J. Chem. Eng. Data **1983**, *28*, 157-160

Excess Volume of Binary Mixtures of 1-Hexanol with Hexane Isomers at 298.15 K[†]

Fumio Kimura[‡] and George C. Benson*

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

Excess volumes, measured at 298.15 K in a successive dilution dilatometer, are reported for binary mixtures of 1-hexanol with the four isomers of *n*-hexane.

This work was undertaken as part of a program to provide accurate experimental information about the changes in the thermodynamic properties of a binary mixture which result from isomeric variations in the molecular configuration of one of its components. For this purpose we have chosen to study binary mixtures of 1-hexanol with the five isomeric hexanes. Measurements of the excess enthalpies of these mixtures have already been described (*1*), and an earlier paper (*2*) reported excess volumes for mixtures of 1-hexanol with *n*-hexane (*n*-C6). Continuing the latter study, we have determined excess volumes for binary mixtures of 1-hexanol with 2-methylpentane (2-MP), 3-methylpentane (3-MP), 2,2-dimethylbutane (2,2-DMB), and 2,3-dimethylbutane (2,3-DMB).

Experimental Section

1-Hexanol (Matheson Coleman and Bell, practical grade) was purified in a preparative gas chromatograph using columns similar to those in our earlier work (*1*). The hexane isomers were Research Grade materials from Phillips Petroleum Co. They were used without further purification. Densities and refractive indices characterizing the samples used for the present measurements are listed in Table I. These agree fairly well with data from the literature (*3*, *4*) and show only minor differences from the properties of the samples used in our excess enthalpy study (*1*).

The changes in volume occurring when the component liquids were mixed at constant pressure were measured in a successive dilution dilatometer (*5*) following the operational procedure described previously (*6*). The temperature was controlled within ±0.0015 K at a value of 298.15 ± 0.01 K (IPTS-68). The imprecision of the mole fraction, x, of 1-hexanol was 2×10^{-5} for the high-dilution region ($x < 0.02$) and 8×10^{-5} for larger mole fractions of 1-hexanol. The experimental error of the molar excess volume, V_m^E, is estimated to be less than $0.0003 + 0.001|V_m^E|$ cm^3 mol^{-1}.

Results

The experimental values of the molar excess volume V_m^E at 298.15 K are listed in Table II and presented graphically in Figures 1 and 2. In all cases, x is the mole fraction of 1-hexanol. To avoid congestion of the points, results for $x < 0.05$ have been omitted from Figure 1 and are shown separately in Figure 2.

Each set of results was fitted with a polynomial in the square root of the mole fraction of 1-hexanol

$$V_m^E = x(1 - x) \sum_{j=1}^{n} v_j x^{(j-1)/2} \qquad (1)$$

Values of the coefficients v_j, and standard deviations σ, determined by the method of least squares with all points weighted equally, are given in Table III. These representations are plotted in Figure 1 and are adequate for most purposes. However, they do not represent the experimental results for small mole fractions ($x < 0.05$) as well as for higher mole fractions, and they are not suitable for calculating the limiting partial molar volume of 1-hexanol at infinite dilution in the various hexane isomers. For $x < 0.1$, the results for V_m^E were fitted with the polynomial

$$V_m^E = \sum_{j=1}^{n} v_j x^j \qquad (2)$$

by the method of least-squares with the points assigned equal weights. Values of the coefficients v_j, and standard deviations σ, are also listed in Table III. In Figure 2, the curves for low x ($x < 0.05$ for 2-MP and 3-MP; $x < 0.035$ for 2,2-DMB; $x < 0.028$ for 2,3-DMB) were calculated from eq 2; at higher x, eq 1 was used.

