Determination of Complex Species by the Method of Continuous Variation Using Infrared Spectroscopy

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The method of continuous variations has been widely used to determine the composition of complex species using such intensive properties of the systems as visible and ultraviolet absorption[1,2] and conductivity.[3] Few studies, however, have used infrared absorption as a basis for this method, apart from those studies where hydrogen bonded systems arise,[4] in which case large shifts are usually found.

In the case of lanthanide salts-TBP(tributyl phosphate) systems, the stoichiometry of the solvates formed have thus far been determined only by liquid-liquid partition methods and solubility methods.[5,6]

Since the organic diluents employed in the above studies dissolve the lanthanide thiocyanates only sparingly or not at all, the method of continuous variations could not be employed. However, such diluents as acetonitrile appear to be compatible with the use of the continuous variation method, provided that an absorption change due to complex formation takes place.

This paper will report the results obtained by the method of continuous variations from an infrared spectroscopic study of the $Ln(SCN)_3$-TBP and -TPPO(triphenyl phosphine oxide) systems using acetonitrile as the diluent.

Experimental

The lanthanide thiocyanates were prepared by dissolving the appropriate oxides in warm, freshly prepared hydrogen thiocyanate and the free water was removed by vacuum evaporation. The TBP was purified by the method of Alcock *et al.*[7] The acetonitrile was purified by distilling it several times from P_2O_5. The TPPO was prepared by the Grignard reaction between phenylmagnesium bromide and phosphorous oxychloride. The resulting product was recrystallized several times from a mixture of ethanol and water. The infrared spectroscopic data were recorded as previously described. Procedure: 0.1 M (0.02 M) of TBP (TPPO) and equimolar lanthanide thiocyanate solutions were equilibrated in varying proportions according to the expression:

$$x = \frac{[\mathrm{Ln}]}{[\mathrm{Ln}] + [\mathrm{TBP(TPPO)}]}$$

Thus, the total concentration was kept at 0.1 M (0.02 M). It was assumed that no appreciable volume change took place on the equilibration.

Results and Discussion

The effect on the infrared spectra of representative lanthanide thiocyanate-TBP(TPPO)-acetonitrile solutions by varying the x parameter is shown in Fig. 1.

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[1] P. Job, *Ann. Chem. Phys.*, **9**, 113 (1928).

[2] W. C. Vosburgh and G. R. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941).

[3] R. Longhi and R. S. Drago, *Inorg. Chem.*, **2**, 85 (1963).

[4] R. A. Zingaro and C. F. Coleman, *J. Inorg. Nucl. Chem.*, **29**, 1287 (1967).

[5] T. Healy and H. A. Mckay, *Trans. Faraday Soc.*, **52**, 633 (1955).

[6] T. Sekine, This Bulletin, **38**, 1972 (1963).

[7] K. Alcock, S. S. Grmley, T. V. Healy, J. Kenedy and H. A. McKay, *Trans. Faraday Soc.*, **52**, 39 (1956).

