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AN INVESTIGATION OF THE DIGITIZED RAMAN BAND PROFILES OF AQUEOUS $\text{Mg}(\text{ClO}_4)_2$ - NaSCN SOLUTIONS

Key words: Raman Spectra, Factor Analysis, Magnesium thiocyanate complexes

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ABSTRACT

Raman spectra, together with factor analysis and band deconvolution procedure, have been used to study formation of magnesium thiocyanate complexes in aqueous solutions at ambient and elevated temperatures. The total salt concentration in solutions, containing different mole ratio of Mg^{2+} to SCN^- , varied between 3.4 and 7.5 mol dm^{-3} . Factor analyses indicated that two linearly independent scattering components in the band envelopes, recorded in the ν_1 and ν_3 stretching regions of SCN^- , for all solutions with total salt concentration of 3.4 mol dm^{-3} . The appearance of a pseudo-isosbestic point in the area normalized spectra supported this result, as well as the band resolution procedure. The latter revealed the third scattering component in the spectra of solutions with total salt concentration above 3.5 mol dm^{-3} . Resolved components have been assigned to the free thiocyanate, the 1:1 and 1:2 magnesium thiocyanate complexes. The equilibrium constant K_C of the 1:1 complex is of an order of $10^{-1} \text{mol dm}^{-3}$.

INTRODUCTION

Factor analysis (FA) is a method of multivariate analysis which has found wide application in several research fields^{1,2}. It is a useful statistical method of extracting information on spectral overlapping³⁻⁶. By application of the method to the analysis of overlapped Raman spectra, each spectrum based on the individually scattering components can be obtained. The method has been used in an investigation of a variety of equilibria involving free and complexed molecules⁷⁻⁹.

In this work, FA is used together with Raman band contour resolution in the study of the number of independently variable components which contribute to the band envelopes arising from the ν_1 and ν_3 stretching vibration of SCN^- ion in aqueous solutions of the mixture of $\text{Mg}(\text{ClO}_4)_2$ - NaSCN .

The work is an extension of our previous Raman spectral study of the ionic interactions in this system¹⁰ with the aim to extract more information. Particular attention was paid to the scope of FA as an unbiased method for determination of number species in solutions and their stability constants.

EXPERIMENTAL

Preparation of solutions. The reagents used were all analytical grade chemicals and were used without further purification.

For measurements at ambient temperature, the solutions were prepared with different $\text{Mg}^{2+}/\text{NCS}$ mole ratios, R , ranging from 0.1 to 9. The total salt concentration of 3.4 mol dm^{-3} was kept constant in all solutions. This concentration was selected previously¹⁰ as the most convenient because the spectral changes were too small to be quantitatively measured when the total molarity was below 3 mol dm^{-3} . However, the preparation of more concentrated solutions was limited by the solubility of the salts.

The measurements at 98°C were carried out on solutions prepared in accordance with molar-ratio method¹¹ having constant Mg^{2+} concentration of 2.5 mol dm^{-3} . These solutions were prepared as described earlier¹⁰.

Raman spectra measurements. Raman spectra were recorded between 700 and 850 cm^{-1} , and between 2000 and 2150 cm^{-1} using a SPEX Model 1401 spectrometer interfaced to Apple IIe Computer. Spectra were excited by Spectra Physics Model 1401 Argon ion laser 514.5 nm line of an effective power of approximately 500 mW at the sample. Band positions were estimated to be accurate within $\pm 1 \text{ cm}^{-1}$.

A data set of 150 wavenumber points of each spectrum from 700 to 850 cm^{-1} and from 2000 to 2150 cm^{-1} , with an interval of 1 cm^{-1} was used for analysis.

METHOD OF DATA ANALYSIS

Factor analysis. As mentioned above, FA is a powerful technique for the analysis of overlapped spectra. It provides the number of scattering individual components (NC) for a series of spectra by an independent method. Rather than assuming a band shape, FA is based upon standard theorems of linear algebra. When a set of constitutive properties is measured for each of a series of solutions, FA is applicable to solve NC⁶.

