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Effects of Phenyl Groups on Thermodynamic Parameters of Lanthanoid(III) Complexation with Aromatic Carboxylic Acids

Yuko Hasegawa,* Nobuhiko Yamazaki, Satoko Usui, and Gregory R. Choppin†
Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162
†Department of Chemistry, The Florida State University, Tallahassee, Fl. 32306-3006, U.S.A.
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The enthalpy changes as well as the stability constants of the complexes between a series of lanthanoid(III) cations and phenylacetate, 3-phenylpropionate, and salicylate ions have been measured using a potentiometer and an isothermal calorimeter, respectively. The data were compared with the data with benzoate ions. The enthalpy changes for formation of the heavier lanthanoid(III) complexes are larger than those for the complexation of the lighter lanthanoids. Also, the complexation heat changes by the carboxylate ions having methylene group(s) between the carboxyl and the phenyl groups are more endothermic than by the anions in which these two groups are joined directly. The results are explained in terms of the differences in the dehydration of the lighter lanthanoid(III) from that of the heavier ones upon complexation and also the different basicities of the carboxylate ions of the ligands.

It has been reported[1)] that the distribution constant of phenylacetic acid is very similar to that of benzoic acid when chloroform is employed as organic solvent, although the constant of aliphatic carboxylic acids increases a factor of 4 with each addition of a methylene group.[2)] It has also been observed[1)] that the adduct formation constants of the chelates between several lanthanoids(III) and 2-thenoyltrifluoroacetone with phenylacetic acid in chloroform as well as the formation constants of the lanthanoid(III) complexes with the acid, in 0.1 M (1 M=1 mol dm^{-3}) sodium perchlorate solution, are smaller than the constants of the corresponding lanthanoid(III) complexes with benzoic acid, in spite of the very similar pK_a values of the acids.

These observations suggest that the presence or absence of a methylene between the carboxyl and phenyl groups in acid may influence the hydration of the anion which also affects the complexation. To study this possibility in more detail, the enthalpy changes as well as the stability constants of a series of lanthanoid(III) complexes with salicylate, phenylacetate, and 3-phenylpropionate ions have been measured in the present work and compared with the data for benzoate complexing. Salicylic acid was chosen for comparison as it also has no -CH_2- between the phenyl and the carboxyl groups, while 3-phenylpropionic acid was chosen for its analogy with phenylacetic acid since the carboxyl group is screened from the phenyl group by methylene groups.

Experimental

Reagents. Lanthanoid(III) perchlorate solutions were prepared by dissolving the weighed lanthanoid oxides (the purities were >99.9%) in perchloric acid. The exact lanthanoid(III) concentrations were determined by titration with EDTA using Xylenol Orange as an indicator and acetate buffer. Phenylacetic acid (Aldrich Chemical Co., Milwaukee WI, U.S.A., the purity: 99%), 3-phenylpropionic acid (Tokyo Kasei Co., Tokyo, the purity: >98%), and salicylic acid (Kanto Chemical Co., Tokyo) were used without purification. These acids were buffered by adding sodium hydroxide solution and these solutions served as the ligand solution in the potentiometric and calorimetric titrations. Sodium perchlorate prepared from sodium carbonate and perchloric acid was recrystallized twice from water. The total ionic concentration was adjusted to 0.1 M with the addition of sodium perchlorate solution.

Procedures. Potentiometric titrations were performed in a similar way to that described elsewhere.[3)] The hydrogen ion concentration was determined potentiometrically using 1.00×10^{-2} M perchloric acid solution (the total perchlorate concentration was 0.1 M) as a standard of $-\log [H^+]=2.00$. Calorimetric titrations were performed on an isothermal calorimeter equipped with a motorized buret (Tronac Model 1250, Utah, U.S.A.). A reaction vessel and a buret were immersed in the water bath of 298 K. The heat was detected as the change in the energy required to maintain the solution at initial temperature. The solution was stirred constantly and vigorously during the measurement. The titrant was injected into a stainless steel reaction vessel at a constant rate. After the first injection of the titrant, approximately 4 minutes were required to stabilize the temperature of the solution. The heat measurement was started after the temperature had been stabilized. In the cup, 75 mL of a lanthanoid perchlorate solution was placed and titrated with the ligand solution. The dilution heats for the ligand solution were determined by titrating a 75 mL of 0.10 M sodium perchlorate solution with the ligand solution. The protonation heats for the carboxylate ions were determined calorimetrically by titrating these buffered solutions with perchloric acid solution. The data from the calorimetric titrations were treated by a linear least-squares analysis.