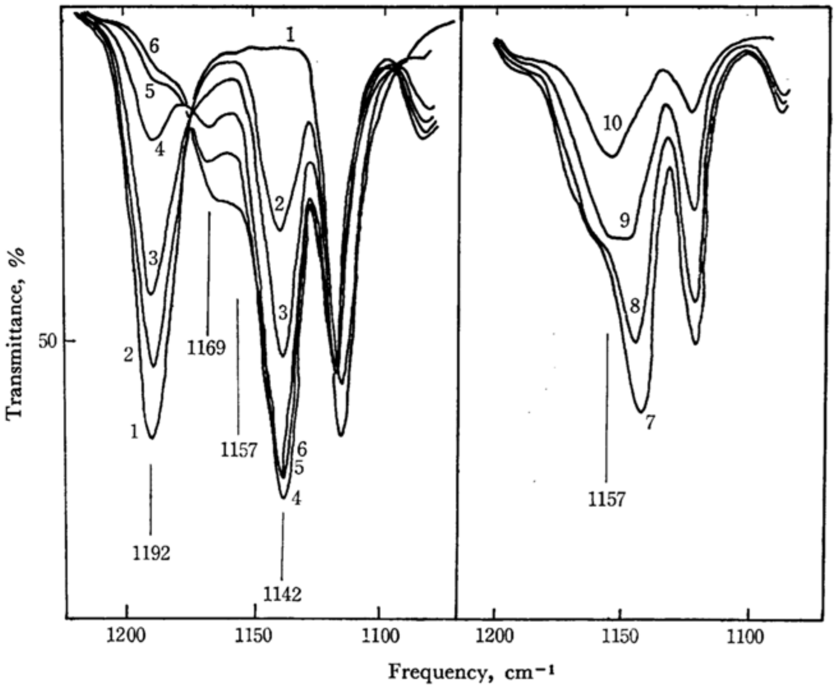

Fig. 1(a). $Er(SCN)_3$-TPPO-CH_3CN

	x
1	0.00
2	0.05
3	0.10
4	0.20
5	0.25
6	0.30
7	0.40
8	0.50
9	0.70
10	0.90

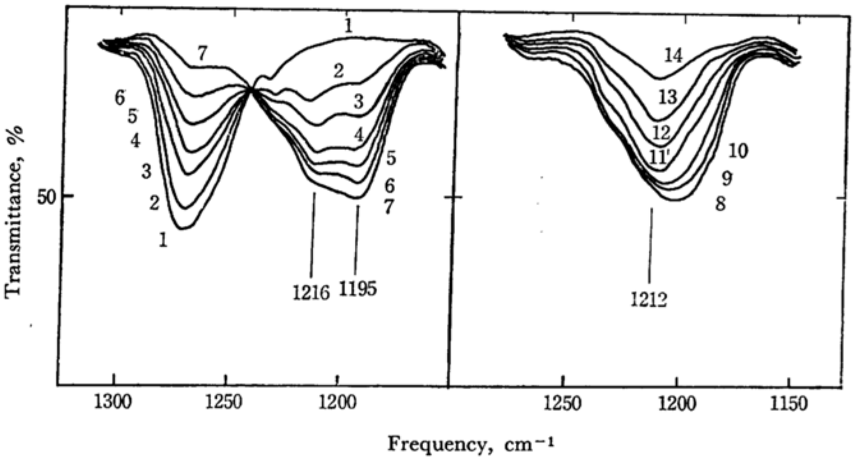

Fig. 1(b). $Dy(SCN)_3$-TBP-CH_3CN

	x
1	0.00
2	0.05
3	0.10
4	0.15
5	0.20
6	0.25
7	0.30
8	0.35
9	0.40
10	0.50
11	0.60
12	0.70
13	0.80
14	0.90

Fig. 1. Infrared spectra of acetonitrile solutions of $Er(SCN)_3$-TPPO and $Dy(SCN)_3$-TBP in the various proportions.

In the erbium thiocyanate-TPPO-acetonitrile system, as x increased, the free TPPO absorption band at 1192 cm^{-1} became increasingly weaker, while new absorption bands, which appeared at lower frequencies, became increasingly stronger. The examination of these new bands suggested that at least three species were present, represented by the absorption bands at 1142 cm^{-1}, 1157 cm^{-1} and 1169 cm^{-1}. A continuous variation analysis of these bands, shown in Fig. 2, indicates that the band at 1142 cm^{-1} represents the tri-solvated species, while the bands at 1157 cm^{-1} and 1169 cm^{-1} may be assigned to the mono- and di-solvated species respectively. The same assignment was found to be applicable for the yttrium and dysprosium systems as well.

In the case of the lighter lanthanide thiocyanate-TPPO complexes (*i.e.*, La and Ce), no distinct absorption bands could be distinguished, indicating that with them complex formation did not occur in distinct steps. For the lighter lanthanide thiocyanates, therefore, the strongest absorption, that at 1140 cm^{-1}, may be attributed to a tri- or tetra-solvated species.

As for the dysprosium thiocyanate-TBP-acetonitrile system, Fig. 1(b) will show that two distinct absorption bands appeared, one at 1216 cm^{-1} and the other at 1195 cm^{-1}, under the experimental conditions of $0.05 \leqq x \leqq 0.15$. This result indicates the coexistence of two species, with the species absorbing at 1216 cm^{-1} predominantly. Under the conditions of $0.20 \leqq x \leqq 0.35$, the band at 1195 cm^{-1} became increasingly stronger, and when $x \geqq 4$, an absorption band appeared at 1212 cm^{-1} and increased in intensity as x increased. Thus, the results demonstrate the formation of at least three species, whose solvation number increases with respect to the observed absorption wavelength in the order: 1216 cm^{-1} > 1195 cm^{-1} > 1212 cm^{-1}.

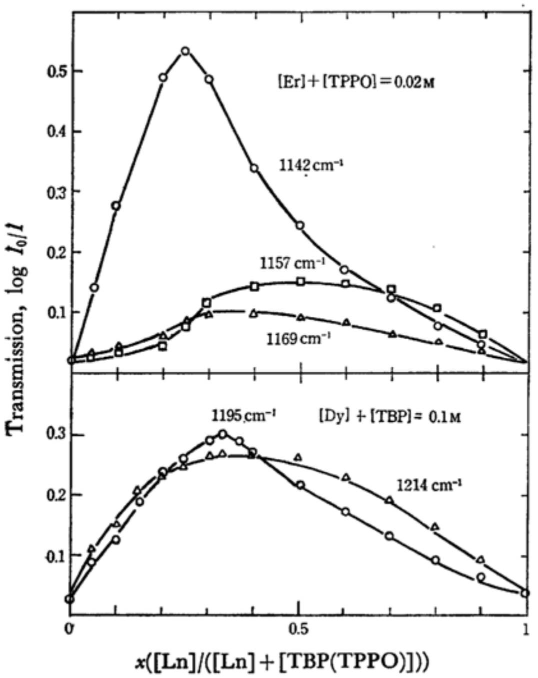

Fig. 2. Continuous variations for acetonitrile solutions of Er(SCN)$_3$-TPPO and Dy(SCN)$_3$-TBP.

A continuous variation analysis in this spectral region is shown in Fig. 2. An examination of Fig. 2 will show that the band at 1195 cm^{-1} may be assigned to the di-solvated species. The band at 1216 cm^{-1} and 1212 cm^{-1} overlap, which makes resolution very difficult. However, in view of the experimental conditions under which these two bands appeared, it is reasonable to assign the band at 1216 cm^{-1} to the tri- or tetra-solvated species, and the band at 1212 cm^{-1} to the mono-solvated species.

This study has revealed many difficulties in connection with the use of infrared spectroscopy on such systems. These difficulties may be listed as below:
1) The absorption shift due to complex formation is small.

2) Because of the strong absorption of the diluents the absorption frequency range for the detection of complex formation and the concentration range available are severely restricted.

3) The NaCl and KCl cells tend to dissolve slightly in polar diluents, and trace amounts of water cause frosting of the optical surface of the cell.

In spite of the above difficulties, however, infrared spectroscopy can be used for the determination of complex species provided that, with the above qualifications in mind, a suitable choice is made of the diluent, the material of construction of the cell, and the range of absorption frequency used for detection.

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