Table I. Densities, ρ, and Refractive Indices, n_D, of Component Liquids at 298.15 K

	ρ/(kg m^{-3})		n_D	
	measd	lit.	measd	lit.
1-hexanol	815.91	816.2 (*3*)	1.416 12	1.416 1 (*3*)
2-methylpentane	648.52	648.52 (*4*)	1.368 67	1.368 73 (*4*)
3-methylpentane	659.79	659.76 (*4*)	1.373 82	1.373 86 (*4*)
2,2-dimethylbutane	644.42	644.46 (*4*)	1.365 90	1.365 95 (*4*)
2,3-dimethylbutane	657.03	657.02 (*4*)	1.372 23	1.372 31 (*4*)

Discussion

The excess volume curves for the present systems are all sigmoid and similar to that found previously for mixtures of 1-hexanol with *n*-C6 (*2*). They are negative over most of the mole fraction range with a minimum near $x = 0.6$; the positive values are limited to $x < 0.1$. At nearly all mole fractions, the curves fall in the order *n*-C6 > 3-MP > 2,3-DMB > 2-MP > 2,2-DMB. However, the curves for 2,3-DMB and 2-MP appear to cross at low x, but the differences between them for $x < 0.04$ are of the same magnitude as their estimated experimental uncertainty.

Curves for the partial molar excess volumes V^E_A and V^E_B (A = 1-hexanol, B = hexane isomer) were calculated from eq 1 and 2. These are not reported in detail here; they are all similar in shape to the results for the *n*-C6 system (*2*) and fall in the same order as listed above for V_m^E. The limiting values $V^E_A{}^\infty$ and $V^E_B{}^\infty$ are given in Table IV.

At present there is no theoretical model which is capable of explaining the differences in thermodynamic behavior exhibited by binary mixtures of 1-hexanol with the various hexane isomers. Previously (*1*) it was noted that there was a roughly linear correlation between the molar excess enthalpies of equimolar mixtures and Z_g, the mean number of gauche conformations of the hexane isomer (coefficient of correlation, $r = -0.92$). However, since the V_m^E curves fall in a very different order, the correlation between V_m^E for equimolar mixtures and Z_g is poor ($r = 0.28$).

[†] Issued as NRCC No. 21052.

[‡] NRCC Research Associate, 1980-82.

0021-9568/83/1728-0157$01.50/0

Table II. Experimental Results for the Molar Excess Volume, V_m^E, of 1-Hexanol-Hexane Isomer Mixtures at Mole Fraction, x, of 1-Hexanol and 298.15 K

