

## Extraction of Zn(II) in Presence of Salicylic Acid, Pyridine, $\beta$ -Picoline & Quinoline

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The extraction of complex  $Zn(HSal)_2$  from Zn(II) and salicylic acid ( $H_2Sal$ ) in aqueous solution has been studied in *n*-butanol. In contrast, extraction by non-hydroxylic solvents (e.g. benzene, chloroform) does not occur in the pH range 4.5-6.0. However, a marked synergism takes place in the presence of nitrogen containing bases (pyridine,  $\beta$ -picoline and quinoline). The synergistic enhancement is found to be due to the displacement of water from the coordination sphere by the base giving the species  $Zn(HSal)_2 \cdot B \cdot H_2O$ . The extraction and formation constants and the effectiveness of the various bases as synergists follow the order  $\beta$ -picoline > pyridine > quinoline.

SEVERAL workers have investigated the extraction of various metals in the presence of salicylic acid and some neutral donors such as tributyl phosphate and nitrogen containing organic bases like pyridine, picolines and quinoline<sup>1-7</sup>. Aggett *et al.*<sup>3</sup>, studied the extraction of zinc salicylate in the presence of tributyl phosphate, but practically no work has been reported on the extraction of zinc salicylate in the presence of nitrogen containing organic bases. By taking different bases a relative idea about their effectiveness as synergists can be obtained.

In the present communication the extraction behaviour of zinc salicylate in *n*-butanol has been studied and the extracted species identified. If *n*-butanol is replaced by a non-hydroxylic solvent such as benzene, no extraction occurs over the pH range studied. However, the addition of nitrogen containing bases like pyridine,  $\beta$ -picoline and quinoline brings about a synergistic enhancement in the extraction. The Zn(II)-salicylate-base species has been identified and the extraction and formation constants calculated. The stability of the different mixed complexes has also been compared.

Over the pH range studied (4.5-6.0), only the species  $H_2Sal$  and  $HSal^-$  of salicylic acid are to be considered in the aqueous phase. Although dimerization of salicylic acid occurs in benzene, it can reasonably be expected to be small or negligible in polar or hydroxylic solvents (such as *n*-butanol) that can act as acceptors for hydrogen bonds<sup>8</sup>.

### Materials and Methods

Zinc sulphate (AR) was dissolved in doubly distilled water and the solution standardized by EDTA. Freshly prepared solution of salicylic acid (AR, BDH) was used. *n*-Butanol, pyridine,  $\beta$ -picoline and quinoline were of AR grade. <sup>65</sup>Zn radioisotope (Bhabha Atomic Research Centre, Bombay) was used for distribution studies.

In each set equal volumes (10 ml) of the aqueous [ $10^{-4}M$  zinc(II) and  $0.0125M$  salicylic acid or any other concentration] and organic phase were shaken

at room temperature  $25^\circ \pm 2^\circ$ . After equilibration the two phases were using a Cambridge bench pH-meter. Suitable aliquots of the two phases were counted using a well-type NaI(Tl) scintillation counter and the distribution ratio calculated by the usual method. The optimum pH for the extraction of Zn(II) in the presence of salicylic acid alone and in the presence of bases extends from 4.5 to 6.0. Optimum concentrations with regard to the bases are 0.5, 1 and 4M for  $\beta$ -picoline, pyridine and quinoline respectively for maximum extraction at an overall salicylic acid concentration of  $0.025M$ . The ionic strength of the aqueous solution was maintained constant ( $0.1M$ ) by adding sodium perchlorate. The partition coefficients of  $\beta$ -picoline, pyridine and salicylic acid between water and benzene were determined by analysing the aqueous phase following standard procedures. It has been observed that the presence of amines do not affect the partition coefficient of salicylic acid and the possibility of the two forming an adduct is ruled out.

### Results and Discussion

The negligible extraction of zinc salicylate in benzene or any solvent other than alcohol indicates that the species is hydrophilic and only alcohol as solvent can replace water molecules from the coordination sphere of the metal. A plot of  $\log D$  versus  $\log [ROH]$  using benzene as a neutral diluent (Fig. 1) was linear with a slope of unity, indicating the ratio 1:1 for zinc to alcohol. Thus assuming the coordination number of zinc to be four the extracting species in *n*-butanol can be represented as  $Zn(HSal)_2 \cdot BuOH \cdot H_2O$ .

