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Application of Regular Solution Theory to Extraction of Salicylaldehyde Oxime Chelates

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The distribution coefficients of salicylaldehyde oxime and its metal chelates, namely of Co(II), Cu(II), and Zn(II) were determined between aqueous acetate phase ($\mu=0.1$) and eight 'inert' organic solvents at 25 °C. On the basis of regular solution theory, the correlation between the distribution coefficients of the ligand (P_{HA}) and that of the metal chelates (P_M) expressed by $\log P_M = n \log P_{HA} + \text{const}$, was shown to be valid satisfactorily in most of the systems. Hexane and cyclohexane showed abnormal behaviour in extraction with Cu(II), while with Zn(II) extraction to the desired level was not possible with these two solvents. A good correlation was also observed between the distribution coefficient of salicylaldehyde oxime and the 'solubility parameter' of the solvents and the solutions are shown to be regular.

In the solvent extraction of metal complexes, studies have been made qualitatively in several systems. Also in many studies the solvents have been chosen semiempirically without understanding what physicochemical properties of the solvent govern the distribution of the species. The solvent plays an important role not only in the effective separation of the species from a mixture but also in synergistic studies, organic phase reactions, kinetics of extraction *etc.* Thus, role of solvent is quite important and a quantitative approach on the basis of regular solution theory[1] has been made. Studies have revealed that the distribution coefficient of a species can be correlated with the solubility parameter of the organic solvent. Also a correlation can exist between the distribution coefficients of the ligand and its metal chelate when the nature of their interaction with solvent molecules are same. Such correlations have been established by Suzuki, Akiba, and others in their studies with thenoyltrifluoroacetone with different metals and different solvents[2–7] and by Honjo *et al.* with thiothenoyl trifluoroacetone.[8] Similar relations for benzoyltrifluoroacetone and for 4-benzoyl-5-methyl-2-phenyl-4-pyrazolin-3-one (BMPP) have been recently established.[9] The present study on above lines has been described with salicylaldehyde oxime as the ligand. Salicylaldehyde oxime has been specifically selected due to its characteristic nature of being biprotonic, and having fair solubility in water, these two properties being absent in the ligands studied so far.

Experimental

Material. Salicylaldehyde oxime (Merck) was used as supplied without further purification.

Carbon tetrachloride, chlorobenzene, cyclohexane (all BDH), chloroform, dichloromethane, hexane (all Merck), benzene (IDPL), and toluene (Rechem) were purified whenever necessary and used.

Co(II), Cu(II), and Zn(II) solutions were prepared from cobalt acetate, copper(II) sulfate, and zinc sulfate respectively (all A. R. grade).

Procedure. *Determination of Distribution Coefficient (P_{HA}) of Salicylaldehyde Oxime*: Aqueous solution of salicylaldehyde oxime of suitable concentration was prepared at pH=1 and its absorbance measured at 258 nm in a spectrophotometer (SP-700A PYE UNICAM) and the molar absorptivity coefficient was determined ($\varepsilon=8400$). Solution of salicylaldehyde oxime of known concentration in the desired organic solvent was equilibrated with aqueous phase (pH=1) and the absorbance of suitable aliquot of aqueous phase was measured. Knowing $\varepsilon=8400$, and the concentration in the aqueous phase, by difference the concentration in organic phase was determined and hence the distribution coefficient. The values of P_{HA} with different solvents are presented in Table 1.

Determination of Distribution Ratio (K_d) of the Metal Salicylaldehyde Oxime Chelate: Ten milliliters of the aqueous phase containing the acetate buffer at appropriate pH and the metal ion at 10—20 ppm level was equilibrated with 10 ml of the desired organic solvent containing salicylaldehyde

Table 1. Distribution coefficients of salicylaldehyde oxime and extraction constants of metal salicylaldehyde oxime

No.	Solvent	δ[a]	ε[b]	$\log P_{HA}$	$\log K_{ex}$		
					Co(II)	Cu(II)	Zn(II)
1	Cyclohexane	8.2	2.0	−0.59	−7.32±0.02	2.62±0.04[c]	d)
2	Hexane	7.3	1.9	−0.53	−7.50±0.02	2.82±0.10[c]	d)
3	Carbon tetrachloride	8.6	2.2	0.104	−7.40±0.02	2.22±0.02	−11.85±0.04[e]
4	Toluene	8.9	2.4	0.58	−8.56±0.02	1.12±0.02	−11.10±0.04[f]
5	Benzene	9.15	2.3	0.98	−9.23±0.02	0.96±0.04	−12.18±0.02[e]
6	Chlorobenzene	9.5	5.6	0.68	−8.30±0.10	1.56±0.04	−12.20±0.10[e]
7	Chloroform	9.3	4.8	1.00	−9.68±0.04	0.86±0.08	−11.14±0.02[f]
8	Dichloromethane	9.7	9.1	1.18	−9.00±0.06	0.60±0.08	−11.30±0.10[f]

a) δ: Solubility parameter. b) Dielectric constant. c) Slope=3. d) No quantitative extraction possible. e) Extracted species contain one ligand molecule. f) Extracted species contain two ligand molecules.

