

## Solvent Extraction of Metal Chelates

### III. A Potentiometric Investigation of Alkali-Ion Extraction by Di-(2-hydroxy-1-naphthyl)methane

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The chelate extractions of Li, Na, and K ions by di-(2-hydroxy-1-naphthyl)methane into butanol, methyl-isobutyl ketone and di-isopropyl ether have been studied by potentiometric measurements. The aim of the investigation has been to identify the species extracted and to characterize them by suitable constants. The formation of polymeric species has been demonstrated in the extraction with methyl-isobutyl ketone as the organic solvent. By variation of the volume ratio between the organic phase and the water phase additional information with regard to equilibrium constants can be obtained. This method has been applied in the simple case of extraction with butanol as solvent.

The formation of an eight-membered chelate ring is postulated and is exemplified by means of other compounds.

Although solvent extraction of metal chelates has for a long time been a well-established procedure for the isolation and purification of different metallic elements, only a single system has so far as is known, been reported useful for the solvent extraction of alkali ions *i.e.* the extraction by means of dipivaloyl methane.<sup>1</sup> This system has found only limited application,<sup>2</sup> but it has the additional theoretical interest that it demonstrates the effect of steric hindrance in chelate formation.<sup>3</sup>

Apart from its analytical and technical aspects, the actual demonstration of such systems, having a certain degree of selectivity towards the different alkali ions, is valuable in providing a model for the phenomena of active transport of alkali ions in biological systems. Few determinations of the stability constants of alkali complexes are reported in literature.<sup>4</sup> Among those are the determinations of Schwarzenbach for different aminopolycarboxylic acids and the determinations for di-benzoyl methane in 75 % dioxane/water by Fernelius and van Uitert. Recently Irving and Da Silva<sup>5</sup> have reinvestigated the alkali complexes with uramildiacetic acid, confirming their abnormally large stability constants.

Several lithium salts as well as some sodium salts are soluble in organic solvents (*e.g.* LiCl in butanol). However this property is not sufficient for a measurable solvent extraction from water into an organic phase to occur, although it is evidently a necessary condition for an extraction to be possible. A search among alkali salts soluble in organic solvents might therefore reveal the existence of useful extractable species.

The alkali salts of di-(2-hydroxy-1-naphthyl) sulphide and di-(2-hydroxy-1-naphthyl) methane (Fig. 1) have been reported to be easily soluble in

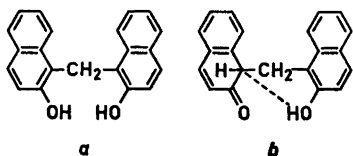


Fig. 1. Alternative formulations of di-(2-hydroxy-1-naphthyl)methane.

diethyl ether and only slightly soluble in water<sup>6</sup> and have been proposed as possible extractants for alkali ions.\* So far no systematic study of the extractive properties of these compounds seems to have been made. As reported in this paper, the said compounds do indeed extract alkali ions from water into different organic solvents. By inspection of Dewar models of the two compounds it is seen that the rotation about the bonds to the bridging groups (*i.e.* —S— and —CH<sub>2</sub>—) is hindered. Since it is not possible to arrange the two naphthyl groups in a plane, any resonance stabilization of the chelates formed can be excluded. Chelate formation seems to involve the formation of an eight-membered ring. Usually chelates forming such a ring are of low stability owing to the great loss in rotational entropy taking place when the rather large extended molecule has to form a ring system. With the present compounds the loss in internal rotational entropy will be appreciably smaller than usual, which may account for the increased stability of the alkali-ion complexes.

On the other hand the model of uramildiacetic acid gives no evidence of hindered rotation; it shows the possibility of formation of chelate rings with eight members. It is therefore probable that the almost purely ionic bonds which must exist in the alkali complexes fit well into the eight-membered ring system, which may give rise to strain in bonds more covalent in character.

