dependent. This has been interpreted as being due to contact ion pairs.^{2,3} In solvents with moderate to high dielectric constants the band frequency being independent of the anion

Table I. Frequencies of Far Infrared Vibrational Bands of Alkali Metal Salts in Liquid 2-Oxazolidones^a

Salt	3Me2Ox	3Et2Ox	3(<i>i</i> -Pr)2Ox	3(<i>t</i> -Bu)2Ox
LiCl	406 \pm 5	399 \pm 5	392 \pm 5	
LiBr	405 \pm 5	406 \pm 5	391 \pm 5	394 \pm 5
LiI	404 \pm 5	403 \pm 5	392 \pm 5	397 \pm 5
LiClO ₄	407 \pm 5	399 \pm 5	394 \pm 5	393 \pm 5
NaI	202 \pm 2	177 \pm 2	186 \pm 2	177 \pm 2
NaBPh ₄	203 \pm 2	180 \pm 2	186 \pm 2	178 \pm 2
NaSCN	204 \pm 2	180 \pm 2	186 \pm 2	176 \pm 2
NaClO ₄	202 \pm 2	182 \pm 2	186 \pm 2	175 \pm 2
KI	154 \pm 2	154 \pm 2	148 \pm 2	
KBPh ₄	152 \pm 2	152 \pm 2	149 \pm 2	
KSCN	153 \pm 2	152 \pm 2	149 \pm 2	154 \pm 2
KClO ₄	153 \pm 2			
RbI	124 \pm 2	126 \pm 2		
RbBPh ₄	126 \pm 2			
RbSCN	126 \pm 2	127 \pm 2	125 \pm 2	
CsSCN	117 \pm 2	117 \pm 2		
NH ₄ I	206 \pm 2	181 \pm 2	185 \pm 2	176 \pm 2
NH ₄ BPh ₄	203 \pm 2	179 \pm 2	185 \pm 2	178 \pm 2
NH ₄ SCN	204 \pm 2	180 \pm 2	186 \pm 2	179 \pm 2
NH ₄ ClO ₄	203 \pm 2	181 \pm 2	184 \pm 2	176 \pm 2

^a BPh₄ = tetraphenylborate.

indicates that the anion does not enter into the inner solvation sphere, as occurs when contact ion pairs are formed. However, as Maxey and Popov⁷ note, the nature and mass of the anion may not influence the vibrational frequency, but it cannot be concluded that the anion is absent from the immediate surroundings of the cation. It does not, however, differentiate between dissociated electrolytes and solvent-separated ion pairs.⁹⁻³¹

Infrared Region. Except for the above there were few other changes between the infrared spectrum of a salt solution and the pure solvent in the 3-substituted liquid 2-oxazolidones investigated. Figure 1 shows the spectrum of a 0.50 M NH_4I solution. A band appears near 3180 cm^{-1} which is the NH_4^+ stretching frequency.³² The band is, within experimental error, independent of the anion as are the far-infrared bands, giving further evidence for the lack of contact ion pairs.

Proton Nuclear Magnetic Resonance. A number of investigators have studied the effect of salts on the pmr spectra of aqueous solutions.³³⁻³⁸ The aqueous proton has been observed to shift either upfield (positive) or downfield (negative) from pure water for various salt solutions. The peak shift is found to be linear with concentration until the solvent molecules are shared by more than one ion.³⁶

Figure 2 shows the shifts for LiI salt solutions in 3Et2Ox. The shifts in peak position are linear with concentration showing the solvent molecules are not shared between ions in the concentration ranges studied. No bulk diamagnetic corrections were made as Hertz and Spalhoff³⁴ indicate they are not necessary when an internal reference is used. The shifts are negative for all protons in the molecule. The largest shifts are observed for the ring methylene protons in the 4 and 5

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(35) V. A. Shcherbakov, *Zh. Strukt. Khim.*, **2**, 484 (1961).

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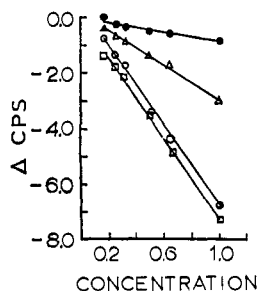


Figure 2. Proton nuclear magnetic resonance vs. moles of LiI in 3-ethyl-2-oxazolidone: (○) 4-methylene protons, (□) 5-methylene protons, (Δ) R-methylene protons, (●) R-methyl protons.

positions. A smaller shift is seen for the methylene protons on the R group substituted on the nitrogen. The methyl group on the R substituent shows only a small shift. This same effect is noted for all 2-oxazolidones studied.