oxime (10^{-2} M; 1 M = 1 mol dm^{-3}) for 5 min. After equilibration, pH of aqueous phase was measured and the concentration of metal in the aqueous phase was determined by atomic absorption spectrophotometer (SP-191 PYE UNICAM) and then the distribution ratio was determined. Experiments were also done with varying ligand concentration (2×10^{-3} M to 10^{-2} M) in the organic phase while maintaining a fixed pH in the aqueous phase.

Results and Discussion

The extraction equilibria for the distribution of a bivalent metal (M) with a ligand (HA) can be written as:

$$HA_{aq} \rightleftharpoons HA_{org} : P_{HA}, \quad (1)$$

$$HA_{aq} \rightleftharpoons H^+_{aq} + A^-_{aq} : K_a, \quad (2)$$

$$M^{2+}_{aq} + nA^-_{aq} \rightleftharpoons MA^{(2-n)+}_{n,aq} : \beta_n, \quad (3)$$

$$MA_{2,aq} \rightleftharpoons MA_{2,org} : P_M, \quad (4)$$

where the subscripts org and aq represent the species in the organic and aqueous phase respectively. The symbol on the right side represents the equilibrium constant for that particular step.

Under the conditions when the concentration of the metal chelate is sufficiently low compared to that of the metal, M^{2+}, in the aqueous phase and if the metal species exist as MA_2 chelate in the organic phase then the distribution ratio, K_d, of the chelate can be given as:

$$K_d = P_M\beta_2(A^-)^2, \quad (5)$$

where A^- is the anion of the ligand and its concentration can be determined from the expression

$$[A^-] = \frac{[HA]_{org,ini}}{[P_{HA}+1][H^+]/K_a+1}. \quad (6)$$

The experimental extraction behaviour of metal complexes can be followed through theoretical plots and slope analysis. Plots of $\log K_d$ *vs.* pH and $\log K_d$ *vs.* log of ligand concentration indicate the number of hydrogen ions released and the number of ligand molecules involved respectively, during the complexation process. Further, plots of $\log K_d$ *vs.* pA (pA = $-\log [A^-]$) can be drawn at fixed pH or at fixed ligand concentration. These plots give negative slopes indicating the number of ligand molecules participating in the simple complexation process. The distribution coefficient (P_M) of the chelate, generally, cannot be measured experimentally and it is related to the measurable distribution ratio, K_d, as a function of pA. Mathematically,

$$K_d = P_M \cdot f[A^-] \quad (7)$$

Thus, if the value of distribution ratio could be known at a fixed pA, it is possible to relate the distribution coefficient of the chelate with the distribution coefficient of ligand and the relation

$$\log P_M = n \log P_{HA} + \text{const}, \quad (8)$$

could be validated as expected from regular solution theory.[12]

In the present work the correlation shown by Eq. 8 has been found to obey satisfactorily with the three metals studied.

Co(II)–Salicylaldehyde Oxime System. The extraction takes place in the pH range 5.6 to 6.6 in all the eight solvents. Slope analysis of plots, discussed already, gave values of two indicating release of two hydrogen ions and involvement of two molecules of salicylaldehyde oxime. It is thus obvious that one hydrogen ion is released from each ligand molecule. The mechanism can be written as:

$$Co^{2+}_{aq} + 2(H_2\cdot sal)_{org} \rightleftharpoons Co(H\cdot sal)_{2\,org} + 2H^+_{aq}, \quad (9)$$

where ($H_2\cdot$sal) represents one salicylaldehyde oxime molecule.

The values of extraction constants, $\log K_{ex}$, for the above reaction for different solvents have been calculated from the relation

$$\log K_{ex} = \log K_d - 2pH - 2\log [H_2\cdot sal] \quad (10)$$

and are presented in Table 1.

Salicylaldehyde oxime has fair solubility in water. A correction is to be applied since the actual value of the ligand concentration will be less than that taken for equilibration in the organic phase. Utilising the P_{HA} values, the solubility correction has been incorporated while computing the values of K_{ex} presented in Table 1.