In a search for other compounds capable of forming an eight-membered chelate ring the following have been investigated: 4-thiazolylazo-1-phenyl-3-methyl pyrazolone-5, salicylideneacetophenone, methylene-bisbarbituric acid and the biologically active compound dicoumarol. Of these the methylene-bisbarbituric acid showed inferior extractive properties, but did form alkali salts slightly soluble in water, and was not investigated further. The other compounds were all effective extractants for alkali ions and will be dealt with in a subsequent paper.

The present paper reports on investigations of di(2-hydroxy-1-naphthyl) methane with different organic solvents and alkali ions. The compound di-

\* Private communication from Th. Rosenberg.

(2-hydroxy-1-naphthyl) sulphide showed extractive properties similar but slightly inferior to those of the methylene derivative and is not dealt with in the paper.

The principle of the investigation was to follow the neutralization of the acid form of the chelating agent in different media. The primary aim was to identify the species extracted and to characterize them by suitable constants.

Generally the formation of polynuclear complexes (in the present case acid salts) cannot be excluded; therefore the concentration of the chelating agent was varied in each case in an attempt to reveal such formation. Only in the extraction with methyl-isobutyl ketone was a more complicated case of polymer formation demonstrated. The equations will only be derived for monomer formation and are exemplified in the treatment of data for the sodium ion extraction. Extensions to the more general case are relatively easy, the resulting equations being, however, somewhat complicated.

### EXPERIMENTAL

*Apparatus and methods.* The combined process of complex formation and solvent extraction was investigated by a titration procedure described previously.<sup>7</sup> In the present case it was found possible to perform the titration directly in a two-phase system. The titrations were made in a slow stream of carbon-dioxide-free nitrogen in a closed thermostated vessel ( $30 \pm 0.05^\circ\text{C}$ ). A weighed amount of the pure compound under investigation was added to equal volumes of 1.0 M  $\text{NaNO}_3$  solution and of the appropriate organic solvent, each saturated with the other. The titration was performed with 4–10 N NaOH added from a syringe with a Teflon piston driven by a micrometer-screw. The pH of the aqueous phase was read on an Electronic Industries Model 39 A pH-meter fitted with a GHS-33 glass electrode and an RSM-23-saturated calomel electrode. After each incremental addition of base the pH was read when the potential, observed on a recorder connected to the pH-meter, was stable. In favourable cases stability was observed after a few minutes, whereas when solid phases took part in the equilibria, periods of up to 1 h were necessary for the potential to become constant. The pH could be read with an accuracy of 0.003–0.005 pH units and the burette readings with an accuracy of less than 0.03  $\mu\text{equiv}$ . The burette system did not show any evidence of leaking when an inverted tip was used as shown by the stable potentials read around  $\text{pH} = 7$  in unbuffered systems.

*Reagents.* Di-(2-hydroxy-1-naphthyl) methane was prepared according to Ref<sup>7</sup>, and melted at  $198^\circ\text{C}$  after two recrystallizations ( $\text{EtOH}$ ). All inorganic reagents were ANALAR reagents. The water was double distilled. The organic solvents were washed with 0.1 N NaOH and water before use to remove any acidic impurities.

### RESULTS AND DISCUSSIONS

*Di-(2-hydroxy-1-naphthyl) methane extraction into butanol.* The titration curve for a simple monobasic acid HA in aqueous solution is described by the equation

$$\bar{n}/(1-\bar{n}) = [\text{OH}^-] (K_a/K_w) \quad (1)$$

where  $\bar{n}$  is the average number of hydroxyl ions "bound" per molecule of acid,  $K_a$  the acid dissociation constant and  $K_w$  the ion product of water. By the introduction of the following equations, defining the distribution

coefficients  $\lambda$ ,  $K_a$  and the complexity product  $\beta$  appropriate for the description of a two-phase complexing and extracting system.