When the method is used for analysis of a complex Raman spectra, the number of scattering components is given by the rank of an intensity matrix I . The I is a product of a number of wavenumbers digitized (NW) and the number of solutions of varying composition (NS)^{1,2}.

The method of finding the rank of I is to examine the eigenvalues and eigenvectors of the second moment matrix¹² $Q = I^T I$, where I^T is transpose of I , and the matrix Q has the rank as I . It can be shown that the number of statistically non-zero eigenvalues (m) of Q equals the rank of I , which is NC. Owing to experimental and computational error, all eigenvalues have finite values and several statistical criteria¹³⁻¹⁶ have been described to determine the value of NC.

Band resolution. Deconvolution of recorded band envelopes in their components is performed using program described elsewhere¹⁷.

RESULTS

Spectral features. Raman spectra of solutions have been recorded in two frequency regions: 700-850 cm^{-1} and 2000-2150 cm^{-1} . The band envelopes in the former region arise from the C=S (ν_3) vibration of SCN^- ion and those in the last region from the C \equiv N (ν_1) vibration.

Figure 1 illustrates the effect of the added Mg^{2+} ions on the both bands of free SCN^- recorded at ambient temperature. For clarity, only several spectra, as an example, are shown. It can be seen that the weak shoulders, appearing on the high frequency side of free thiocyanate bands at 747 cm^{-1} and 2068 cm^{-1} , develop into distinguishable bands at ca. 785 cm^{-1} and 2110 cm^{-1} with increasing R. Concurrently, the intensity of the original of free NCS^- ν_1 and ν_3 bands at 747 cm^{-1} and 2068 cm^{-1} , respectively, decreased. The new features changed in intensity with variation of R, but they remained at the same wavenumber positions within experimental precision. This fact supported formation of the nitrogen bonded species existing in different amounts in the investigated mixtures.

The same effect was observed in the spectra of solutions recorded at 98°C.

FA and band resolution technique have been used to determine the number of independent scattering species

Factor analysis. FA has been applied to ten spectra measured at ambient temperature. Due to limited solubility of the salts we have been not able to prepare all necessary molar-ratio solutions at elevated temperature for successful application of FA. The spectra of these solutions have been studied using band resolution technique.

In applying FA, we have used three statistical tests for determining NC or real factors: the imbedded error (IE)^{2,13}, the indicator function (IND)^{2,13}, and the residual standard deviation (RSD)^{14,15}. When the value of m is equivalent to NC, IE and IND

