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# Physico-chemical Studies of Metal Extractants: Hydroxamic Acids

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This paper presents the results of the determination of various physical parameters of N-arylsubstituted/hydroxamic acids. The parameters investigated are densities, molar volumes and their partition data between different organic solvent-aqueous systems. An attempt is made to correlate these data with theoretical calculations based on regular solution theory, and to investigate solubility parameters of these reagents. These reagents behave as organic bases in presence of strong acidic solutions. Thus, their protonation has been studied in aqueous hydrochloric acid solutions. The relevant $pK_{BH^+}$ values have been calculated according to Hammett acidity function method (HAFM), Bunnett olsen method (BOM) and excess acidity method (EAM) methods.

## INTRODUCTION

The versatile metal extractants, N-arylsubstituted hydroxamic acids of the general formula RNOH-R′C=O (where R and R′ are phenyl or substituted phenyl groups), besides their tremendous applications in all spheres of life[1–6], their physico-chemical properties have received little attention[7–10]. The solvent extraction is one of the most widely used separation methods, but the factors that affect the magnitude of the distribution constants are not completely understood. In chelate extraction systems, inert solvents are mainly used. Many papers appeared in the literature describing the reaction between reagent and metal ions[1, 2, 11–15]; nevertheless, the effect of solvent on distribution constant has not been treated theoretically, though it constitutes one of the fundamental features of solvent extraction. With this view in mind, we had undertaken the work and determined the various physical parameters of these metal extractants. Densities of these reagents have been computed for the first time to calculate molar volumes. Solubilities in water and various organic solvents and their distribution constants between different organic solvent-aqueous systems have been determined. An attempt is made to correlate these partition data with theoretical calculations based on regular solution theory. In solvent extraction systems, if we can know the fundamental parameters of the solvent, the aqueous solutions and the solute, we shall be able to pre-estimate the behaviour of solute and, moreover, the role of solvent or diluent. The knowledge of solubility parameter values will prove fruitful not only in choosing proper solvent for extraction but also in extending the range of extraction method as well.

These metal extractants serve as weak organic bases in presence of acidic solutions. Since, as metal extractants, most of the studies were carried out in hydrochloric acid medium, the protonation behaviour of these reagents has been studied in aqueous hydrochloric acid at 25 ± 1°C. Relevant $pK_{BH^+}$ values were calculated according to Hammett acidity function method (HAFM), Bunnett Olsen method (BOM) and excess acidity method (EAM) to compare between them.

## EXPERIMENTAL

Hydroxamic acids were prepared according to the method reported[16] and purified by crystallisation from benzene. C.P. grade hydrochloric acid was used for extraction work, because iron(II) present in it does not interfere. A.R. hydrochloric acid was used for determining distribution ratios. Hydrochloric acid-water mixtures were prepared by dilution of A.R. concentrated, standardised acid, with glass-distilled water. Saturated solution of ammonium metavanadate was prepared in glass-distilled water. Chloroform used was shaken five or six times with equal volumes of water to remove the ethanol (present as preservative) and distilled. We stored this in an amber bottle in a cool place.

Spekol molde EK-1 (Carl Zeiss, Jena) was used for the measurement of absorbance and DMS 100S UV-VIS Varian spectrophotometer was used for recording ultra-violet spectra using 10 mm matched silica cells. All the calculations were carried out on a Wipro SX-386 computer under MS-DOS.

**Measurement of $K_D$ and D:** Distribution constants, $K_D$, in between water and various organic solvents, were determined by taking, 10 to 15 mL of solution of the compound of known concentration (*ca.* 50 mg) in an organic solvent. This was shaken with 25 to 100 mL of aqueous phase. Although the complete equilibration was attained in less than 20 min, the shaking time of 30 min was chosen for the present work. The solutions were allowed to stand for about 1 h and then the phases were separated and analysed by colorimetric method using vanadium(V). Distribution ratio, D, as a function of hydrochloric acid concentration was determined by a quick technique[7] to avoid hydrolysis.

**Analysis of the Samples:** The determination of reagent content by its absorbance in UV gave unsatisfactory results because of variation of its spectral characteristics in pure solvent and in aqueous acidic solutions. The reagent concentrations were therefore determined colorimetrically using vanadium(V) method[2]. This method has the advantage that side reactions do not necessarily invalidate the measurements.

**Density measurements:** Hydrostatic weighing method was used for density measurements. Repeated weighings were performed to record the accurate results. All the weighings were corrected for air buoyancy.