The replacement of *n*-butanol by a non-hydroxylic solvent like benzene leads to practically negligible extraction over the pH range 4.5-6.0. But the addition of neutral donors like pyridine,  $\beta$ -picoline and aquinoline to benzene has a striking effect on the extraction and the metal gets extracted to the extent of 80-90%. Obviously this happens by replacement of the water by the neutral donor and

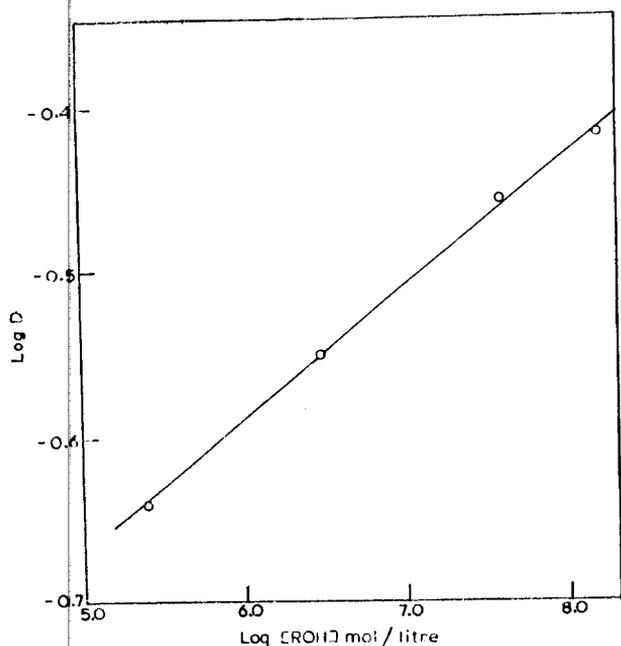


Fig. 1—Effect of varying *n*-butanol concentration on the extraction of  $Zn^{2+}$  with salicylic acid

rendering the species less hydrophilic thereby facilitating extraction into benzene.

The plots of  $\log D$  against experimentally determined values of  $\log [HSal^-]$  at constant  $pH$  and  $[B]_{aq}$ , (Fig. 2A) were linear with slope  $\sim 2$ . This indicates that in the formation of mixed complex two acid molecules are used. The plot of  $\log D$  versus  $\log [B]_{aq}$  at constant  $pH$  and  $[HSal^-]_{aq}$ , (Fig. 2B) was linear with a slope of unity showing the utilization of one base molecule per zinc atom. Thus the ratio zinc: salicylic acid: base: water is 1:2:1:1 and the extracting species may be represented as  $Zn(HSal)_2 \cdot B \cdot H_2O$ . The presence of water molecule in the species is indicated by the fact that in the presence of above bases quantitative extraction of zinc does not occur and the species has still some hydrophilic character. For the extraction of zinc salicylate in tributyl phosphate Aggett and coworkers<sup>3</sup> observed  $Zn(HSal)_2 \cdot 2 TBP$  as the extracting species where both the water molecules in the coordination sphere were replaced by the neutral donor. It has been noticed that out of the different nitrogen containing organic bases used in the study  $\alpha$ -picoline is quite unable to enhance extraction. This may be due to the poor

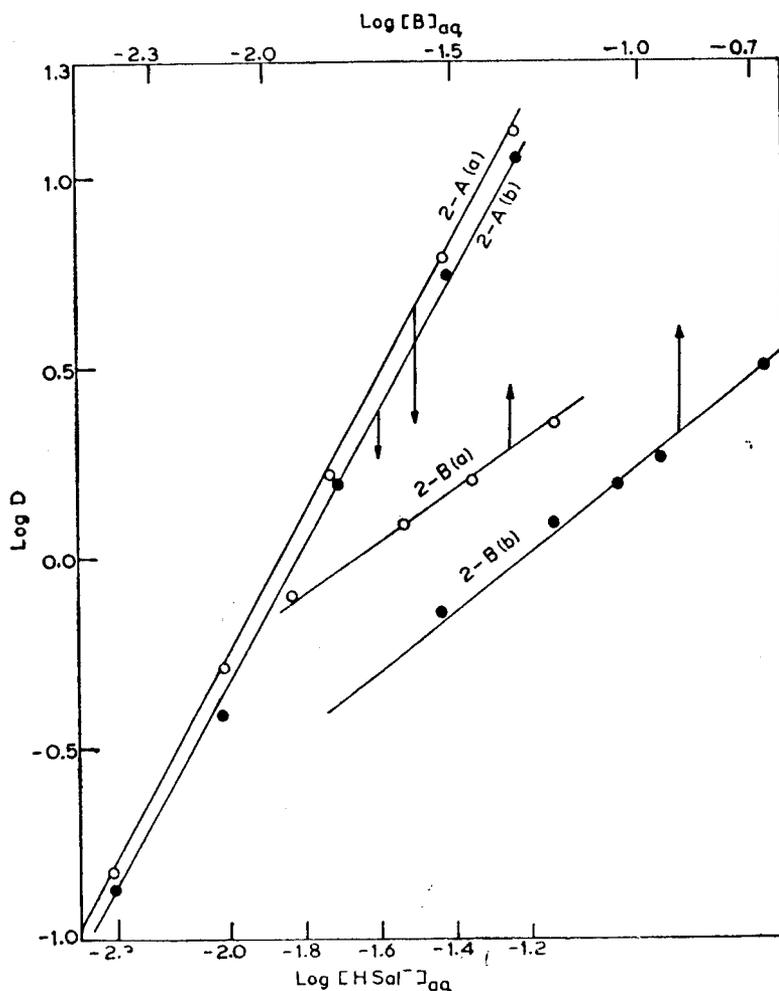
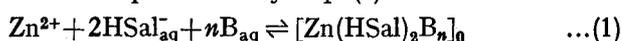