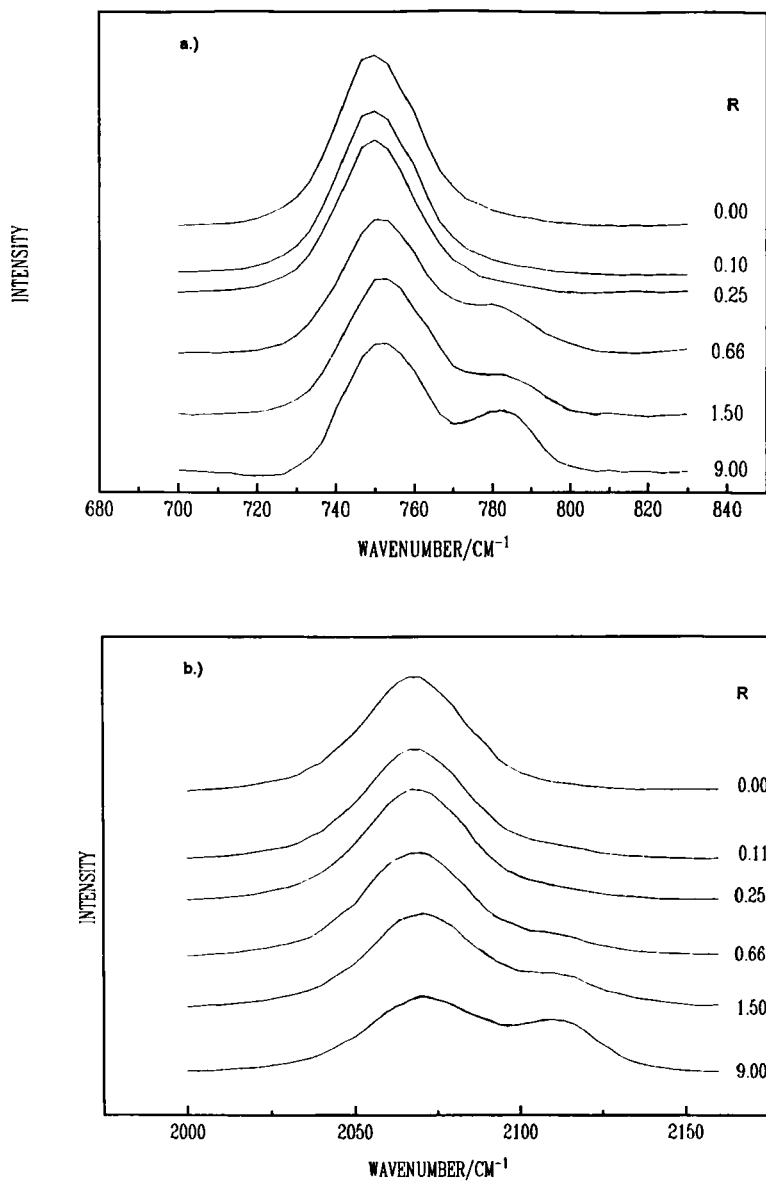


Fig. 1. Experimental Raman spectra of several solutions with the specified values of R in the region of ν_3 (a) and ν_1 (b) vibrations of SCN^- ion

have their minimum values, while RSD show no significant change after all real factors are included in calculation. The last criterion indicates that only eigenvalues greater than their standard errors can be considered as real factors.

The results of the FA of C=S and C≡N band envelopes of the Raman spectra of investigated solutions are summarized in Tables 1 and 2.

It is evident from both Tables that only first two eigenvalues are greater than their standard errors, suggesting $NC = 2$. The IE falls by a factor of ≈ 2 (Table 1) and by a factor of ≈ 4 (Table 2) between $m = 1$ and $m = 2$ and then levels off as well as RSD. In the same time IND shows a slight minimum at $m = 2$.

Thus, the FA indicates that two scattering components contribute to the C=S and C≡N stretching band envelopes in the Raman spectra. The existence of only two species was supported by appearance of pseudo-isosbestic points at 2083 and 762 cm^{-1} (Fig. 2a and 2b) which show normalized spectra of solutions to the same area (free SCN^- band).

Band resolution. The band envelopes obtained in the spectra of all solutions with various R ranging from 2.0 to 0.3 recorded at 98°C, have been resolved into three components. Figure 3 shows resolved spectra in C-N stretching regions for solutions with the highest (b) and the lowest R (a). The resolved bands at 2068 cm^{-1} , 2087 cm^{-1} and 2108.5 cm^{-1} are attributed to free SCN^- , the 1:1 and 1:2 complexes, respectively.

Stability constant calculation. The equilibrium constant of $[\text{Mg}(\text{SCN})]^+$ complex formation is found by using target factor analysis method². The essential problem in quantitative factor analysis is how to get physically meaningful eigenvectors. The eigenvectors obtained by decomposition of Q matrix, which are supposed to represent component bands and concentration distribution of components in solutions, have profiles differing significantly from real component band contours. Matrices formed from these eigenvectors must be rotated to get their physically real profiles. Results of appropriate rotation are band profiles that are very close to component bands and their intensities give distribution of species in solutions. Target factor analysis is a method in which it is necessary to know band profile of investigated component. This band serves as 'target' in which eigenvector matrix should be rotated by least squares

Table 1: Factor analysis results of the $\text{C}=\text{S}$ band envelopes

m	eigenvalue	error of eiv.	IE·10	RSD·10	IND·100
1	11220.07	25.5234	3.829	11.489	1.7952
2	393.77	24.7308	1.507	3.197	0.6524
3	18.54	24.4506	1.183	2.049	0.5692
4	4.38	25.8140	1.125	1.688	0.6752
5	2.85	25.0438	0.994	1.333	0.8337
6	2.52	24.5674	0.915	1.120	1.2452