2-MP		3-MP		2,2-DMB		2,3-DMB	
x	V_m^E/(cm^3 mol^{-1})	x	V_m^E/(cm^3 mol^{-1})	x	V_m^E/(cm^3 mol^{-1})	x	V_m^E/(cm^3 mol^{-1})
0.002 85	0.0091	0.002 94	0.0115	0.002 81	0.0061	0.002 80	0.0089
0.005 52	0.0159	0.005 40	0.0181	0.005 50	0.0097	0.005 57	0.0153
0.009 52	0.0205	0.008 23	0.0236	0.008 27	0.0108	0.008 13	0.0189
0.013 74	0.0215	0.010 98	0.0259	0.011 13	0.0098	0.011 04	0.0207
0.017 55	0.0208	0.013 62	0.0273	0.016 46	0.0054	0.013 55	0.0208
0.021 76	0.0193	0.016 20	0.0283	0.027 47	−0.0085	0.016 22	0.0205
0.027 03	0.0156	0.018 85	0.0283	0.040 60	−0.0288	0.018 92	0.0196
0.032 34	0.0115	0.021 54	0.0282	0.077 87	−0.0881	0.024 30	0.0171
0.040 00	0.0055	0.024 06	0.0277	0.123 73	−0.1604	0.031 90	0.0127
0.052 59	−0.0061	0.026 79	0.0269	0.164 96	−0.2207	0.039 62	0.0066
0.069 80	−0.0233	0.032 03	0.0253	0.219 99	−0.2941	0.054 50	−0.0060
0.093 24	−0.0471	0.039 75	0.0221	0.283 06	−0.3674	0.080 72	−0.0302
0.121 89	−0.0764	0.052 27	0.0152	0.348 80	−0.4314	0.120 57	−0.0682
0.162 71	−0.1167	0.076 49	0.0004	0.403 53	−0.4748	0.161 23	−0.1058
0.217 33	−0.1678	0.120 99	−0.0297	0.449 78	−0.5031	0.215 25	−0.1528
0.279 94	−0.2211	0.161 57	−0.0582	0.458 75	−0.5085	0.277 60	−0.2042
0.345 41	−0.2705	0.215 84	−0.0950	0.478 48	−0.5173	0.342 73	−0.2510
0.400 13	−0.3064	0.278 18	−0.1350	0.489 38	−0.5214	0.397 09	−0.2854
0.442 28	−0.3294	0.343 49	−0.1745	0.508 90	−0.5281	0.443 14	−0.3101
0.446 28	−0.3319	0.397 88	−0.2046	0.523 63	−0.5316	0.450 97	−0.3132
0.452 67	−0.3342	0.444 01	−0.2275	0.543 54	−0.5357	0.472 62	−0.3227
0.480 03	−0.3467	0.451 39	−0.2305	0.553 28	−0.5364	0.482 67	−0.3276
0.485 82	−0.3499	0.473 19	−0.2396	0.570 33	0.5375	0.502 64	−0.3341
0.511 25	−0.3583	0.483 54	−0.2443	0.583 32	0.5373	0.516 97	−0.3396
0.520 08	−0.3618	0.503 10	−0.2510	0.629 32	−0.5287	0.536 86	−0.3441
0.546 84	−0.3679	0.517 83	−0.2564	0.683 23	−0.5036	0.546 66	−0.3470
0.549 79	−0.3691	0.537 37	−0.2616	0.747 16	−0.4520	0.560 13	−0.3497
0.564 76	−0.3718	0.547 56	−0.2646	0.807 69	−0.3795	0.576 37	−0.3509
0.587 73	−0.3736	0.562 56	−0.2683	0.850 97	−0.3138	0.621 75	−0.3516
0.635 29	−0.3719	0.576 65	−0.2699	0.859 99	−0.2990	0.674 95	−0.3416
0.691 17	−0.3573	0.622 12	−0.2739	0.898 70	−0.2283	0.738 34	−0.3139
0.757 96	−0.3206	0.675 24	−0.2697	0.941 09	−0.1409	0.798 06	−0.2713
0.821 32	−0.2657	0.738 37	−0.2512	0.975 65	−0.0618	0.849 61	−0.2203
0.876 31	−0.2014	0.798 06	−0.2186			0.887 63	−0.1747
0.917 19	−0.1437	0.849 37	−0.1792			0.929 40	−0.1171
0.962 35	−0.0700	0.887 69	−0.1427			0.965 79	−0.0602
		0.929 41	−0.0961				
		0.963 40	−0.0529				

Table III. Coefficients v_j and Standard Deviation σ for Least-Squares Representations of V_m^E for 1-Hexanol–Hexane Isomer Mixtures at 298.15 K by Eq 1 in the Range $0 < x < 1$ and by Eq 2 in the Range $0 < x < 0.1$

	2-methylpentane		3-methylpentane		2,2-dimethylbutane		2,3-dimethylbutane	
	eq 1	eq 2	eq 1	eq 2	eq 1	eq 2	eq 1	eq 2
v_1	7.1397	4.0809	7.8738	4.7977	5.7466	2.9305	6.9469	3.8971
v_2	−79.7661	-2.7010×10^2	−84.7011	-3.1653×10^2	−74.6891	-2.5555×10^2	−77.8833	-2.4710×10^2
v_3	371.8022	8.0084×10^3	403.4900	10.7044×10^3	354.6736	7.6161×10^3	366.3677	6.5347×10^3
v_4	−1018.738	-1.3101×10^5	−1124.812	-2.0374×10^5	−988.372	-1.1167×10^5	−1010.321	-8.2932×10^4
v_5	1708.827	1.0947×10^6	1910.731	2.0056×10^6	1685.130	6.0875×10^5	1701.176	3.9371×10^5
v_6	−1726.733	-3.6272×10^6	−1947.936	-7.9008×10^6	−1729.343		−1722.754	
v_7	960.132		1090.432		975.452		959.433	
v_8	−224.641		−256.623		−231.201		−224.820	
σ	0.0005	0.0003	0.0004	0.0002	0.0004	0.0002	0.0005	0.0004