Plots of $\log K_d$ *vs.* pA also give negative slope of two for all solvents. Figure 1 indicates such plots for some solvents. From these plots, the values of $\log K_d$ at a fixed pA were plotted against $\log P_{HA}$, and it was found that there is a satisfactory regularity with most of the solvents.

Cu(II)–Salicylaldehyde Oxime System. The extraction takes place in acidic range *i.e.*, pH range 1 to 2 in all solvents. Slope analysis confirms the mechanism similar to the extraction in Co(II) system shown in Eq. 9, in all solvents except hexane and cyclohexane. These two solvents, however, show different behaviour and they give slope value of ≈3 in $\log K_d$ *vs.* pH and $\log K_d$ *vs.* $\log [H_2\cdot sal]$ plots. This indicates involve-

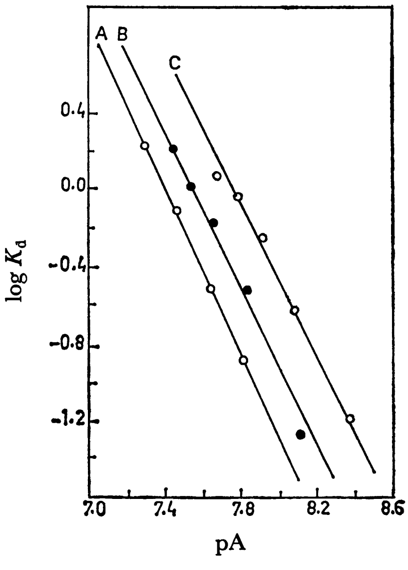

Fig. 1. Variation of distribution ratio of cobalt-salicylaldehyde oxime chelate as a function of pA.
A: Benzene; $(HA)_0 = 10^{-1}$ M, B: chlorobenzene; pH = 6.4, C: dichloromethane; pH = 6.6.

ment of three molecules of ligand and release of three hydrogen ions and the complex will be anionic. Since extraction does take place into the organic phase, this anion perhaps forms an ion pair chelate, of the type $Cu(H\cdot sal)_3^-\cdot H^+$ where the H^+ probably coming from the aqueous phase. The mechanism is probably

$$Cu^{2+}_{aq} + 3(H_2\cdot sal)_{org} \rightleftharpoons 3H^+_{aq} + Cu(H\cdot sal)^-_{3,aq} \longrightarrow Cu(H\cdot sal)_3^-\cdot H^+_{org}. \quad (11)$$

The formation of higher complexes involving three ligand molecules may be due to nature of these two solvents. These two solvents, show more resemblance to aqueous phase so far as the distribution coefficient of salicylaldehyde oxime with these two solvents are concerned. The P_{HA} values are so low that the anion concentration of salicylaldehyde oxime can be expected to be high in the aqueous phase resulting in the formation of higher complexes. In the case of both solvents at higher pH (>2) the extraction declines and this can be attributed to low availability of H^+ to form ion pair. The values of log K_{ex} with different solvents are given in Table 1.

In the log K_d *vs.* log P_{HA} plot, shown in Fig. 2, there is satisfactory regularity. Hexane and cyclohexane show abnormal deviation and it is difficult to pinpoint the reason with the present information.

Zn(II)–Salicylaldehyde Oxime System. Dahl, in his studies[10] has emphasized the importance of reagent concentration in the extraction of Zn(II) with various solutions of salicylaldehyde oxime. The present studies also indicated requirement of different ligand concentration in different solvents, 5×10^{-2} M solution of salicylaldehyde oxime in benzene, toluene, chlorobenzene, and carbon tetrachloride and 10^{-1} M solution were needed in chloroform and dichloromethane for extraction which was in the pH range 6.4 to 7.6; in case of cyclohexane, however, it was noted that quantitative extraction could not be achieved with 10^{-1} M or even slightly higher concentration. Still higher concentration rendered the ligand insoluble in these two solvents and hence no satisfactory extraction could be done with hexane and cyclohexane.

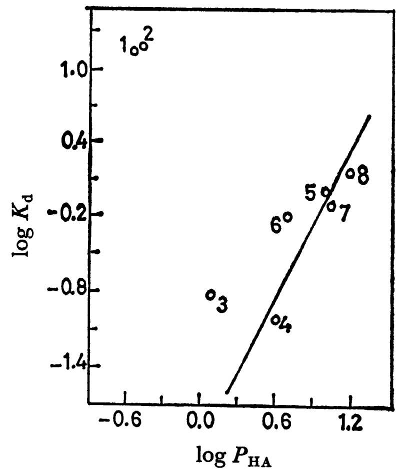

Fig. 2. Correlation between the distribution coefficient of salicylaldehyde oxime and that of its copper chelate. The numbers in the figure correspond to those in Table 1.

