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THE COEXTRACTION OF WATER WITH ALKALI AND ALKALINE EARTH METALS HEXANITRODIPHENYLAMINATES AND ANALOGOUS AMINATES

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Alkali and alkaline earth metal salts of hexyl (2,4,6,-2',4',6'-Hexanitrodiphenylamine), α-hexyl (N-(2,4,6-trinitrobenzo)-2,4-dinitro-1-naphthylamine), and thiohexyl (1,3,7,9-Tetranitrophenothiazine-5-oxide) were extracted into nitrobenzene. The water in the nitrobenzene solution was determined by means of the Karl-Fischer method. It was found that the water content in the extract was greater than that in nitrobenzene which did not contain these salts. The behavior of water in nitrobenzene phase was discussed on the basis of absorption spectra in near infrared region and of proton magnetic resonance spectra.

Recently the interest in the coextraction of water into solvents along with ion pairs is increasing.[1-5] In a previous paper,[6] it has been reported that water is coextracted into nitrobenzene with alkali metal hexylates. In the present paper, the coextraction of water with some other polynitrocompounds analogous to hexyl will be discussed. The coextraction of water can be considered to be caused by the hydration of cations. Optical and NMR absorption spectra confirm the occurrence of hydration.

1) Experimental. Chemicals of reagent-grade were used throughout. Thiohexyl was prepared by the nitration of phenothiazine[7,8] and α-hexyl, by the nitration of the condensation product of picrylchloride with 1-naphthylamine.[9] Nitrobenzene was washed with a sodium hydroxide solution, then with water, and subsequently distilled under reduced pressure.

Extraction procedures were as follows: Into a 50-ml separatory funnel, 10 ml of an aqueous solution of hydroxide or carbonate of alkali and alkaline earth metals (about 0.1 M) were transferred. The pH of the solutions was kept at above 12. Then, 10 ml of a nitrobenzene solution containing polynitrocompounds ($2 \times 10^{-3} - 10^{-2}$M) were added. The resultant mixture of the aqueous and the nitrobenzene solutions was shaken moderately for an hour at 25°C.

The concentration of the alkali and alkaline earth metals in the nitrobenzene solution was determined spectrophotometrically, assuming that a stoichiometric relationship will hold between the cations and the anions of the polynitrocompounds.

The concentration of water in the organic extracts was determined by means of the Karl-Fischer method.

2) Results and Discussion. Nitrobenzene dissolves about 0.17 M water at 25°C, while the extracts dissolve a slightly greater quantity of water. The water-increment is plotted against the concentration of the alkali and alkaline earth metals in the organic extract, as is shown typically in Fig. 1. From the slopes of these lines the quantity of the coextracted water is calculated. The values obtained are listed in Table 1. These values were reproducible to about ± 2 percent on repeated runs. The reproducibility was invariably poor for the salts of heavy alkali metals. With thiohexyl it was difficult to find the water-increment, because the distribution ratio of the salts was very small.

Table 1 shows that cations have great effect on the quantity of water coextracted. The quantity increases linearly with the ratio of the charge to the ionic radii of the cations, $z^2/r_{cryst.}$, except in the case of the heavy alkali metals. The table also shows that, contrary to the case of cations, anions used virtually have little effect on the coextraction of water. In general, the bulky univalent anions can be believed not to be hydrated in a solution. Therefore, the values of the table can be replaced by the hydration number of the cations in the nitrobenzene phase. The hydration numbers in an aqueous solution of the chlorides of alkali and alkaline earth metals obtained by the method of activity measurements[10] are similar to the values listed in Table 1.

