CHEMISTRY LETTERS, pp. 1415-1418, 1983. © The Chemical Society of Japan 1983

COMPLEXATION OF "CROWNED" DINITROPHENYLAZOPHENOL WITH ALKALI AND ALKALINE EARTH METAL IONS AND ITS APPLICATION TO THE COLORIMETRIC DETERMINATION OF Rb(I) AND Cs(I)

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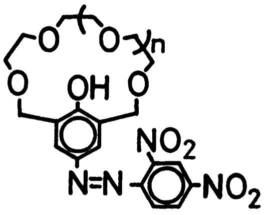
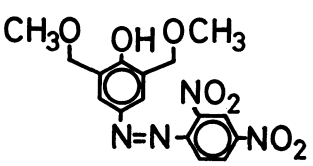
Complexation of "crowned" dinitrophenylazophenol (CDPA) with alkali and alkaline earth metal ions in $CHCl_3$ – MeOH – triethylamine was examined. The ionic radii of these metal ions correlated linearly both with the wave numbers of absorption maxima and with the molar absorption coefficients of the resulting complexes except for Be(II). The colorimetric determination of Rb(I) and Cs(I) by using CDPA was practical.

"Crowned" dinitrophenylazophenols (abbreviations: CDPA for n=1 and I for n=2; see below) were synthesized, and these compounds showed the complexation with alkali and alkaline earth metal ions.1) Recently, CDPA has been used for the sensitive spectrophotometric determination of Li(I) in $CHCl_3$ – dimethylsulfoxide – triethylamine (TEA) and was applied successfully to the analysis of commercial preparations, *e.g.*, Li_2CO_3 (tablet).2)

Here, the complexation of CDPA with alkali and alkaline earth metal ions in $CHCl_3$ – MeOH – TEA was studied, and two kinds of linear relationships were found in the absorption spectra. In addition, a new sensitive spectrophotometric method was developed for the determination of Rb(I) and Cs(I), separately, by using CDPA.



n = 1: CDPA
n = 2: I



II

The absorption spectra of the complexes of CDPA with the alkali and the alkaline earth metal ions were measured in $CHCl_3$ – MeOH – TEA according to the procedure as described below for the determination of Rb(I). The longest-wavelength peaks (λ_{max}) and the molar absorption coefficients (ε) of the complexes are shown in Table 1. As shown in Figs. 1 and 2 both $\tilde{\nu}_{max}$ ($=1/\lambda_{max}$) and ε are linearly dependent on the ionic radius of the metal ions of each of the alkali and alkaline earth groups, Be(II) being an exception, and the alkaline earth metal ions behave individually as a separate group. It is interesting that a red shift and a hyperchromic effect are observed with the increase in ionic size. The above behavior is correlated with the structure of the complexes in the solution. A relatively small ion [*e.g.*, Li(I) or Mg(II)] fits well into the cavity[3] and seems to be subjected to somewhat strong interaction with the phenolate anion conjugated

Table 1. Spectral data of the complexes[a]

Ion	λ_{max}/nm	$\varepsilon \times 10^{-4}$/mol^{-1}dm^{3}cm^{-1}	Ionic radius/Å
Li^+	547	3.41	0.60
Na^+	562	4.27	0.95
K^+	573	4.18	1.33
Rb^+	575	4.26	1.48
Cs^+	580	4.66	1.69
Be^{2+}	560	0.51	0.31
Mg^{2+}	542	5.04	0.65
Ca^{2+}	556	6.31	0.99
Sr^{2+}	560	7.49	1.33
Ba^{2+}	563	8.91	1.35

a) CDPA: 1×10^{-4}mol dm^{-3}; TEA: 0.5 v/v%.

Table 2. The mole ratio of metal ion to CDPA[a]

Ion	([CDPA] + [M^{n+}])/mol dm^{-3}	Mole ratio
Li^+	5.0×10^{-5}	1 : 0.93
Na^+	5.0×10^{-5}	1 : 1.06
K^+	2.5×10^{-5}	1 : 0.93
Rb^+	2.5×10^{-5}	1 : 1.06
Cs^+	2.5×10^{-5}	1 : 1.00
Ca^{2+}	2.5×10^{-5}	1 : 2.33
Sr^{2+}	2.5×10^{-5}	1 : 2.28
Ba^{2+}	2.5×10^{-5}	1 : 2.33

a) Absorbance was measured at λ_{max} described in Table 1, and square brackets denote the amount-of-substance concentration.

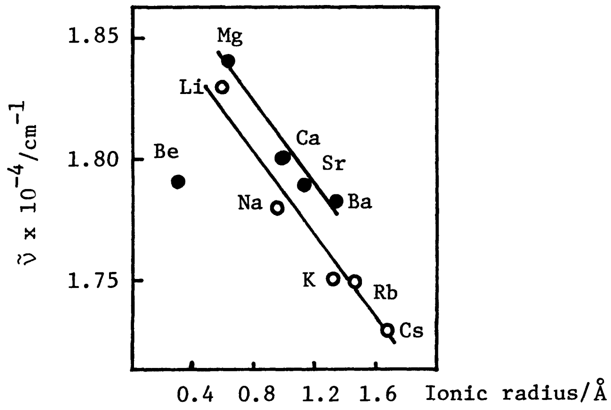


Fig. 1. $\tilde{\nu}$ *vs*. Ionic radius.