Analysis of plots reveal interesting results. With toluene, chloroform, and dichloromethane the extraction mechanism was similar to those noted in Co(II) and Cu(II) system. But with carbon tetrachloride, benzene and chlorobenzene slope analysis indicated release of two hydrogen ions and involvement of only one ligand molecule in the complexation. This indicates the release of the two hydrogen ions from the same salicylaldehyde oxime molecule and the mechanism can be written as:

$$Zn^{2+}_{aq} + (H_2\cdot sal)_{org} \rightleftharpoons Zn(sal)_{org} + 2H^+_{aq}. \quad (12)$$

The extraction constant values are shown in Table 1.

In the plots of log K_d *vs.* log P_{HA}, slope of two was observed for toluene, chloroform, and dichloromethane while for carbon tetrachloride, benzene, and chlorobenzene slope of one was noted. This is in conformity with the predicted mechanism of involvement of only one molecule of ligand for the latter three solvents. It can be seen from Fig. 3 that there is good regularity with all solvents.

The molar volume of salicylaldehyde oxime was determined to be 100±5.0 through density measurement using petroleum ether as solvent. This experimental value was checked to be correct by the graphical method employed for β-diketones by Wakahayashi *et al.*[11,12] and later by Kojima *et al.*[13] Knowing the molar volume, the solubility parameter (δ) of salicylaldehyde oxime in different solvents, using hexane as standard, was calculated employing Siekierski-Olszer equation.[14] The solubility parameter value was found to be 13.0±0.8. A plot between the distribution coefficient of the ligand and the solubility parameter of the solvents gave a parabolic curve, as Fig. 4 shows, and this is in accordance with regular solution theory. The points in the figure for different solvents are on the same side since $\delta_{ligand}>\delta_{solvent}$ for all the solvents and since all points fall in the parabola with no deviation it can be concluded that the solutions of salicylaldehyde oxime in different solvents are regular.

The basis for regular solution theory is on the concept of solubility parameter. The importance of this in relation to other parameters like dielectric constant was also investigated, on the basis of Pearson's cor-

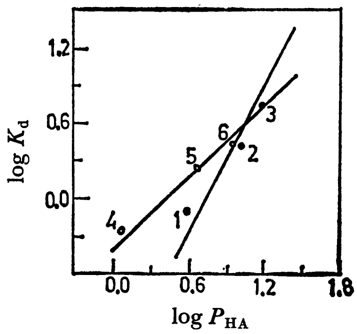

Fig. 3. Correlation between the distribution coefficient of salicylaldehyde oxime and that of its zinc chelate at a fixed pA.

1: Toluene, 2: chloroform, 3: dichloromethane (at pA=6.2), 4: carbon tetrachloride, 5: chlorobenzene, 6: benzene (at pA=15.0).

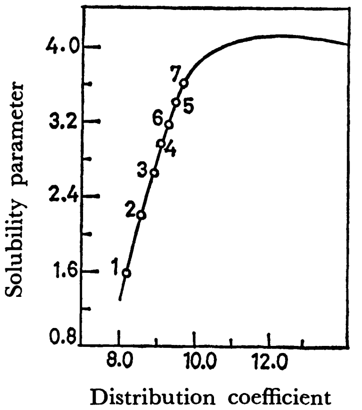

Fig. 4. Distribution of salicyladehyde oxime as a function of solubility parameter of organic solvents based on Siekierski-Olszer equation using Hexane as standard.
1: Cyclohexane, 2: carbon tetrachloride, 3: toluene, 4: benzene, 5: chlorobenzene, 6: chloroform, 7: dichloromethane.

relation coefficient. The correlation coefficient is used to measure the degree of linear correlation between two variables. Pearson's correlation coefficient is given by

$$\text{Correlation coefficient} = \frac{\sum \delta x . \delta y}{\sqrt{\sum(\delta x)^2 \times \sum(\delta y)^2}},$$

where δx is deviation from the mean of one of the first variable and δy is the deviation from the mean of the corresponding second variable. When the correlation coefficient is +1 there is a positive correlation between the two variables and all the points fall exactly on a line. If the points are completely random on the graph the correlation coefficient will be zero. In the present study, in the plot between $\log P_{HA}$ and δ, the solubility parameter, the correlation coefficient is obtained as +0.88 while in the plot of $\log P_{HA}$ *vs.* ε, the dielectric constant the value is +0.58. Thus, the values P_{HA} are much better correlated with solubility parameter than with dielectric constant.

In conclusion, it may be said that for a ligand like salicylaldehyde oxime, regular solution theory appears to be valid from the present studies and it is thus possible to make choice of appropriate solvent for extraction.

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