Table IV. Partial Molar Excess Volumes $V^E{}_A{}^\infty$ of 1-Hexanol and $V^E{}_B{}^\infty$ of Hexane Isomer at Infinite Dilution in 1-Hexanol-Hexane Isomer Mixtures at 298.15 K

isomer	$V^E{}_A{}^\infty$/(cm^3 mol^{-1})	$V^E{}_B{}^\infty$/(cm^3 mol^{-1})
n-hexane	4.7[a]	−1.5[a]
2-methylpentane	4.1	−2.0
3-methylpentane	4.8	−1.5
2,2-dimethylbutane	2.9	−2.6
2,3-dimethylbutane	3.9	−1.9

[a] Treszczanowicz and Benson (*2*).

The closeness of the V_m^E results for 3-MP to those for *n*-C6 indicates that these molecules have very similar interactions with 1-hexanol, at least as far as the excess volume is concerned. This is consistent with the observation of Ott et al. (*7*), who found that, within the limits of their experimental technique, the molar excess volume of *n*-C6–3-MP mixtures was zero.

It is evident from our results that branching of the hexane molecule makes a negative contribution to V_m^E in mixtures with 1-hexanol and that the presence of a tertiary configuration leads to a larger decrease than one or two secondary branches. Similar behavior has been reported for mixtures of the isomeric hexanes with *n*-hexane (*7*), *n*-hexadecane (*8*), cyclohexane (*9*), nitroethane (*10*), and 1-chloropentane (*10*).

Brennan et al. (*11*) noted that V_m^E for binary mixtures of cyclopentane with the isomeric octanes correlated reasonably well with the molar enthalpy of vaporization or solubility parameter of the branched hydrocarbon. Evidence of similar correlations for the excess volumes of *n*-hexadecane–hydrocarbon mixtures was also reported by Fenby et al. (*12*). In Figure 3, our results for the molar excess volumes, V_m^E (0.5),

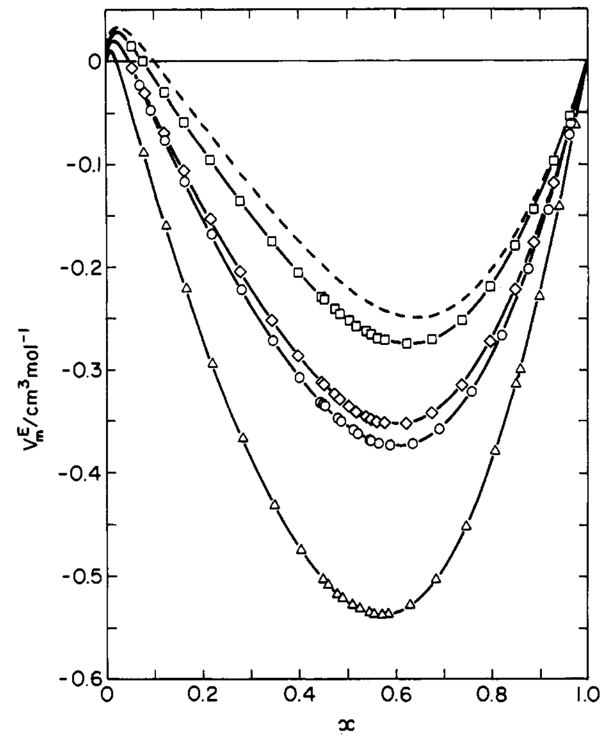


Figure 1. Molar excess volume, V_m^E, of 1-hexanol-hexane isomer mixtures at mole fraction, x, of 1-hexanol and 298.15 K: (○) 2-MP; (□) 3-MP; (△) 2,2-DMB; (◇) 2,3-DMB. Curves are least-squares representations of our results by eq 1. (- - -) Results for n-C6 are taken from Treszczanowicz and Benson (*2*).

