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Properties of Cycloalkylhydroxamic Acids and Their N-Substituted Derivatives as New Extractants for Metal Ions

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The results of the chemical and thermal stabilities as well as the solubility measurements of 14 cycloalkylhydroxamic acids and their N-substituted derivatives are presented and discussed. These results are useful for the preliminary evaluation of the title compounds as new extracting agents.

Hydroxamic acids were previously known as good extracting agents with a number of metal ions (*1*). They were used successfully for the colorimetric determination and selective extractants for various metal ions (*2-4*). Among the factors used to evaluate new extractants are the following: (i) solubility in both organic and aqueous media, (ii) thermal stability, and (iii) chemical stability toward a number of mineral acids as well as the extraction power toward metal ions (*5*). In the present work, the results of study of the above behaviors (i-iii) of recently (*6*) synthesized cycloalkylhydroxamic acids (I-XV, Table I) are presented.

Solubility Behaviors. The results (Table III) showed that, in general, the solubility behaviors are greatly improved (i.e., increases and decreases in organic and aqueous solvents, respectively) upon N-substitution and in the following order

$$\text{N-H} > \text{N-CH}_3 > \text{N-C}_6\text{H}_{11} \quad \text{(in aqueous media)}$$

$$\text{N-CH}_3 > \text{N-C}_6\text{H}_{11} > \text{N-H} \quad \text{(in organic solvents)}$$

except in ethanol where the following order is valid

$$\text{N-CH}_3 > \text{N-H} > \text{N-C}_6\text{H}_{11}$$

The lower solubility of the *N*-cyclohexyl derivative in aqueous and hydroxylic solvents could be attributed to the increase in the C content of the molecules beside steric factors. Moreover, the results showed that within a particular substitution series, as the solubility in water decreases with increasing the ring size, no clear relation was observed for their solubilities in certain organic solvents.

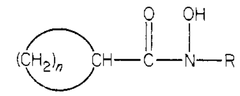
Thermal Stability. The results showed that, in general, N-substitution increases the thermal stability of cycloalkylhydroxamic acids in the following order

$$\text{N-C}_6\text{H}_{11} > \text{N-CH}_3 > \text{N-H}$$

and the stability is not affected by the ring size (Figure 1).

Chemical Stability. The results of contact of compounds I-XV with different mineral acids (3 M HNO_3, 5 M HCl, and 5 M $HClO_4$) showed that, in general, N-substituion enhanced the chemical stability of hydroxamic acids. Greater enhancement is observed for *N*-cyclohexyl derivatives toward hydrochloric and perchloric over nitric acid. This could be attributed to the oxidizing nature and the presence of nitrous acid in the latter (*7*). Moreover, as no sign of degradation was observed with the *N*-cyclohexyl derivatives (IX, XII, and XV) and only 20% degradations with VI and III, respectively, upon contact with 5 M HCl and 5 M $HClO_4$ for 10 days, the rest of the hydroxamic acid series were fully degraded within 1-5 days. Furthermore, with the exception of the C_7 ring compounds (XIII-XV) which have generally good chemical stabilities toward the above three mineral acids, the rest of the hydroxamic acids were fully degraded within 2-5 days upon contact with 3 M HNO_3.

Table I



	R		
n	H	methyl	cyclohexyl
2	I	II	III
3	IV	V	VI
4	VII	VIII	IX
5	X	XI	XII
6	XIII	XIV	XV

Table II. Visible Spectra of Ferric Hydroxamates

hydroxamic acid	λ_{max}, nm	ϵ_{max} (EtOH)	hydroxamic acid	λ_{max}, nm	ϵ_{max} (EtOH)
I	550	1200	IX	545	1433
II	540	1300	X	535	1181
III	555	1300	XI	535	1266
V	540	1140	XII	540	1395
VI	545	1300	XIII	520	1230
VII	520	1245	XIV	530	1272
VIII	535	1026	XV	530	1384

In conclusion, we feel that these results are useful in deciding the appropriate conditions to be used for the above hydroxamic acid reagents in the field of solvent extraction or chemical analysis.

Experimental Section

Ultraviolet and visible spectra were recorded on a DU-Beckman spectrophotometer. Solubility and thermal stability measurements were carried out by using a Baird and Tatlock thermostat bath with an accuracy of ±1 °C. The chemical stability was carried out by using a Tecam-SB.4 shaking bath connected to a Tecam-C400 circulator and Tecam-1000 heat exchanger, with an accuracy of ±0.1 °C.