$$[\text{NaA}]_{\text{org}}/[\text{NaA}] = \lambda \quad (2) \quad [\text{HA}]_{\text{org}}/[\text{HA}] = K_a \quad (3)$$

$$[\text{NaA}]/[\text{Na}^+][\text{A}^-] = \beta \quad (4)$$

instead of eqn. (1) is obtained

$$\bar{n}/(1-\bar{n}) = [\text{OH}^-] \frac{K_a(1 + [\text{Na}^+]\beta(1 + \lambda V_o/V_w))}{K_w(1 + K_a V_o/V_w)} \quad (5)$$

which is the equation describing the titration curve for the acid in a two-phase system with extraction of both the undissociated acid and its sodium

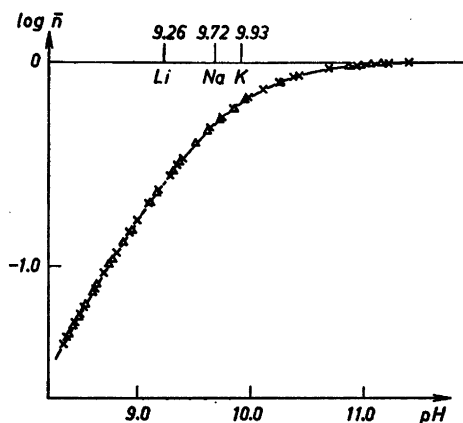


Fig. 2. The titration curves for the complex-extraction of the sodium salt of di-(2-hydroxy-1-naphthyl)methane into butanol at total concentrations  $C_B = 0.0835 \text{ M}$  ( $\times$ ) and  $C_B = 0.0417 \text{ M}$  ( $\Delta$ ).

complex. In this expression  $V_o$  and  $V_w$  are the volumes of the organic phase and the water phase, respectively. All concentrations in eqn. (5) refer solely to the water phase.

With the sodium-ion concentration kept reasonably constant the new titration curve is identical in shape with that corresponding to eqn. (1), only displaced a distance of

$$\log \frac{1 + [\text{Na}^+]\beta(1 + \lambda V_o/V_w)}{1 + K_a V_o/V_w}$$

along the pH axis. In Fig. 2 the actual data for titrations at two different total concentrations of di-(2-hydroxy-1-naphthyl)methane in the butanol-water system are shown in a  $\log \bar{n}$  versus pH plot. The total concentrations are designated  $C_B$  and refer to the water phase. From these data it is concluded that the compound acts as a monobasic acid with an apparent acid dissociation constant of  $\text{p}K_a = 9.72$ . The sodium salt extracted can therefore be formulated as  $\text{NaHA}$ , where  $\text{H}_2\text{A}$  is the di-(2-hydroxy-1-naphthyl) methane. The magnitude of the acid dissociation constant does not deviate from that expected for a naphthol in a water phase. Two prove that extraction occurred,

the two-phase system was centrifuged and a sample of the organic phase withdrawn. By backtitration of the sample with nitric acid, in the presence of water, the proper indicator as determined from Fig. 2 (*e.g.* bromothymol blue, pH = 7.0) being used, the amount of base extracted could be determined. In the present case the extraction of the sodium salt was found to be almost quantitative. From this it is concluded that  $\lambda$  is at least  $10^2$ , but may be appreciably larger if  $\beta$  is very small. These conclusions have been drawn from eqn. (6), which expresses the ratio between the amounts of sodium complex extracted into the organic phase and sodium salt in the water phase:

$$\frac{[\text{NaHA}]_{\text{org}}/([\text{HA}^-] + [\text{NaHA}])}{[\text{Na}^+]} = \lambda\beta[\text{Na}^+]/(1 + \beta[\text{Na}^+]) = \lambda\beta/(1 + \beta) \quad \text{for} \quad (6)$$

$$[\text{Na}^+] = 1.0$$

By comparison with other solvents (methyl-isobutyl ketone, di-isopropyl ether, benzene, chloroform, etc.) butanol shows far better solvent properties than the others, which suggests that it might function as an active ligand in complex formation and extraction. If the following reaction scheme is assumed:



where  $N$  is the number of solvent molecules  $\text{S}$  bound per complex, and if the equations

$$[\text{NaHAS}_N]/[\text{NaHA}][\text{S}]^N = \beta_s \quad (8)$$

$$[\text{NaHAS}_N]_{\text{org}}/[\text{NaHAS}_N] = \lambda' \quad (9)$$

defining a new complexity product  $\beta_s$  and distribution coefficient  $\lambda'$  are introduced into eqn. (1) together with eqns. (3) and (4), the following expression is obtained:

$$\bar{n}/(1-\bar{n}) = [\text{OH}^-] \left( \frac{K_a(1 + \beta[\text{Na}^+](1 + \beta_s[\text{S}]^N(1 + \lambda'V_o/V_w)))}{K_w(1 + K_dV_o/V_w)} \right) \quad (10)$$

which, for  $\beta_s[\text{S}]^N \gg 1$ ,  $\beta[\text{Na}^+] \gg 1$ ,  $K_d \gg 1$ , and  $\lambda' \gg 1$ , can be simplified to

$$\bar{n}/(1-\bar{n}) = [\text{OH}^-] \left( \frac{K_a\beta\beta_s\lambda'[\text{Na}^+][\text{S}]^N}{K_wK_d} \right) \quad (11)$$

From this equation is seen that, for  $\bar{n}/(1-\bar{n})$  being constant or almost so, the following relation holds with approximation:

$$\text{pH} = -N \log [\text{S}] - B, \quad \text{where } B \text{ is a constant} \quad (12)$$

To determine the value of  $N$ , a normal two-phase titration with benzene, (be), as organic solvent was performed to a certain intermediary value of  $\bar{n}$ . The pH of this point was noted. To this system incremental amounts of butanol, (bu), were added, and the pH of the water phase was measured after each addition.

As seen from eqn. (10), when  $[\text{S}]$  is small, *i.e.* when  $\beta_s[\text{S}]^N(1 + \lambda'V_o/V_w)$  is smaller than unity, only slight changes in pH should be expected, whereas when this expression is appreciably larger than unity eqn. (11) should hold approximately.

Fig. 3 shows experimental points for two independent titrations with butanol plotted as pH *versus*  $\log [S]$ , where  $[S]$  has been calculated on the assumption that all the butanol is in the organic phase, *e.g.*  $[S] = bu/(bu + be)$ ,

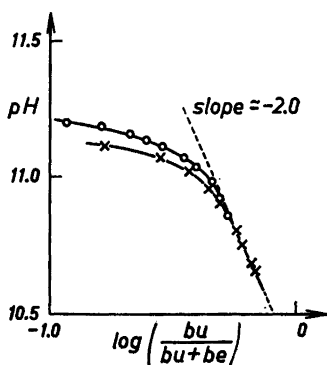
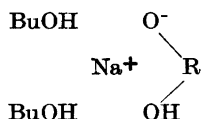


Fig. 3. The variation of pH with the concentration of butanol in benzene at two arbitrary values of  $\bar{n}$ .

which is probably the case in the present system. The curves show exactly the expected dependence merging into linear plots for large  $[S]$ . The limiting slope is  $-2.0 \pm 0.1$ , corresponding to  $N=2$ . With the additional assumption that the ratio  $\lambda'/K_a$  is almost constant, even when the original solvent is changed by dilution with butanol, and that the uncomplexed acid is not extracted as a butanol complex, one may therefore deduce that two molecules of butanol are bound per sodium ion in the organic solvent. Even if the latter condition were not fulfilled, the slope would indicate the additional number of solvent molecules being bound per complex. The formula for the sodium complex will therefore be