Table 2: Factor analysis results of the $\text{C}\equiv\text{N}$ band envelopes

m	eigenvalue	error of eiv.	IE·10	RSD·10	IND·100
1	33371.77	59.3346	4.113	13.007	1.6058
2	728.16	57.0983	0.955	2.136	0.3337
3	8.63	59.4793	0.899	1.643	0.3352
4	4.82	57.8929	0.777	1.223	0.3412
5	3.76	58.0155	0.755	1.068	0.4217
6	3.55	57.9086	0.733	0.947	0.5918

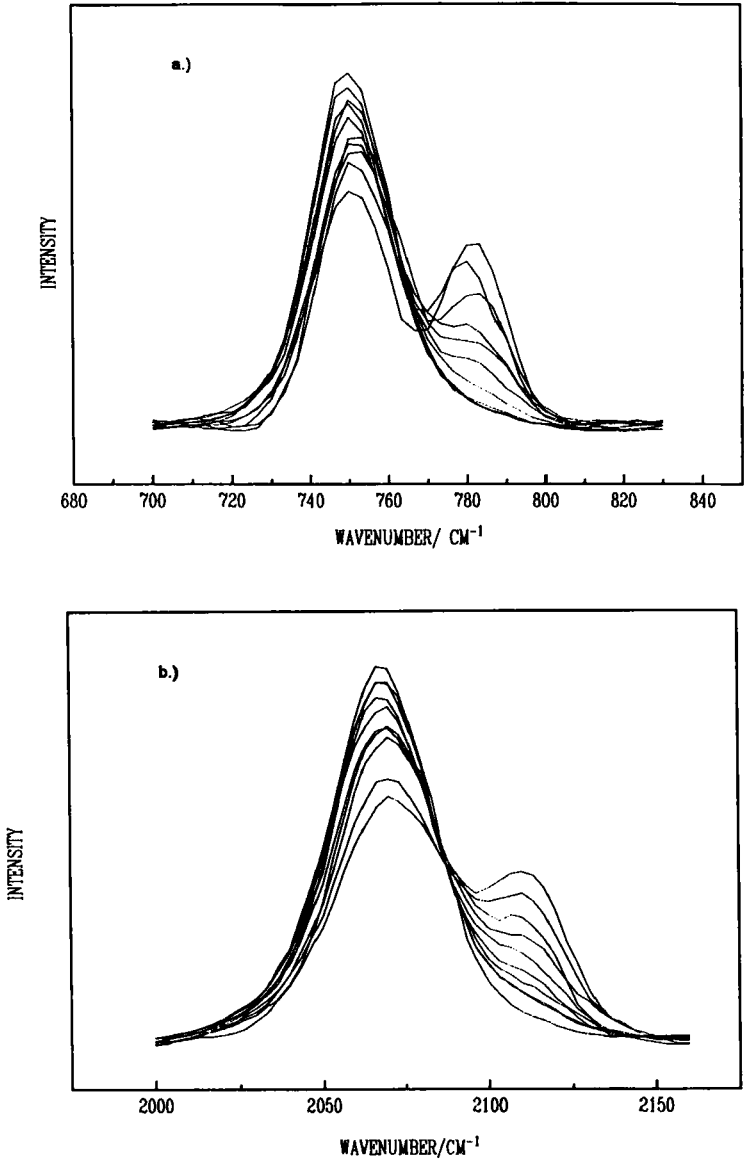


Fig. 2. Normalized Raman spectra of ten solutions in region of ν_3 (a) and ν_1 (b) vibration of SCN^- ion