## RESULTS AND DISCUSSION

The solvent extraction method[2] was successfully used for determining the concentration of the reagent in all experiments.

The distribution constants, $K_D$, for the partition of four hydroxamic acids between aqueous phase and various immiscible organic solvents are given in Table 1, along with the relevant data on densities, molar volumes and solubility parameters.

$K_D$ values can be regarded as the distribution constants for the monomeric form of these reagents, as there is no significant variation in $K_D$ involved with

### TABLE-1
### VARIOUS PHYSICAL PARAMETERS OF N-ARYL-SUBSTITUTED-HYDROXAMIC ACIDS

| Hydroxamic acid / Solvents | N-phenyl-4-nitro-benzo- | | N-phenyl-*o*-chloro-benzo- | | N-*p*-chloro-phenyl-*p*-methoxy-benzo- | | N-*p*-chloro-phenyl-cinnamo- | |
|---|---|---|---|---|---|---|---|---|
| | $K_D$ | $\delta_c$ | $K_D$ | $\delta_c$ | $K_D$ | $\delta_c$ | $K_D$ | $\delta_c$ |
| Benzene | 99.55 | 14.98 | 67.87 | 14.78 | 712.07 | 14.59 | 2044.00 | 14.71 |
| Chloro benzene | 79.83 | 14.96 | 2.26 | 15.21 | 291.00 | 14.66 | 1540.38 | 14.73 |
| *o*-Di chloro benzene | 47.50 | 15.47 | 130.79 | 14.94 | 387.09 | 15.32 | 1333.13 | 15.05 |
| Toluene | 48.19 | 14.89 | 50.90 | 14.66 | 1220.00 | 14.40 | 859.19 | 14.67 |
| *n*-Hexane | 10.12 | 14.27 | 1.24 | 14.03 | 10.92 | 14.16 | 19.95 | 14.23 |
| Cyclo hexane | 75.68 | 14.53 | 2.31 | 15.19 | 28.29 | 14.95 | 45.28 | 15.02 |
| Carbon tetrachloride | 10.57 | 14.91 | 20.83 | 14.58 | 96.85 | 14.58 | 155.71 | 14.67 |
| Chloroform | 240.00 | 14.97 | 212.37 | 14.74 | 226.32 | 14.81 | 7000.00 | 14.69 |
| 1,2-Dichloro ethane | 79.23 | 15.26 | 222.40 | 14.88 | 206.25 | 15.02 | 713.00 | 15.08 |
| Density ($gm^{-1}$) | 1.0105 | | 1.5784 | | 1.4410 | | 1.0417 | |
| Molar volume [$v_1$] | 255.32 | | 156.81 | | 192.57 | | 262.53 | |

TABLE-2

D AND % PROTONATION OF N-ARYL SUBSTITUTED/HYDROXAMIC ACIDS AS A FUNCTION OF HYDROCHLORIC ACID CONCENTRATION

| Hydroxamic acid / Hydrochloric acid, M | N-Phenyl-4-nitro-benzo- | | N-Phenyl-*o*-chloro-benzo- | | N-*p*-chloro-phenyl-*p*-methoxy-benzo- | | N-*p*-Chloro-phenyl-cinnamo- | |
|---|---|---|---|---|---|---|---|---|
| | D | % Protonation | D | % Protonation | D | % Protonation | D | % Protonation |
| 1. | 10.70 | 10.51 | 24.90 | 5.85 | 131.54 | 5.85 | 360.00 | 2.79 |
| 2. | 10..43 | 18.23 | 24.60 | 10.56 | 117.04 | 10.56 | 335.61 | 5.18 |
| 3. | 9.37 | 28.93 | 19.20 | 17.74 | 102.04 | 17.74 | 290.40 | 9.07 |
| 4. | 4.87 | 50.00 | 15.60 | 34.63 | 88.01 | 34.63 | 240.00 | 19.68 |
| 5. | 3.46 | 66.61 | 12.00 | 51.38 | 69.77 | 51.38 | 170.67 | 32.82 |
| 6. | 2.26 | 79.55 | 9.40 | 67.33 | 43.69 | 67.33 | 135.40 | 48.79 |
| 7. | 1.23 | 88.82 | 6.50 | 80.80 | 27.93 | 80.80 | 100.22 | 67.84 |
| 8. | 0.74 | 93.67 | 4.60 | 88.68 | 15.95 | 88.68 | 70.60 | 78.37 |
| 9. | 0.38 | 96.57 | 2.50 | 93.72 | 8.41 | 93.72 | 46.31 | 87.35 |
| 10. | 0.26 | 98.25 | 1.50 | 96.75 | 4.01 | 96.75 | 26.05 | 93.23 |