where the coordination number four for the sodium ion is satisfied. Similar experiments have been performed with Li and K, the aqueous phase and titrant being 1 M  $\text{LiNO}_3$  and  $\text{LiOH}$ , 1 M  $\text{KNO}_3$  and  $\text{KOH}$ , respectively, giving the apparent acid dissociation constants  $\text{p}K_a(\text{Li}) = 9.26$  and  $\text{p}K_a(\text{K}) = 9.93$ . The data obtained in this way indicate that Li is extracted far better than the two other alkali ions and the sodium ion slightly better than the potassium ion. However, the data are not directly comparable, primarily because appreciable differences may exist between the activity coefficients in the different systems. The observed trends do, however correspond to what would be expected if real complex formation occurred, although their relative magnitudes may not correspond to actual separation factors. An attempt to measure the separation factors in a butanol-chelate extraction from a mixed Li, Na, K-nitrate water phase by flame-spectroscopy was unsuccessful because the neutral alkali nitrates were also extracted in amounts comparable to those encountered in the chelate system, which are small as compared with the salts.

A possible way of resolving the apparent acid dissociation constants for the two-phase system into its components would be to determine  $K_a$ ,  $K_d$ ,  $\beta$ , and  $\lambda$  separately. In principle this can be done if a base can be found whose cation does not form any complexes or association products with the acid. Tetramethyl-ammonium hydroxide might be supposed to be such a base. By titration in a water phase with constant ionic strength regulated by, e.g. tetramethyl-ammonium chloride it should be possible to determine  $K_a$  and  $\beta$ . By a similar two-phase titration  $K_d$  and  $\lambda$  could be determined. However, experiments have shown that the acid is extremely insoluble in water so that in practice  $K_a$  cannot be determined especially because the titrations take place in a difficult pH range. By a two-phase titration it should, however, be possible to determine  $K_a/(1+K_d)$ . In an actual titration with tetramethyl-ammonium hydroxide as a base and distilled water as inorganic phase it was shown that the salt formed was also extracted into the organic phase, in this case probably as an ion-pair. By this titration, therefore, only a new apparent acid dissociation constant of the type expressed in eqn. (5) could be determined. Since it has thus been impossible to find a reference system in which to calculate the usual complexity constants, only the apparent acid dissociation constants will be presented.

In an effort to resolve the latter constants into their components an analysis based on the variation of the volume ratio  $V_o/V_w$  has been developed.

By rearrangement of eqn. (5) the following expression is obtained:

$$[\text{H}^+]\bar{n}/(1-\bar{n}) = K_a(1+\beta) \left( \frac{1+\lambda\beta V_o/V_w(1+\beta)}{1+K_d V_o/V_w} \right) \text{ for } [\text{Na}^+] = 1.0 \quad (13)$$

A plot of  $[\text{H}^+]\bar{n}/(1-\bar{n})$  versus  $V_o/V_w$  would thus lead to a curve whose shape is determined by the constants  $\lambda\beta/(1+\beta)$  and  $K_d$  and whose position along the  $[\text{H}^+]\bar{n}/(1-\bar{n})$  axis is determined by the constant  $K_a(1+\beta)$ .

It is seen that eqn. (13) can be solved for the unknowns  $K_a(1+\beta)$ ,  $K_a\beta\lambda$ , and  $K_d$  by the insertion of three corresponding values of  $V_o/V_w$  and  $[\text{H}^+]\bar{n}/(1-\bar{n})$ . Considerations on the precision obtainable show that large uncertainties are connected with both very large and very small values of  $K_d$  and  $\lambda\beta/(1+\beta)$ .

In the experimental determination of  $[\text{H}^+]\bar{n}/(1-\bar{n})$  it is important to correct for changes in  $\bar{n}$ , which are quite large in this pH range. It is easily accomplished graphically.