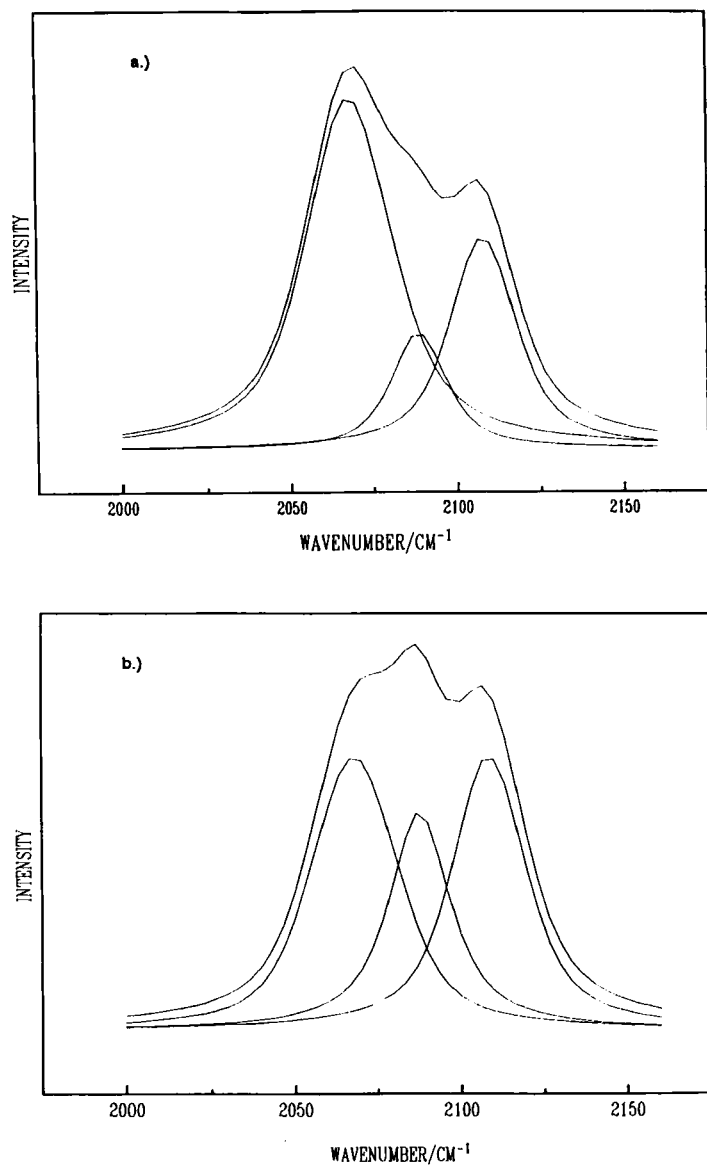


Fig. 3. Resolved ν_1 band envelopes of solutions with $R = 2$ (a) and $R = 0.5$ (b)

procedure. Here, the bands of free SCN^- were 'targets' in both ν_1 and ν_3 spectral region respectively. The complex bands on 2109 cm^{-1} and 785 cm^{-1} were used as 'targets' too. Since bands of free SCN^- ion dominate in all recorded spectra, data obtained from their analyses are more reliable than data obtained from analyses of complex bands and they are used in calculation of equilibrium constant

$$K = \frac{C_{[\text{Mg}(\text{SCN})]^+}}{C_{\text{Mg}^{2+}} C_{\text{SCN}^-}}$$

The equilibrium concentration of complex $[\text{Mg}(\text{SCN})]^+$ is obtained as difference of total concentration and that of free SCN^- ion, while the equilibrium Mg^{2+} concentration is found from the relation

$$C_{\text{Mg}^{2+}} = C_{\text{totalMg}^{2+}} - C_{[\text{Mg}(\text{SCN})]^+}$$

The equilibrium constant calculated by the above expressions is found to be $0.150\text{ dm}^3\text{ mol}^{-1}$ for solutions with $R > 1$. For solutions in which R is less than one, it is not possible to calculate concentration of bound SCN^- and for these solutions the equilibrium constant are not calculated.

DISCUSSION

In the present study, FA indicates that two independent species exist in solutions with R range of 0.1 - 9 and total salts concentration of 3.5 mol dm^{-3} . This conclusion was supported by the observation of pseudo-isosbestic point (Fig. 2a and Fig. 2b) in the area of normalized spectra.

Resolved spectra recorded at 98°C revealed two new bands in addition to the free SCN^- ion bands, which are attributed to the 1:1 and 1:2 complex.