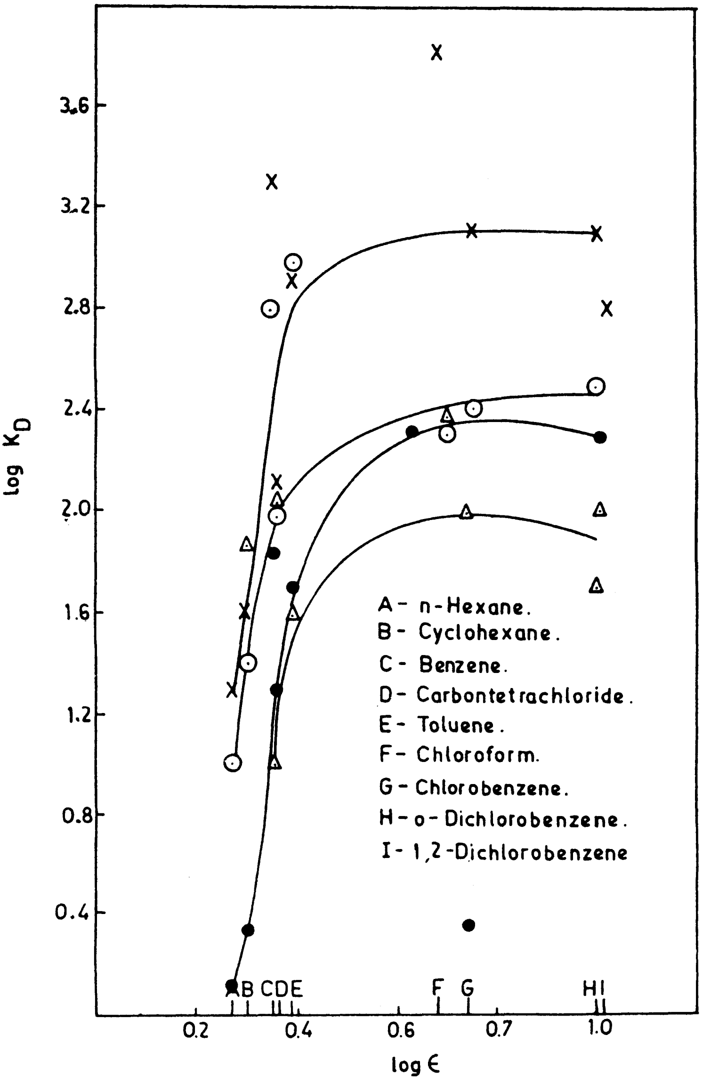

Fig. 1. Log-log plot of $K_DV_s\varepsilon$.
△—△-N-Phenyl-4-nitrobenzo-; ●—●-N-Phenyl-*o*-chloro-benzo; ⊙—⊙-N-*p*-Chloro-*p*-methoxy-benzo; ×—× N-*p*-Chloro-phenyl-cinnamohydroxamic acids.

total reagent concentration. At the same time, the ionisation constants of these reagents in water are small, $pK_a$ being between 8–1, and so the concentration of their anionic species in the aqueous phase is negligible. $K_D$ values were determined to get information about the suitability of the solvent for extraction work and these values are further helpful to calculate the solubility parameters and thus can be correlated with regular solution theory.

A regular solution is defined as one which has no chemical interaction between solute and solvent molecules and no change in states of association and orientation by mixing. To such solutions, Hildebrand's theory of regular solution[17] can be applied according to which solubility parameter, δ, of a substance is defined as $-\delta = (\delta E^v/V)^{1/2}$, where $\delta E^v/V$ is energy of vapourization per unit volume.

Heat of mixing of solute and solvents depends on the difference of their δ values. The solubility parameters of hydroxamic acids are calculated following the equation:

$$\ln \frac{\phi_{1,\,org}}{\phi_{2,\,aq}} = \frac{V_1}{RT}[(\delta_c - \delta_{aq})^2 - (\delta_c - \delta_{org})^2] + V_1\left[\frac{1}{V_{org}} - \frac{1}{V_{aq}}\right] \qquad \ldots(1)$$

where, $\delta_c$ = solubility parameter of solute, $\phi_1$ = volume fraction of solute, $\phi_2$ = volume fraction of the solvent in the solution, $V_1$ = molar volume of the solute, $\delta_{aq}$ = solubility parameter of aqueous phase, $V_{aq}$ = volume of aqueous phase for all organic solvents and $V_{org}$ = volume of organic solvent.