Fig. 2—(A) Variation of distribution ratio with  $[HSal^-]_{aq}$  in the extraction  $Zn^{2+}$  with salicylic acid. [(a) benzene- $\beta$ -picoline; and (b) benzene-pyridine] (B) Variation of distribution ratio with  $[B]_{aq}$  in the extraction of  $Zn^{2+}$  with salicylic acid [(a) benzene- $\beta$ -picoline; and (b) benzene-pyridine]

basicity of  $\alpha$ -picoline and the steric factors may also play a role.

The reaction for the mixed complex formation can be represented by Eq. (1).



The equilibrium constant for the extraction ( $K_{\text{ex}}$ ) is given by Eq. (2).

$$K_{\text{ex}} = \frac{[\text{Zn}(\text{HSal})_2\text{B}_n]_0}{[\text{Zn}^{2+}]_{\text{aq}} [\text{HSal}^-]_{\text{aq}}^2 [\text{B}]_{\text{aq}}^n} \quad \dots(2)$$

Hence,

$$\log D = \log K_{\text{ex}} + 2 \log [\text{HSal}^-]_{\text{aq}} + n \log [\text{B}]_{\text{aq}} \quad \dots(3)$$

$$\text{where } D = \frac{[\text{Zn}(\text{HSal})_2\text{B}_n]_0}{[\text{Zn}^{2+}]_{\text{aq}}}$$

Mass balance for salicylic acid is given by the relation (4)

$$\begin{aligned} [\text{H}_2\text{Sal}]_{\text{total}} &= [\text{H}_2\text{Sal}]_0 + [\text{H}_2\text{Sal}]_{\text{aq}} + [\text{HSal}^-]_{\text{aq}} \\ &+ 2[\text{Zn}(\text{HSal})_2\text{B}_n]_0 + 2[(\text{H}_2\text{Sal})_2]_0 \\ &= [\text{HSal}^-]_{\text{aq}} \{ (\rho s + 1) ([\text{H}^+]/K_1) + 1 \} \\ &+ 2[\text{Zn}(\text{HSal})_2\text{B}_n]_0 + 2K_{\text{dim}}[\text{H}_2\text{Sal}]_0^2 \quad \dots(4) \end{aligned}$$

where  $\rho s$  is the partition coefficient,  $K_1$  is first dissociation constant and  $K_{\text{dim}}$  is the dimerization constant in benzene of salicylic acid.

Since the values of  $[\text{H}_2\text{Sal}]_{\text{aq}} \ll 1$ ,  $[\text{H}_2\text{Sal}]_0^2$  term can be neglected and the relation (4) simplifies to Eq. (5)

$$[\text{HSal}^-]_{\text{aq}} = \frac{[\text{H}_2\text{Sal}]_{\text{total}} - 2[\text{Zn}(\text{HSal})_2\text{B}_n]_0}{\{ (\rho s + 1) ([\text{H}^+]/K_1) + 1 \}} \quad \dots(5)$$

Mass balance for the base is given by the expression (6).

$$[\text{B}]_{\text{total}} = [\text{B}]_{\text{org}} + [\text{B}]_{\text{a1}} + [\text{BH}^+]_{\text{aq}} + n[\text{Zn}(\text{HSal})_2\text{B}_n]_0 \quad \dots(6)$$

Hence,

$$[\text{B}]_{\text{aq}} = \frac{[\text{B}]_{\text{total}} - n[\text{Zn}(\text{HSal})_2\text{B}_n]_0}{\{ P_{\text{B}} + 1 + [\text{H}^+]/K_{\text{BH}^+} \}} \quad \dots(7)$$

where  $P_{\text{B}}$  and  $K_{\text{BH}^+}$  are the partition coefficient and ionization constant respectively of  $\text{BH}^+$  of the base.  $K_{\text{BH}^+}$  values are taken from literature<sup>9,10</sup>. Equilibrium concentrations  $[\text{HSal}^-]$  and  $[\text{B}]_{\text{aq}}$  are calculated making use of Eqs. (5) and (7).