Figure 3 shows the shifts due to sodium tetraphenylborate in 3Me2Ox. These are positive and much larger than for lithium iodide. The same is observed for the relative shifts. The ring protons have a larger shift than the R-methyl group protons. Table II gives the

Table II. Proton Nuclear Magnetic Resonance Shift Data in Hertz for 3-Methyl-2-oxazolidone^a

Salt	<i>M</i>	δ_{4-CH_2}	δ_{5-CH_2}	δ_{R-CH_3}
LiCl	0.25	-1.9	-1.7	-0.8
LiCl	0.50	-2.5	-2.2	-1.0
LiCl	1.00	-3.2	-3.0	-1.3
LiBr	0.25	-1.7	-1.6	-1.0
LiBr	0.50	-2.0	-2.5	-1.3
LiBr	1.00	-4.6	-5.4	-2.7
LiI	0.25	-0.7	-1.4	-0.5
LiI	0.50	-2.1	-3.3	-0.9
LiI	1.00	-4.9	-6.4	-2.2
LiClO ₄	0.25	-0.7	-1.2	-0.2
LiClO ₄	0.50	-1.5	-1.5	-1.0
LiClO ₄	1.00	-3.1	-3.3	-2.2
LiClO ₄	2.00	-5.3	-5.9	-4.6
NaI	0.25	-0.3	-1.5	-0.9
NaI	0.50	-2.5	-2.9	-1.6
NaI	1.00	-4.7	-5.5	-2.8
NaClO ₄	0.25	-0.4	-0.5	-0.8
NaClO ₄	0.50	-1.2	-1.5	-1.2
NaClO ₄	1.00	-1.5	-2.0	-1.6
NaSCN	0.25	-0.1	-1.1	-0.8
NaSCN	0.50	-1.4	-2.3	-1.0
NaSCN	1.00	-2.7	-3.6	-1.2
NaBPh ₄	0.25	+3.2	+4.5	+1.7
NaBPh ₄	0.50	+7.6	+9.9	+4.5
NaBPh ₄	1.00	+20.2	+23.4	+11.1
KI	0.25	-0.8	-1.2	-0.8
KI	0.50	-2.6	-2.7	-2.0
KI	1.00	-4.4	-4.9	-2.5

^a (-) indicates a downfield shift and (+) indicate an upfield shift.

pmr shift data for all salts studied in 3Me2Ox and is representative of the data observed for the other solvents.³⁹ All salts with the exception of the tetraphenylborates show negative shifts whereas the tetraphenylborate salts of all cations produce a positive shift.

The shifts are not anion independent as are the bands

(39) See paragraph at end of paper regarding supplementary material.

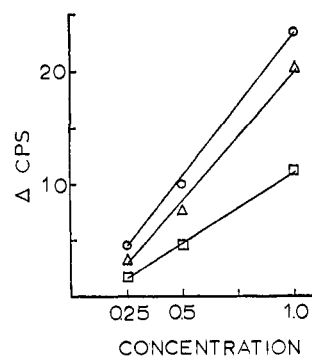


Figure 3. Proton nuclear magnetic resonance shift vs. moles of NaBPh₄ in 3-methyl-2-oxazolidone: (Δ) 4-methylene protons, (○) 5-methylene protons, (□) R-methyl protons.

in the far-infrared spectra. Each salt solution produces its own characteristic shift. Since this is the case, it would appear that both ions are interacting with solvent molecules. The differences in peak location are due to the electron density around the protons. When a cation interacts with a solvent, it withdraws electron density from the proton causing a downfield shift as the proton is deshielded. The anion would be expected to produce the opposite effect. In most salts the cation is strongly solvated with the anion having a secondary effect. In the tetraphenylborate salt solutions it is possible the anion is appreciably solvated. It has been stated that for aqueous solutions when both cation and anion are solvated the anion has a larger effect on the pmr spectrum.¹⁹ This seems plausible for the tetraphenylborate salts.

Sodium-23 Nuclear Magnetic Resonance Spectra.

Table III gives the results for sodium-23 nuclear magnetic resonance spectra. No bulk diamagnetic susceptibility corrections were made so the shift data differ from the true values by about 1 ppm. The results are similar to those reported by Popov and coworkers.^{20-22,40} In their studies it was found that for a large number of solvents the sodium-23 nmr shift is concentration independent for NaBPh₄ and NaClO₄ indicating solvent-separated ion pairs or dissociated ions while NaSCN and NaI peaks are concentration dependent. These results were identical with those found in this study with the four oxazolidones. The concentration dependence of NaSCN and NaI has been interpreted as due to the anion entering the inner solvation sphere of the cation.^{21-23,40}

Correlation of Spectral Data. The far-infrared data for salt solutions in liquid-2-oxazolidones are similar to those found by other workers in a variety of solvents.²⁻⁷ As indicated by Edgell and coworkers,^{3a} there must be structure at the cation. The theory advocated is that the cation vibrates in a cage composed of solvent molecules and anions. For such a structure the vibrational frequency would be anion dependent. If the frequency is anion independent, then only solvent molecules make up the cage. This appears to be the most important one in the liquid 2-oxazolidones although we cannot conclude that the anion is absent from the immediate vicinity of the cation at all times as the maximum lifetimes for such structures are estimated as

(40) M. S. Greenberg, R. L. Bodner, and A. I. Popov, *J. Phys. Chem.*, **77**, 2449 (1973).