The results of both procedures are consistent with those obtained previously¹⁰. They can be explained in terms of stepwise substitution in coordination sphere of magnesium.

The magnesium (II) cation is aquated by six molecules of water in the presence of noncoordinated anions, such as perchlorate and nitrate¹⁷⁻²⁰. On addition of

thiocyanate ion the hexaaquomagnesium (II) cation undergoes successive substitution to give complexes of the type $[\text{Mg}(\text{H}_2\text{O})_{6-n}\text{NCS}]^{(2-n)+}$.

It appears from the results obtained from both procedures that the SCN^- ion is the preferred ligand in competition with the water molecule in ligand exchange process over the whole concentration range. Since the replacement of one water molecule by NCS^- in the first hexahydrated sheath of Mg^{2+} ²¹⁻²³ is statistically more probable event in less concentration solution than the replacement of two or more, the formation of 1:1 complex species is dominant. The next NCS^- ion enters the first coordination sphere of Mg^{2+} only when water to total salt concentration drops below certain levels. It is shown that if total salt concentration is above 3.5 mol dm^{-3} .

On the basis of the magnitude of equilibrium constant K_c , which is of an order of $10^{-1} \text{ dm}^3/\text{mol}$, it can be concluded that 1:1 complex species formed between magnesium and thiocyanate ions in aqueous solutions is relatively weak complex.

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REFERENCES

1. H. H. Harman, *Modern Factor Analysis*, University of Chicago Press, Chicago (1967)
2. E. R. Malinowski, *Factor Analysis in Chemistry*, Wiley, New York (1991)
3. J. T. Bulmer, Ph D Thesis, Queen's University, Kingston, Canada 1973
4. J. T. Bulmer and H. F. Shurvell, *J. Phys. Chem.* 1973; 77, 256
5. J. T. Bulmer and H. F. Shurvell, *J. Phys. Chem.* 1973; 77, 2085
6. J. T. Bulmer and H. F. Shurvell, in *Vibrational Spectra and Structure*, ed. by J. R. Durig, Vol. 6, Chap. 2 pp 91-172
7. T. Ozeki, H. Kihara and S. Hikime, *Bunseki Kagaku* 1986; 35, 885
8. T. Ozeki, H. Kihara and S. Hikime, *Anal. Chem.*, 1987;59, 945

9. T. Ozeki, H. Kihara, S. Hikime and S. Ikeda, *Anal. Sci.*, 1987; **59**, 945
10. A. Antić - Jovanović, M. Jeremić, M. Lalić and D. A. Long *J. Raman Spectrosc.* 1989; **20**, 253
11. T. Beck, *Chemistry of Complex Equilibria*, p.86, Van Nostrand, London, 1970
12. E. R. Malinowski, *Anal. Chem.*, 1977; **49**, 606
13. E. R. Malinowski, *Anal. Chem.*, 1977; **49**, 612
14. J. J. Kankare, *Anal. Chem.*, 1970; **42**, 1322
15. Z. Z. Hugus and A. A. El-Awady, *J. Phys. Chem.*, 1971; **76**, 2954
16. S. Alex and R. Savole, *Can. J. Spectrosc.*, 1989; **34**, 27
17. I. A. Slavić and S. Šašić, *Spectrosc. Lett.*, 1995; **28**, 783
18. A. Fratiello, R. E. Lee, N. M. Nishida and R. E. Schuster, *J. Chem. Phys.* 1971; **76**, 2954
19. T. H. Cannon and R. E. Richards, *Trans. Faraday Soc.*, 1966; **62**, 1378
20. A. Fratiello, D. D. Davis, S. Peak and R. R. Schuster, *Inorg. Chem.*, 1971; **10**, 1627
21. D. P. Strommen and R. A. Plane, *J. Chem. Phys.* 1965; **60**, 2643
22. R. L. Frost, D. W. James, R. Appleby and R. E. Mayers, *J. Phys. Chem.*, 1982; **86**, 3840
23. A. G. Miller and J. W. Macklin, *J. Phys. Chem.*, 1982; **89**, 1193

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