In Fig. 4 experimentally determined values of  $-\log([\text{H}^+]\bar{n}/(1-\bar{n}))$  have been plotted versus  $\log(V_o/V_w)$ . The slope of the curve is negative. It is found from eqn. (13) by differentiation that a negative slope means that  $\lambda\beta/(1+\beta) > K_d$ , from which result is deduced that  $\lambda > K_d$  irrespective of the magnitude of  $\beta$  which is still unknown. From the determined value of  $\lambda\beta/(1+\beta) = c$  (=constant) one may deduce  $\lambda > c$  as  $\beta$  must have a finite value, although it may be very small. By variation of the sodium-ion concentration  $[\text{Na}^+]$  it is theoretically possible to resolve the expression  $\lambda\beta/(1+\beta)$  if constancy of  $\lambda$  and  $\beta$  during this operation can be assumed. Normally one may keep the ionic strength almost constant in a solution by adding a large surplus of neutral alkali salts and thus ensuring the constancy of formation constants

of species not involving the alkali ion. This procedure is obviously not applicable in the present case. Therefore one cannot evaluate the relative magnitudes of  $\lambda$  and  $\beta$ .

By the present procedure the same information was obtained as would have been found if alternate single-phase and two-phase titrations had been performed. For the final resolution of the apparent acid dissociation constants a base with a non-complexing cation is still lacking.

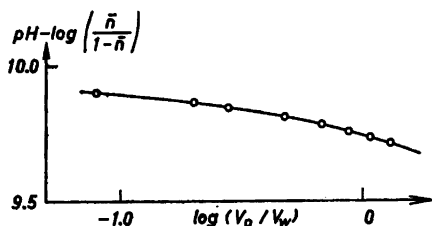


Fig. 4. The variation of  $\text{pH} - \log \left( \frac{\bar{n}}{1-\bar{n}} \right)$  with  $\log (V_o/V_w)$  in the extraction of sodium ions by di-(2-hydroxy-1-naphthyl) methane into butanol.

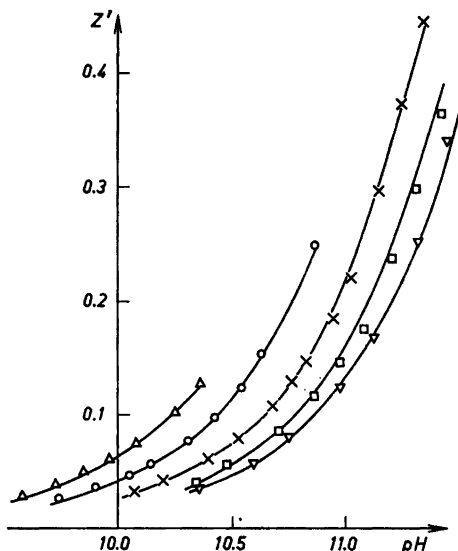


Fig. 5. Titration data for sodium-ion extraction by di-(2-hydroxy-1-naphthyl) methane into methyl-isobutyl ketone at total concentrations  $C_B = 0.667 \text{ M}$  ( $\Delta$ ),  $C_B = 0.333 \text{ M}$  ( $\circ$ ),  $C_B = 0.167 \text{ M}$  ( $\times$ ),  $C_B = 0.0844 \text{ M}$  ( $\square$ ) and  $C_B = 0.0422 \text{ M}$  ( $\nabla$ ). The curves have been calculated on the basis of the apparent acidity constants  $\log \beta_{1,1}^* = 11.96$ ,  $\log \beta_{1,2}^* = 11.03$  and  $\log \beta_{3,3}^* = 32.66$ .

For the extraction of di-(2-hydroxy-1-naphthyl)methane into butanol the following constants were found

$$\begin{aligned} \log K_a(1 + \beta) &= 9.17 \pm 0.03 \\ \log K_a\beta\lambda &= 9.68 \pm 0.02 \\ K_a &= 0.81 \pm 0.1 \end{aligned}$$

whence  $\lambda\beta/(1 + \beta) = 1.76$  and  $\lambda > 1.76 > K_a$  as predicted.

It is seen that at least part of the effectivity of the compound as alkali-ion extractant is due to a favourable distribution coefficient for the salts



between the two phases. The theoretical curve calculated by means of the above set of constants is shown in solid line in Fig. 5.