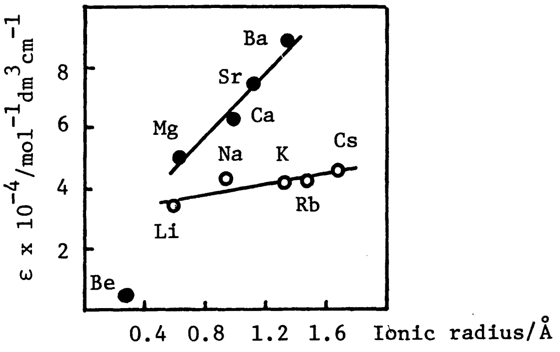


Fig. 2. ε *vs*. Ionic radius.

to the dinitrophenylazo group.[4)]

The anomalous behavior of Be(II) is believed to be largely caused by its extremely small ionic size.

The larger molar absorption coefficients for the alkaline earth metal complexes (Fig. 2) can be attributed to the fact that these metal ions form 1 (metal): 2 (ligand) complexes while the alkali metal ions form 1 : 1 complexes, as is evidenced by the stoichiometric ratios determined by means of the continuous variation method (Table 2).

The absorption spectra of CDPA were recorded as a function of pH to determine the acid dissociation constant (pK_a).[5)] An isosbestic point was observed at 463 nm (Fig. 3). The pK_a values of CDPA, I, and II were determined by using the absorbance at λ_{max}. The order of the acidity was II > I > CDPA (Table 3).

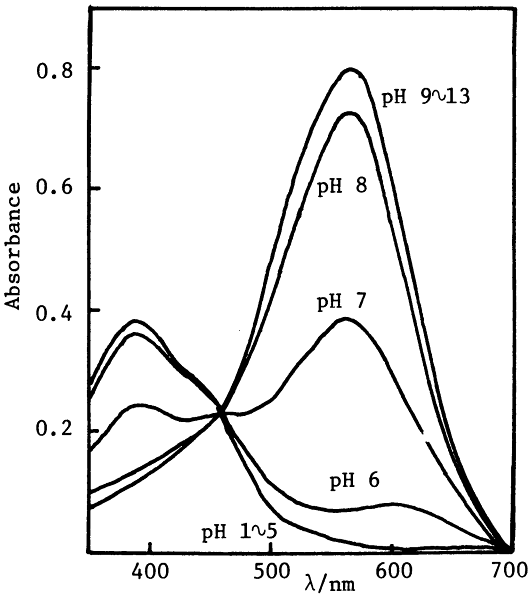


Fig. 3. Absorption spectra of CDPA as a function of pH (25°C).

Table 3. Acid dissociation constants[a)]

Compound	pK_a	λ_{max}/nm
CDPA	7.05	565
I	6.69	550
II	6.23	545

a) concentration, 2×10^{-5} mol dm^{-3}; ionic strength, 0.09–0.24 mol dm^{-3}; 25°C.

A new sensitive method for the spectrophotometric determination of Rb(I) and Cs(I) with CDPA in $CHCl_3$–MeOH–TEA is proposed. A recommended procedure is as follows. To a solution of RbCl [$\leq$ 25 μg as Rb(I)] or CsCl [$\leq$ 30 μg as Cs(I)] in MeOH (0.5 ml) in a 10 ml volumetric flask, a solution of CDPA in $CHCl_3$ (2.5×10^{-4} M, 1 M = 1 mol dm^{-3}, 3.0 ml) is added, and the whole is diluted to *ca.* 9 ml with $CHCl_3$. To the mixed solution is added TEA (0.05 ml) and the total volume is adjusted finally to 10 ml with $CHCl_3$. The solution is mixed and allowed to stand for 10 min, then the absorbance is measured at 575 nm for Rb(I) or at 580 nm for Cs(I) against the reagent blank.[6)] The resulting color was fairly stable and a constant absorbance was obtained during 10 – 60 min after the coloration reaction. The calibration curves for Rb(I) and Cs(I) were linear from 0.03 to 2.5 ppm and 0.25 to 3 ppm, respectively.[7)]

So far few instances of the colorimetric determination of Rb(I) or Cs(I) have been reported.[8)] The sensitivity and the precision of the present method are superior to the conventional methods; however, its selectivity is not always good because of interference with other alkali and alkaline earth metal ions. This method is especially well suited for the determination of a single compound of Rb(I) or Cs(I).

This work was partly supported by the Grant-in-Aid for Scientific Research (Nos. 56470022 and 57540287) from the Ministry of Education, Science and Culture.

References

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3) Measurements on space-filling models of CDPA indicate that the shortest transannular distance between the surface of the oxygen atoms is 1.6 – 1.8 Å, which is suitable to accommodate Li(I) or Mg(II).

4) The mechanism of the coloration of the complexes has been discussed.[1)]

5) A dioxane solution (10 v/v%) was used for the measurement; Buffers: pH 1 – 3, 0.1 M Sodium citrate + 0.1 M HCl; pH 4 – 5, 0.1 M Acetic acid + 0.1 M Sodium acetate; pH 6 – 9, 0.1 M KH_2PO_4 + 0.05 M $Na_2B_2O_7$; pH 10 – 11, 0.05 M $Na_2B_2O_7$ + 0.05 M Na_2CO_3; pH 12 – 13, 0.1 M Na_2HPO_4 + 0.1 M NaOH.

6) Constant absorbances were obtained in the following concentration ranges: MeOH, 4 – 16 v/v%; TEA, 0.1 – 1.0 v/v%; CDPA, (4 – 16) x 10^{-5} M for Rb(I). MeOH, 4 – 20 v/v%; TEA, 0.2 – 1.0 v/v%; CDPA, (2 – 15) x 10^{-5} M for Cs(I).

7) The coefficients of variation for the five replicated experiments were 1.56% for Rb(I) (1 ppm) and 3.03% for Cs(I) (1.5 ppm).

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(Received June 13, 1983)