The extraction constant ( $K_{\text{ex}}$ ) is computed using Eq. (3) and the formation constant ( $K$ ) by the relation  $\log K = \log K_{\text{ex}} - \log P_{\text{complex}}$ . Partition coefficient values of the complex ( $P_{\text{complex}}$ ) are calculated from the limiting values of its percent extraction. The results for  $\beta$ -picoline and pyridine systems are given in Tables 1 and 2. The data for quinoline are not given as in view of its distribution<sup>9</sup> being highly in favour of organic phase ( $\rho s > 100$ ) as compared to other bases, it is quite likely that a mixed complex is formed in the organic phase in this case.

The extraction data reveals that the effectiveness of the bases as synergists follows the sequence:  $\beta$ -picoline  $>$  pyridine  $>$  quinoline; the concentrations required for a particular extraction (%) are in the reverse order. The stabilities of the mixed complexes follow the order:  $\beta$ -picoline  $>$  pyridine  $>$   $\alpha$ -picoline. A similar sequence of stability of complexes has been observed in other

TABLE 1 — VARIATION OF  $[\text{HSal}^-]_{\text{aq}}$  AT CONSTANT  $[\text{B}]_{\text{Total}}$  AND  $\rho\text{H}$  ON THE EXTRACTION Zn(II)

$\log [\text{H}_2\text{Sal}]_{\text{Total}}$	$\log D$	$\log [\text{HSal}^-]_{\text{aq}}$	$\log [\text{B}]_{\text{aq}}$
$\beta$ -PICOLINE $[\text{B}]_{\text{Total}} = 0.3M$ AND $\rho\text{H} = 5.0$ (a)			
-2.30	-0.834	-2.311	-1.375
-2.00	-0.294	-2.011	-1.375
-1.70	0.211	-1.710	-1.375
-1.40	0.772	-1.408	-1.375
-1.22	1.121	-1.232	-1.375
PYRIDINE $[\text{B}]_{\text{Total}} = 0.625M$ AND $\rho\text{H} = 5.0$ (b)			
-2.30	-0.873	-2.315	-0.844
-2.00	-0.422	-2.011	-0.844
-1.70	0.197	-1.710	-0.844
-1.40	0.744	-1.408	-0.844
-1.22	1.055	-1.232	-0.844

(a)  $\log K_{\text{ex}} = 5.04$ ; and  $\log K = 4.27$

(b)  $\log K_{\text{ex}} = 4.45$ ; and  $\log K = 3.71$ .

TABLE 2 — VARIATION OF  $[\text{B}]_{\text{aq}}$  AT CONSTANT  $[\text{H}_2\text{Sal}]_{\text{Total}}$  AND  $\rho\text{H}$  ON THE EXTRACTION OF Zn(II)

$\log [\text{B}]_{\text{Total}}$	$\log D$	$\log [\text{B}]_{\text{aq}}$	$\log [\text{HSal}^-]_{\text{aq}}$
$\beta$ -PICOLINE $[\text{H}_2\text{Sal}]_{\text{Total}} = 0.02M$ AND $\rho\text{H} = 5.0$ (a)			
-1.40	-0.334	-2.251	-1.71
-1.10	-0.098	-1.949	-1.71
-0.80	0.080	-1.649	-1.71
-0.62	0.203	-1.472	-1.71
-0.40	0.358	-1.250	-1.71
PYRIDINE $[\text{H}_2\text{Sal}]_{\text{Total}} = 0.02M$ AND $\rho\text{H} = 5.0$ (b)			
-0.90	-0.134	-1.554	-1.71
-0.60	0.094	-1.242	-1.71
-0.42	0.195	-1.066	-1.71
-0.30	0.254	-0.941	-1.71
0.00	0.505	-0.640	-1.71

(a)  $\log K_{\text{ex}} = 5.18$ ;  $\log K = 4.41$ .

(b)  $\log K_{\text{ex}} = 4.68$ ;  $\log K = 3.94$ .

systems also on considerations of both the strength of the base and steric factors<sup>11</sup>.

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