*Di-(2-hydroxy-1-naphthyl)methane extraction into methyl-isobutyl ketone.* The titration curves for sodium-ion extraction by di-(2-hydroxy-1-naphthyl)methane into hexone are shown in Fig. 5 for different total concentrations of ligand. Since the curves do not coincide, the extraction mechanism obviously involves species polynuclear with respect to the reagent.

Back-extraction experiments show that the base added is practically quantitatively extracted, and the deductions made in the following concerning the composition of the complexes will therefore very probably correspond to the composition of the complexes extracted. The application of the limiting-slope method of Ref.<sup>8</sup> suggests the two species  $\text{NaHA}$  and  $\text{NaH}_3\text{A}_2$ . However, it was found impossible to obtain a reasonable fit between calculated curves and experimental points, assuming these two species to be the only products formed.

By a trial programme other probable species in different combinations were suggested and tested in a "LETAGROP" calculation. (The LETAGROP programme of Sillén<sup>9,10</sup> has been translated into ALGOL for use in the GIER computer, with slight modifications.) Among the combinations tested the following was found to give the best fit with experimental data as shown by the solid curves in Fig. 6. The constants are given as apparent "acid dissociation" constants  $\beta_{x,r}^*$  defined by

$$\beta_{x,r}^* = [\text{H}^+]^x [\text{A}_r \text{H}_{2r-x}] / [\text{H}_2\text{A}]^r$$

$$\begin{aligned} \log \beta_{1,1}^* &= 11.96 \pm 0.02 \\ \log \beta_{1,2}^* &= 11.03 \pm 0.5 \\ \log \beta_{3,3}^* &= 32.66 \pm 0.03 \end{aligned}$$

Species
$\text{NaHA}$
$\text{NaH}_3\text{A}_2$
$\text{Na}_3\text{H}_3\text{A}_3$

Although the analysis of data cannot be said to be rigorous, the constants found do represent experimental data rather well and may be taken as an indication of which species are extracted. It should be noted, however, that the incorporation of a second acid function in the molecule (*i.e.* the formation of a complex  $\text{Na}_2\text{A}$ ) leads to an equally acceptable fit between experimental data and theoretical curves. The relatively low order of precision of the data (due to the extreme pH values) does not allow a decision between the two cases, but by analogy with other solvents the representation involving only a single acid function will be favoured. In the case of butanol the tendency to polymerization is masked by solvent coordination with the sodium ion which apparently is not possible with hexone. The methyl-isobutyl ketone molecule is perhaps too bulky to gain access to the central atom so as to saturate a coordinate bond, and thus the complex tends to polymerize. The residual multipolar forces extending outside the primary polymerization products are neutralized by the rather polar organic solvent, molecules, now in a sterically less hindered sphere.

The general expression for extraction of polynuclear complexes will be similar to that representing a single-phase system, the concentration of each species being multiplied by  $(1 + \lambda_{x,r} V_o / V_w)$  in the two-phase system.

In this expression  $\lambda_{x,r}$  means the distribution coefficient of the species of composition  $B_rA_x$ , where B is the central atom and A the ligand. The expressions for  $Z$  and  $Z'$  (the average number of ligand molecules bound per central atom B) in a single-phase and a two-phase system, respectively, will be

$$Z = \frac{\sum_r \sum_x x [B_r A_x]}{C_B} \quad (15)$$

$$Z' = \frac{\sum_r \sum_x x (1 + \lambda_{x,r} V_o / V_w) [B_r A_x]}{C_B} \quad (16)$$

Owing to the restricted range of  $V_o/V_w$  accessible experimentally (about two decades), an analysis of a complicated extraction system, such as that discussed here, based on the volume ratio variation is almost impossible and has not been attempted.