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Table III. Solubility (mmol/L (g/L)) of Cycloalkylhydroxamic Acids at 25 °C

hydroxamic acids	solvent	ethanol	chloroform	xylene	mesitylene	*n*-heptane	*n*-dodecane	1 M HNO_3	water
	dielectric constant	24.4	4.0	2.35	2.27	1.92	2.002		80.37
I		$>10^3$	20.00 (2.02)	0.42 (0.042)		0.04 (0.004)			$>10^3$
II		$>10^3$	$>10^3$	153.75 (17.68)		65.00 (7.48)			$>10^3$
III		$>10^3$	$>10^3$	5.40 (0.99)		2.00 (0.37)			9.23 (1.69)
V		$>10^3$	$>10^3$	$>10^3$		86.25 (11.13)			solid formation
VI		756.25 (148.98)	$>10^3$	2.25 (0.44)		2.90 (0.57)			2.00 (0.39)
VII		$>10^3$	11.20 (1.45)	4.90 (0.63)	2.00 (0.26)	0.2 (0.02)		$>10^3$	888.6 (114.63)
VIII		$>10^3$	$>10^3$	$>10^3$	$>10^3$	106.7 (15.25)	91.60 (13.09)	429.30 (61.39)	532.90 (76.20)
IX		540.7 (114.08)	985.50 (207.93)	27.60 (5.82)	17.50 (3.69)	3.70 (0.78)	3.30 (0.69)	insoluble	0.70 (0.15)
X		$>10^3$	84.6 (12.1)	3.00 (0.43)	2.75 (0.39)	0.22 (0.03)	0.29 (0.04)	270.80 (38.72)	160.75 (22.99)
XI		$>10^3$	$>10^3$	29.07 (4.56)	18.53 (2.91)	2.28 (0.35)	2.20 (0.34)	28.83 (4.52)	15.36 (2.41)
XII		171.29 (38.54)	213.22 (47.97)	4.20 (0.95)	3.41 (0.77)	0.72 (0.16)	0.49 (0.11)	insoluble	insoluble
XIII		$>10^3$	105.37 (16.54)	4.63 (0.72)	3.31 (0.52)	0.40 (0.06)	0.2 (0.03)	80.15 (12.58)	70.07 (11.09)
XIV		$>10^3$		$>10^3$	29.46 (5.03)	38.49 (6.58)	8.05 (1.37)	46.35 (7.92)	35.35 (6.04)
XV		487.50 (116.51)	$>10^3$	24.00 (5.73)	16.50 (3.94)	3.10 (0.74)	2.50 (0.59)	insoluble	insoluble

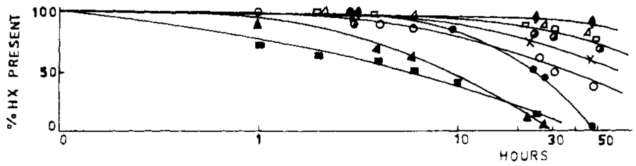

Figure 1. Thermal stability of cycloalkylhydroxamic acids at 80 °C: (♦) I; (◑) II; (×) V; (●) VII; (○) VIII; (▲) X; (△) XI; (■) XIII; (□) XIV. HX = hydroxamic acid. Compounds III, VI, IX, XII, and XV showed no degradation at 80 °C over 50 h.

Preparation of Hydroxamic Acids. The hydroxamic acids I–XV were prepared and purified following the general procedure reported recently (*6*).

Colorimetric Determination of Hydroxamic Acids. To a set of different concentrations of hydroxamic acids I–XV in ethanol, an alcoholic solution of ferric perchlorate was added. The absorbances at the indicated wavelengths (Table II) were considered and the concentrations of hydroxamic acids were thereby determined from the appropriate standard calibration curves plotted for this purpose.

Solubility Measurements. Saturated solutions of hydroxamic acids in different solvents were placed in stoppered test tubes and left in a thermostated bath for 2 h. The amount of hydroxamic acid in the centrifuged solution was determined by iron colorimetry from the calibration curves and the results are tabulated (Table III).

Thermal Stability Measurements. Hydroxamic acid in chloroform (0.01 M) was placed in a number of volumetric flasks. After evaporation of the chloroform, the flasks were placed in a thermostated bath at 80 °C. At regular intervals the remaining hydroxamic acid was determined by iron colorimetry in order to follow the variation of hydroxamic acid concentration as a function of time (Figure 1).

Chemical Stability Measurements. Hydroxamic acids (I–XV) in chloroform (0.05 M) were mixed with an equal volume of each of the mineral acids (3 M HNO_3, 5 M HCl, and 5 M $HClO_4$) and then placed in a thermostated shaking bath at 25 °C. At regular intervals the concentrations of the undergraded hydroxamic acid in the organic and aqueous phases were measured as a function of contact time.

Registry No. I, 5687-86-5; II, 77317-95-4; III, 77317-96-5; IV, 77317-97-6; V, 77317-98-7; VI, 77317-99-8; VII, 64214-51-3; VIII, 77318-00-4; IX, 77318-01-5; X, 13810-02-1; XI, 66107-13-9; XII, 84027-65-6; XIII, 84027-66-7; XIV, 84027-67-8; XV, 84027-68-9; ethanol, 64-17-5; chloroform, 67-66-3; xylene, 1330-20-7; mesitylene, 108-67-8; heptane, 142-82-5; dodecane, 112-40-3.

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