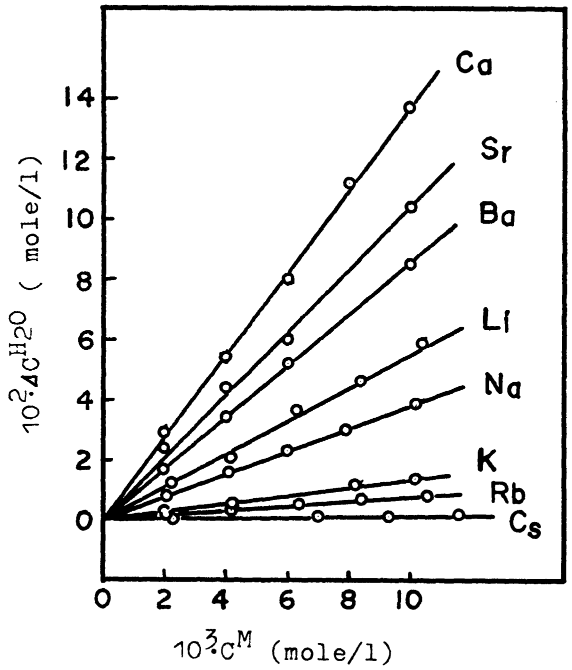

Fig. 1. Coextraction of water wit α-hexylates of alkali and alkaline earth metals

Table 1. COEXTRACTED WATER
(numbers of water molecules/ion)

	Cs^+	Rb^+	K^+	Na^+	Li^+	Ba^{2+}	Sr^{2+}	Ca^{2+}
$z^2/r_{cryst.}$	0.59	0.66	0.75	1.03	1.47	2.94	3.58	4.04
hexyl	0.7[6]	0.7[6]	1.3[6]	3.5[6]	5.5[6]	9.4	12.1	13.3
α-hexyl	0.1	0.8	1.4	3.8	5.5	8.6	10.4	13.8
thiohexyl	-	-	-	2	5	13	14	13

These findings suggest that the cations form ion pairs of outer sphere complex with the anions and carry water into the nitrobenzene phase without being stripped of their hydrated water when they pass through the interface.

Water absorbs light at about 1900 and 1400 nm, the molar extinction coefficient being about 3 and 0.5 respectively. Calcium hexylate anhydride (CaR_2)

was dissolved into dry nitrobenzene to give a 1 x 10^{-2}M water-free nitrobenzene solution. To the solution small portions of water were added and the spectra at 1900 nm were observed (Fig. 2). Up to a water concentration of about 0.1 - 0.13 M, which corresponds to the hydration numbers 10 - 13, the location of the peak shifts slightly toward a shorter wavelength, accompanying the increase in the peak height as the water concentration increases. When the water concentration exceeds 0.13 M, an increase in the peak height alone is observed. The gradual shift of the absorption spectra suggests that the chemical species in the solution changes gradually; that is, the hydration number of calcium may increase with the water concentration. The solution prepared by dissolving calcium hexylate ($CaR_2 10H_2O$) into dry nitrobenzene gives a spectrum identical with that obtained for the solution containing the same quantity of water prepared by the procedures mentioned above. This fact also supports the view that the spectral shifts may be ascribed to the selective hydration of water added.

NMR studies may also give valuable information concerning the behavior of water in a nitrobenzene solution. The NMR spectra of calcium hexylate solutions were also obtained with the same solutions employed for the measurements of the absorption spectra (Fig. 2). The peaks due to water appear in the ppm 3.31 - 4.41 region. The location of the peak shifts toward a higher field as the water concentration increases. This fact may be explained by assuming a coulombic interaction between the water molecules and calcium cations. The tendency can be shown approximately