*Di-(2-hydroxy-1-naphthyl)methane extraction into di-isopropyl ether.* The titration curves for sodium-ion extraction by di-(2-hydroxy-1-naphthyl)methane into di-isopropyl ether at two different total concentrations of ligand are shown in Fig. 6. As diethyl ether is known to extract large amounts of sodium complex, it is surprising that only very small amounts can be extracted into di-isopropyl ether as demonstrated by back-titration. When a certain concentration of anion  $HA^-$  (or sodium complex  $NaHA$ ) is reached, a third liquid phase is separated (marked by  $\rightarrow$  in Fig. 6.) This phase is rather viscous,

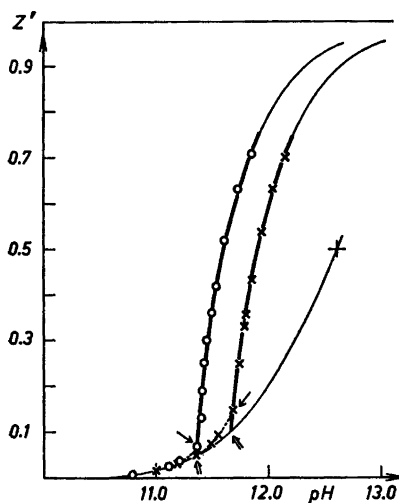


Fig. 6. Titration data for sodium-ion extraction by di-(2-hydroxy-1-naphthyl)methane into di-isopropyl ether at total concentrations  $C_B = 0.167$  M (O) and  $C_B = 0.0835$  M (x).

The solid curves have been calculated on the assumption of an apparent acid dissociation constant  $pK_a = 12.60$  and an apparent solubility product  $K_s = [Na^+][HA^-] = 8.4 \times 10^{-3}$ .

which is considered to be due to the presence of highly polymeric species. The titration curves in the presence of the third phase do follow the expression for infinite polymerization, *i.e.* a precipitation reaction, well, but no conclusions can be drawn about the degree of polymerization, except that it is larger than 30 because the precision of the potentiometric measurements is such that it is impossible to distinguish between degrees of polymerization higher than that value. For very low values of  $Z'$  the curves coincide, which

indicates that the primary product of neutralization is a monomer that can be characterized by an apparent acid dissociation constant  $pK_a = 12.6 \pm 0.1$ . Before the third phase is separated the titration curves show evidence of another sort of polymerization reaction, the exact nature of which cannot be determined with certainty as few data are available. This polymerization is of low order, however, and may be  $Na_2H_2A_2$ .

Since the formation curve for the third phase is identical with that of a solid precipitate of composition  $NaHA$  the third phase may be characterized by an apparent "solubility product"  $K_s$ :

$$K_s = [Na^+][HA^-] = 8.4 (\pm 0.4) \times 10^{-3} \quad (17)$$

The magnitude of  $[HA^-]$  at the point marked  $\blacktriangleright$  in Fig. 6 was calculated at  $8.4 (\pm 0.4) \times 10^{-3}$ . With  $[Na^+] = 1.0$ , eqn. (17) is obtained.

### CONCLUSIONS

The present investigation has revealed the existence of a new class of compounds capable of forming chelates with alkali ions. The trends in the apparent stabilities of the alkali-ion complexed, although not strictly comparable, lend support to the assumption that the "salts" formed are real complexes (*i.e.*, that they are formed by a replacement reaction of water of hydration and thus involve a direct interaction between cation and ligand) and not ion-association products.

The data presented show that the mechanism of extraction may in some cases be more complicated than the simple extraction of electroneutral monomers, as is usually assumed in work on chelate extraction. According to its preparation and formula (Fig. 1a) di-(2-hydroxy-1-naphthyl)methane would be expected to act as a dibasic acid. The present investigation, however, only reveals the existence of a single acid function per molecule, which suggests the alternative formulation (Fig. 1b), proposed by Evans and Smiles<sup>6</sup> to explain the very weak acid character of the second proton — or indicates the formation of an extremely strong hydrogen bond of the second proton.

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