At low concentration of solute, $\phi_{aq} = \phi_{org} = 1$, and for low concentration of solute used in the present investigation, it can be assumed that $\frac{\phi_{1,\,org}}{\phi_{1,\,aq}} = K_D$, where $K_D$ is experimental distribution constant; $K_D$ can thus be related directly to the right hand side terms of equation (1).

A log-log plot of $K_D$ values against the dielectric constants of the organic solvents gives an approximately parabolic relationship as shown in Fig. 1.

To calculate the molar volume, $V_1$, densities of these hydroxamic acids were determined following hydrostatic weighing method at ±30°C. The method was found convenient as well as accurate provided the following precautions were taken. Like, weighings were done at such an interval of time that the air density remained alomost constant. The glass tube was weighed in water with and without the sample so that its buoyancy was cancelled. Solubility parameter for water and for organic solvents, δ, were obtained from literature. The data on solubility parameters of these reagents showed that the calculated values of $\delta_c$ for the solvents investigated here, are reasonably constant. This indicates that properties of hydroxamic acid solutions in these solvents are at least qualitatively similar to those postulated for regular solutions.

In solvent extraction systems, if we can know the fundamental parameters of the solvent, the aqueous solutions and the solute, we shall be able to pre-estimate the behaviour of solute and, moreover, the role of solvent or diluent.

Table 2 represents the data of percentage protonation and distribution ratios, D, between an organic solvent carbon tetrachloride and increasingly hydrochloric acid concentration (1 to 10 M). Percentage of protonated hydroxamic acids is calculated following the equation, % protonated $= \frac{h_0}{h_0 + K_{BH^+}} \times 100$, where $H_0 = -\log h_0$. The percentage of protonated species increases and D decreases with increasing hydrochloric acid concentration. This suggests that the protonated species or conjugate acid has a hydrophilic character. Carbon tetrachloride was found to be the most suitable solvent for physico-chemical studies because of its favourable physical properties.

In acidic solutions, $HA + H^+ \overset{pK_{BH^+}}{\rightleftharpoons} H_2A^+$, where, HA is the base (hydroxamic acid) and $H_2A^+$ is the protonated species or a conjugate acid of base HA. Ionisation ratio, $I = C_{H_2A^+}/C_{HA}$, where $C_{HA}$ and $C_{H_2A^+}$ are the molar concentration of the hydroxamic acid and protonated species, respectivley, and $I = K_D - D/D$, where $K_D$ is the thermodynamic distribution constant of hydroxamic acids between the organic layer and aqueous acid in the region where appreciable protonation is occurring and is estimated by the equation $D = K_D - Dh_0/K_{H_2A^+}$, where $K_{H_2A^+}$ can be written as $K_{BH^+}$ ($pK_{BH^+} = -\log K_{BH^+}$) or from the intercept of a plot D *vs.* $Dh_0$ or by calculating from least square method. All the three methods used here, gave the closely matched results. The protonation analysis of these reagents is done by three classical procedures to compare between them.

The first method is the traditional Hammett acidity function method, (HAFM)[18], suitably modified by using acidity function appropriate to the class of bases under consideration. For each compound $pK_{BH^+}$ was obtained by plotting log I against $H_0$ according to the equation $\log I = pK_{BH^+} - H_0$. Because of the structural similarity of hydroxamic acids to amides, it is of interest to analyse the ionisation data in terms of amide acidity function, $H_A$, in the equation

$$\log I = pK_{BH^+} - H_A \qquad \ldots (2)$$

The second and more general method of determining $pK_{BH^+}$ is to use the linear free energy approach originally proposed by Bunnett and Olsen. Bunnett- Olsen method (BOM)[19] provided that the plot of left hand side of equation (3).

$$\log I + H_0 = \phi(H_0 + \log C_{H^+}) + pK_{BH^+} \qquad \ldots (3)$$

against $(H_0 + \log C_{H^+})$ is linear, $C_{H^+}$ is proton concentration and slope $\phi$ is a measure of susceptibility of the equilibrium to changing acid concentration.