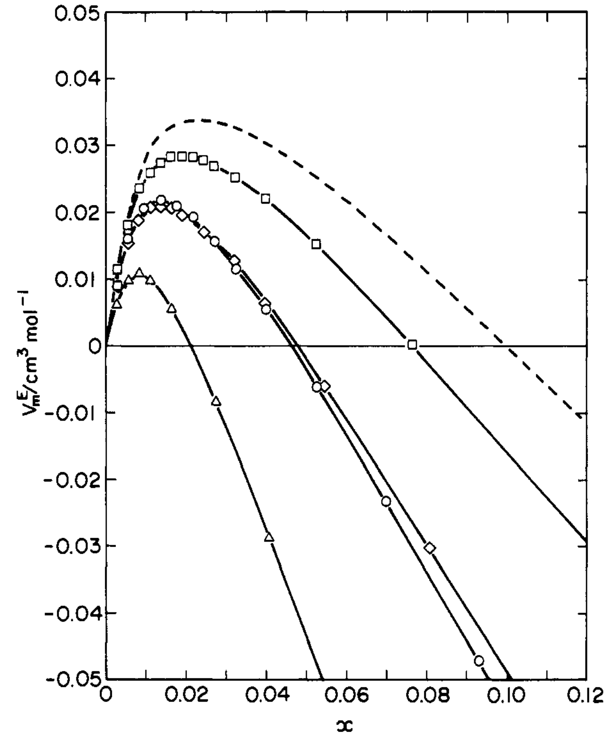


Figure 2. Molar excess volume, V_m^E, of 1-hexanol-hexane isomer mixtures at low mole fraction, x, of 1-hexanol and 298.15 K: (○) 2-MP; (□) 3-MP; (△) 2,2-DMB; (◇) 2,3-DMB. Curves calculated from combination of eq 1 and 2. (- - -) Results for n-C6 are taken from Treszczanowicz and Benson (*2*).

of equimolar mixtures are plotted against values of the solubility parameter

$$\delta = [(\Delta H_m^v - RT)/V_m]^{1/2} \qquad (3)$$

calculated for the isomeric hexanes at 298.15 K from values of the standard molar enthalpy of vaporization ΔH_m^v and the molar volume V_m (*4*). The least-squares line in this figure corresponds to a high degree of correlation (r = 0.98).

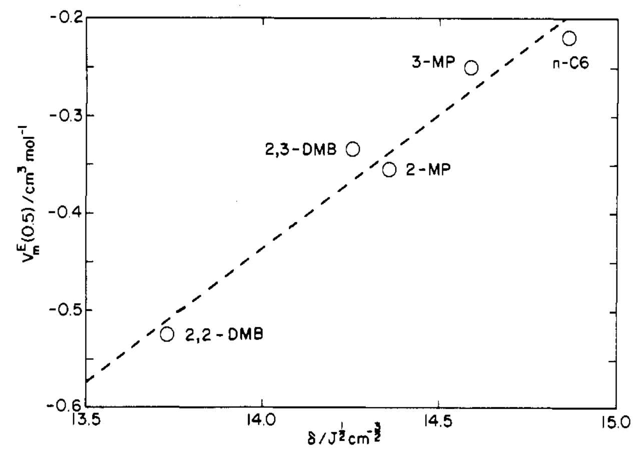


Figure 3. Plot of V_m^E (0.5), the molar excess volume of an equimolar 1-hexanol-hexane isomer mixture, against δ, the solubility parameter of the isomer: (- - -) least-squares line with coefficient of correlation = 0.98. The point for n-C6 is taken from Treszczanowicz and Benson (*2*).