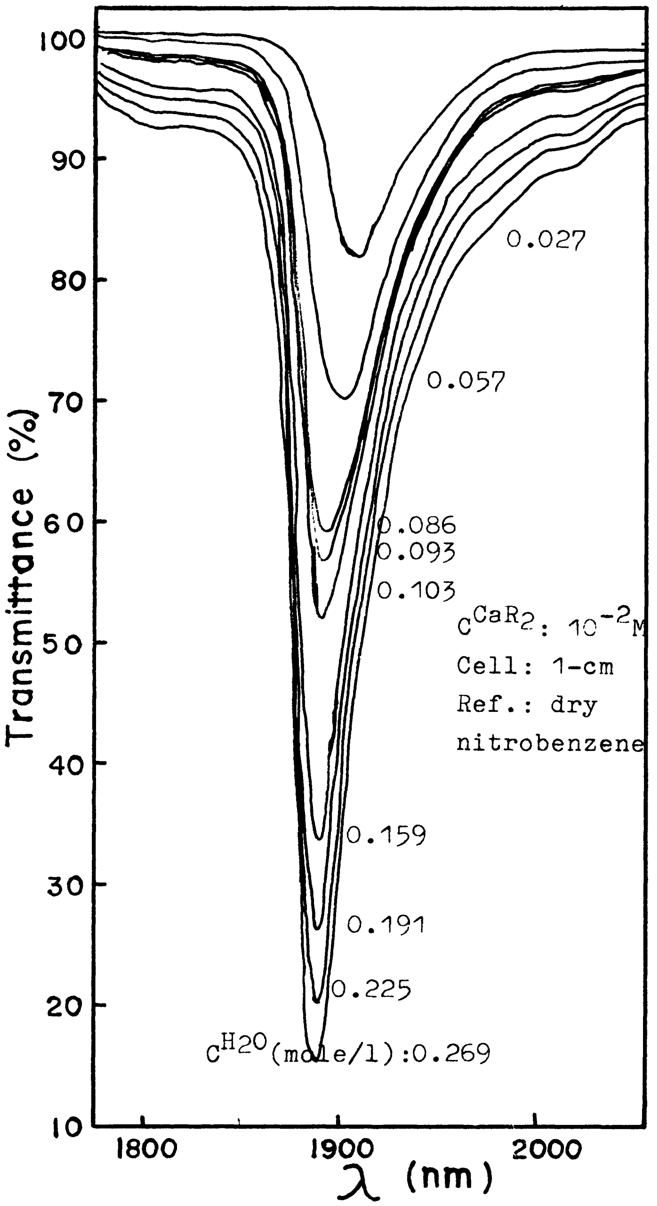

Fig. 2. The spectra of water in nitrobenzene solutions.

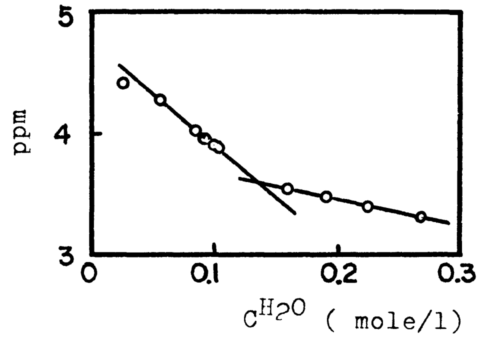

Fig. 3. The dependence of chemical shift on the water content.

by two line portions, as is shown in Fig. 3. The water concentration at the intersection of the two lines corresponds very well to the hydration number of calcium ions obtained by the Karl-Fischer method. The NMR spectra may give a simple method to determine the hydration number in such a solution. Until the water concentration reaches about 0.13 M, water causes a great chemical shift toward the higher field. This means that the field about calcium cations is weakened greatly by the coordination of the water. Hence, both the steep fall in Fig.3 and the gradual shift of absorption curves in Fig. 2 are considered to reveal the hydration process in the nitrobenzene phase. On the other hand, the gradual chemical shift and the increase in the peak height without shift in the absorption spectra, which were observed in the case of a water concentration above 0.13 M, may also reveal the extremely weak interactions between the water molecules and the cations.

From the spectra of the light absorption and of the NMR, it can be concluded that, when water is added successively to the water-free nitrobenzene solution, the water hydrates selectively to the cations, and then disperses into nitrobenzene, the solvent. Such behavior of the water in the nitrobenzene phase may support the formation of a water-separated ion pair, which was proposed by the authors in order to elucidate the association constant obtained with these salts in a nitrobenzene solution.

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