Another extrapolative method is the excess acidity method, EAM, which is an earlier approach proposed by Marziano and Passerini[20], developed by Yates and Cox[21]. This method involves proton concentration, $C_{H^+}$, and concept of excess medium acidity, X, is summarised as

$$\log I = pK_{BH^+} + \log C_{H^+} + m^*X \qquad \ldots (4)$$

where X is excess acidity. Values of X as a function of weight per cent composition are available for the aqueous hydrochloric acid systems[22], as well as, these are calculated using the formula $X = -(H_A + \log C_{H^+})$, or by substituting the reported estimates of $pK_{BH^+}$ and m* for each base in the equation $X = (\log I - \log C_{H^+} - pK_{BH^+})/m^*$ and on the basis of data available for 35 conjugate acids of hydroxamic acids. The X values calculated tally very closely as shown in Table-3.

TABLE-3
VALUES OF X AS A FUNCTION OF HYDROCHLORIC ACID

| HCl, M | X | |
|---|---|---|
| | $-[H_A + \log C_{H^+}]$ | $-(\log I - \log C_{H^+} - pK_{BH^+})/m$ |
| 1. | 0.50 | 0.54 |
| 2. | 0.48 | 0.49 |
| 3. | 0.56 | 0.55 |
| 4. | 0.83 | 0.83 |
| 5. | 1.03 | 1.06 |
| 6. | 1.24 | 1.26 |
| 7. | 1.48 | 1.52 |
| 8. | 1.70 | 1.73 |
| 9. | 1.93 | 1.97 |
| 10. | 2.18 | 2.23 |

Table-4 is a summary table presenting a comparative data of $pK_{BH^+}$ determined in 4–10 M hydrochloric acid solution, by HAFM, BOM and EAM methods, along with the values of slope (m), coefficient of correlation (r) and standard deviation ($\sigma$). Insufficient protonation at lower acidity hinders the experimental determination of $pK_{BH^+}$. An examination of data reveals that for weak bases, the three different approaches give different $pK_{BH^+}$ values. The values of $pK_{BH^+}$ determined by EAM are most negative among the three methods. It is interesting that the $pK_{BH^+}$ values of structurally similar compounds, amides also furnished different $pK_{BH^+}$ values by different procedures[23]. Difference in $pK_{BH^+}$ values has been found for other weak bases also. In case of halogen substituents, when chlorine is present at *ortho-* position in the phenyl ring, it increases the basicity of the protonated reagent whereas, conjugate acid of that hydroxamic acid is less basic where chlorine is present at *para* position and presence of methoxy group in it further decreases the basicity of the reagent. Nitro groups are strongly electron-withdrawing oxygen-containing groups, which would be expected to interact strongly and specifically with the solvent through formation of strong O—H—O type hydrogen bonds. With increasing acidity the water content decreases and thus solvation decreases and influence of substituents on reaction centre should go up. So the conjugate acids of nitro substituted hydroxamic acids are strong acids as compared to halo derivatives, and the parent product PBHA. Although the chloro-derivatives are also electron-withdrawing, it would be expected to produce weaker and less specific solute-solvent interaction.

In those cases in which disagreement between the three methods is observed, the question arises, as to which method gives the more accurate estimate of the real thermodynamic quantity. However, it has been observed that particularly in case of weak organic bases HAFM method works better than BOM and EAM. At the same time, EAM method is capable of providing mechanistic information, which the other methods cannot.

TABLE-4
$pK_{BH^+}$ OF N-ARYL SUBSTITUTED/HYDROXAMIC ACIDS BY HAFM, BOM AND EAM METHODS

| Hydroxamic acid | HAFM | | | | BOM | | | | EAM | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $pK_{BH^+}$ | m | r | σ | $pK_{BH^+}$ | ϕ | r | σ | $pK_{BH^+}$ | m* | r | σ |
| N-Phenyl-4-nitrobenzo- | −1.43 | 0.94 | 0.997 | 0.05 | −1.20 | 0.16 | 0.907 | 0.04 | −1.74 | 1.20 | 0.994 | 0.07 |
| N-Phenyl-2-chlorobenzo- | −1.93 | 0.89 | 0.997 | 0.05 | −1.65 | 0.19 | 0.954 | 0.03 | −2.11 | 1.09 | 0.997 | 0.04 |
| N-*p*- chlorophenyl-4-methoxybenzo- | −1.71 | 1.03 | 0.999 | 0.02 | −1.43 | 0.20 | 0.999 | 0.03 | −1.87 | 1.03 | 0.999 | 0.02 |
| N-*p*-chlorophenyl-cinnamo- | −2.04 | 0.97 | 0.982 | 0.14 | −1.56 | 0.29 | 0.973 | 0.03 | −2.15 | 1.08 | 0.990 | 0.08 |

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