Acknowledgment

We are indebted to Dr. A. J. Treszczanowicz for helpful discussion and to Mr. C. J. Halpin and Mr. P. J. D'Arcy for technical assistance.

Glossary

ΔH_m^v	standard molar enthalpy of vaporization, J mol^{-1}
n	number of coefficients in eq 1 or 2
n_D	refractive index for sodium light
r	coefficient of correlation
R	gas constant, J K^{-1} mol^{-1}
T	thermodynamic temperature, K
v_1, v_2, ..., v_j	coefficients in representation of molar excess volume by eq 1 and 2
V_m	molar volume, cm^3 mol^{-1}
V_m^E	molar excess volume, cm^3 mol^{-1}
x	mole fraction of 1-hexanol
Z_g	mean number of gauche conformations of hexane isomer

Greek Letters

δ	solubility parameter, J$^{1/2}$ cm$^{-3/2}$
ρ	density, kg m^{-3}
σ	standard deviation

Subscripts

A	component 1-hexanol
B	component hexane isomer

Registry No. 1-Hexanol, 111-27-3; 2-methylpentane, 107-83-5; 3-methylpentane, 96-14-0; 2,2-dimethylbutane, 75-83-2; 2,3-dimethylbutane, 79-29-8.

Literature Cited

(1) Kimura, F.; Benson, G. C. *J. Chem. Eng. Data* **1981**, *26*, 317.
(2) Treszczanowicz, A. J.; Benson, G. C. *J. Chem. Thermodyn.* **1980**, *12*, 173.
(3) Wilhoit, R. C.; Zwolinski, B. J. *J. Phys. Chem. Ref. Data* **1973**, *2*, Supplement No. 1.
(4) "Selected Values of Properties of Hydrocarbons and Related Compounds", American Petroleum Institute Research Project 44; Thermodynamics Research Center, Texas A & M University: College Station, TX; see Table 23-2-(1.201)-a dated Oct 31, 1952, and Table 23-2-(1.201)-m dated Oct 31, 1965.
(5) Tanaka, R.; Kiyohara, O.; D'Arcy, P. J.; Benson, G. C. *Can. J. Chem.* **1975**, *53*, 2262.

(6) Treszczanowicz, A. J.; Benson, G. C. *J. Chem. Thermodyn.* **1977**, *9*, 1189.
(7) Ott, J. B.; Grigg, R. B.; Goates, J. R. *Aust. J. Chem.* **1980**, *33*, 1921.
(8) Reeder, J.; Knobler, C. M.; Scott, R. L. *J. Chem. Thermodyn.* **1975**, *7*, 345.
(9) Romani, L.; Paz Andrade, M. I. *An. Quim.* **1975**, *71*, 3.
(10) Handa, Y. P.; Knobler, C. M.; Scott, R. L. *J. Chem. Thermodyn.* **1977**, *9*, 451.
(11) Brennan, J. S.; Hill, R. J.; Swinton, F. L. *J. Chem. Thermodyn.* **1978**, *10*, 169.
(12) Fenby, D. V.; Khurma, J. R.; Kooner, Z. S.; Block, T. E.; Knobler, C. M.; Reeder, J.; Scott, R. L. *Aust. J. Chem.* **1980**, *33*, 1927.

Received for review April 13, 1982. Accepted December 1, 1982.

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

Hikmat N. Al-Jallo,* Shakir S. Ahmed, Faris I. Saleh, and Fatima M. Abbas
Department of Chemistry, Nuclear Research Center, Tuwaitha, Baghadad, Iraq

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

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

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

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.

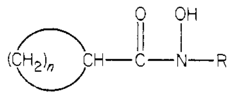
Thermal Stability. The results showed that, in general, N-substitution increases the thermal stability of cycloalkylhydroxamic acids in the following order

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

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



n	R: H	R: methyl	R: 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.