Table III. Sodium-23 Nuclear Magnetic Resonance Shift with Change in Concentration for 3-Substituted Liquid 2-Oxazolidones

Salt	Concn, <i>M</i>	Δ , ppm
3-Methyl-2-oxazolidone		
NaBPh ₄	0.25	12.76
NaBPh ₄	0.50	11.40
NaBPh ₄	1.00	12.55
NaClO ₄	0.25	15.00
NaClO ₄	0.50	15.27
NaClO ₄	1.00	15.53
NaI	0.25	15.00
NaI	0.50	12.38
NaI	1.00	9.12
NaSCN	0.25	11.24
NaSCN	0.50	10.45
NaSCN	1.00	8.11
3-Ethyl-2-oxazolidone		
NaBPh ₄	0.25	13.00
NaBPh ₄	0.50	12.37
NaBPh ₄	1.00	12.62
NaClO ₄	0.25	12.73
NaClO ₄	0.50	12.84
NaClO ₄	1.00	12.97
NaI	0.188	11.94
NaI	0.375	8.18
NaI	0.750	6.67
NaSCN	0.25	10.49
NaSCN	0.50	9.79
NaSCN	1.00	5.05
3-Isopropyl-2-oxazolidone		
NaBPh ₄	0.188	12.75
NaBPh ₄	0.375	12.95
NaBPh ₄	0.750	12.66
NaClO ₄	0.25	10.15
NaClO ₄	0.50	10.66
NaClO ₄	1.00	10.11
NaSCN	0.33	6.45
NaSCN	0.67	0.50
NaSCN	1.00	-1.89
3- <i>tert</i> -Butyl-2-oxazolidone		
NaBPh ₄	0.188	11.69
NaBPh ₄	0.375	11.46
NaBPh ₄	0.750	11.05
NaClO ₄	0.188	11.55
NaClO ₄	0.375	11.49
NaClO ₄	0.750	11.22
NaSCN	0.25	11.29
NaSCN	0.50	4.41
NaSCN	1.00	3.57
NaI	0.188	9.34
NaI	0.375	5.44
NaI	0.750	1.36

10^{-7} sec.^{3a,41} The infrared studies reinforce the far-infrared studies at least for this NH₄⁺ cation.

The pmr studies support an interaction by the tetraphenylborate anion with the solvent molecule by giving a large positive peak shift. This would be indicative of increased electron density around the solvent

(41) M. Eigen, "Coordination Chemistry: Seventh International Conference," Butterworths, London, 1963.

protons which would be expected from an anionic interaction. All other salts produce negative shifts showing that the cation is more strongly solvated. The anions do interact with the solvent molecules because the shifts observed are not independent of anion as was observed for the band frequencies in the far-infrared studies. The linearity of these peak shifts *vs.* concentration plots shows that the solvent molecules are not shared with more than one ionic species in the regions studied. This rules out the possible formation of polymeric ion aggregates.

The sodium-23 nmr shows that iodide and thiocyanate anions influence the immediate environment of the cation since a peak shift with concentration is observed. Popov and coworkers have noted similar effects in other solvents.⁴⁰ These data probably reflect a greater sensitivity to the immediate environment of the cation than do the far-infrared measurements (as indicated earlier no shifts in the far-ir band positions were observed for sodium salt solutions; also the far-ir bands are quite broad and a shift of 3 or 4 cm⁻¹, as might be expected, would be virtually undetectable within experimental error). The nmr experimental data reflect an "averaged" situation with respect to the cation environment since the time scale is much slower than for vibrational spectroscopy where the lifetime of the proposed "cage" structure is $\leq 10^{-7}$ sec.^{3a,41}

The tetraphenylborate anion has shown unusual solvation behavior by pmr studies. The cations also interact with the solvent molecules as shown by far-infrared studies. There is no effect seen between this anion and various cations by sodium-23 nmr. Salts of this anion are probably completely dissociated or form solvent-separated ion pairs with both cation and anion solvating independently with the solvent molecules.

The perchlorate anion shows no effect on the sodium-23 resonance. The infrared data indicate no interaction between the anion and the solvent as occurs for the tetraphenylborate anion. The cations from perchlorate salts solvate as is seen from the far-infrared studies. The pmr shows a less negative shift than for any other salt solutions except for the tetraphenylborates which are positive. It is possible that the perchlorate anion either solvates very weakly as a dissociated ion or forms solvent-separated ion pairs with the cations of the perchlorate salts.

Supplementary Material Available. Additional tabulated data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-6033.