Results and Discussion

Table 1 shows the typical experimental conditions which were used in the potentiometric titrations to determine the stability constants. The symbol n denotes the average number of ligand molecules bound to a metal ion. The potentiometric data were analyzed on the basis of the Bjerrum formation func-

Table 1. Typical Experimental Conditions Employed in Potentiometric Titrations for the Lanthanoids(III)-Phenylacetate System[a)] (I=0.10 M ($NaClO_4$); T=298 K)

Ln^{III}	Volume added /ml	$-\log[H^+]$	$[A^-]$ /10^{-4} M	n
Pr	2.4-8.0	3.81-3.78	2.64-8.16	0.029-0.082
Nd	1.8-8.0	3.81-3.75	1.88-7.63	0.020-0.074
Sm	2.6-6.5	3.77-3.74	2.44-5.97	0.033-0.074
Gd	1.3-6.5	3.88-3.80	1.57-7.05	0.015-0.064
Tb	2.0-7.5	3.86-3.83	2.61-8.78	0.017-0.055
Dy	2.0-7.0	3.86-3.83	2.65-8.50	0.016-0.046
Ho	1.0-7.0	3.94-3.87	1.47-9.84	0.009-0.047
Er	0.5-6.5	4.01-3.88	0.82-8.59	0.004-0.040
Tm	2.0-7.0	3.87-3.84	2.73-8.65	0.014-0.042
Lu	1.0-7.0	3.94-3.86	1.47-8.69	0.009-0.051

a) Initial Conditions. In the cup: $[Ln^{3+}]=1.0\times10^{-2}$ M, volume=50.0 mL. In the buret: $A_T=2.0\times10^{-2}$ M.

Table 2. Thermodynamic Parameters for Protonation of Carboxylate Anions (I=0.1 M ($NaClO_4$); T=298 K)

Anion	$\log\beta_{011}\pm\delta$[a)]	$\Delta G_{011}\pm\delta$	$\Delta H_{011}\pm\delta$	$\Delta S_{011}\pm\delta$
		kJ mol^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}
Phenylacetate	4.00±0.03[1)]	−22.8±0.2	1.72±0.01	82.2±0.7
3-Phenylpropinate	4.40±0.01	−25.1±0.1	1.06±0.01	87.9±0.3
Benzoate[5)]	3.99±0.05	−22.8±0.3	−0.87±0.05	74 ±5
Salicylate	2.72±0.01[3)]	−15.5±0.1	−3.95±0.01	38.7±0.3

a) δ donotes error limits based on the agreement in repetitive titrations.

Table 3. Calorimetric Titration Data for the Praseodymium(III)-Phenylacetate System[a)] (I=0.1 M ($NaClO_4$); T=298 K)

Titrant	Q(corr)[b)]	Q(calcd)[c)]	$-\log[H^+]$	$[LnA^{2+}]$	n
ml	mJ	mJ		10^{-2} mmol	
4.41	−26.65	−27.74	3.805	4.195	0.070
4.73	−53.60	−55.15	3.803	4.458	0.074
5.04	−80.60	−82.26	3.802	4.718	0.078
5.36	−106.95	−109.06	3.801	4.975	0.082
5.67	−134.31	−135.57	3.800	5.229	0.087
5.99	−161.74	−161.79	3.800	5.480	0.091
6.30	−188.04	−187.72	3.800	5.729	0.095
6.62	−212.50	−213.38	3.799	5.975	0.099
6.93	−237.98	−238.76	3.799	6.218	0.103
7.25	−262.81	−263.88	3.799	6.459	0.107
7.56	−287.47	−288.73	3.800	6.697	0.111
7.88	−312.68	−313.32	3.800	6.933	0.115
8.19	−337.95	−337.66	3.800	7.167	0.119

a) Initial Conditions: In the cup: $[Pr^{3+}]=8.05\times10^{-3}$ M, $-\log[H^+]=4.07$, volume=75.0 mL. In the buret: $A_T=4.14\times10^{-2}$ M, $[A^-]=2.06\times10^{-2}$ M. b) Q(corr) is the observed heat corrected for dilution and protonation. c) Q(calcd) is the heat calculated using the stability constants and the enthalpy changes observed.

tion[4)] and the mass balance equations of the relevant species. Table 2 lists the thermodynamic parameters for protonation of the four carboxylate ions. A notable point in these constants is that the protonation heats for benzoates are exothermic while those for the carboxylates having methylene group(s) between the carboxyl and phenyl groups are endothermic. Although the cause of the difference is not clear, it can be explained by a difference of the hydration of ligand anions. In phenylacetate and 3-phenylpropionate anions, the inductive effect of phenyl ring should be weaker due to the shielding of the methylene group and these anions can be expected to be more basic than that of benzoate anions. Consequently, the hydration of these anions having methylene group(s) should be greater than that of benzoate, and the enthalpy change in the protonation of the carboxylate ion joined to methylene groups would be larger than that of benzoate ion. This interpretation is supported by the more positive values of ΔS for the phenylacetate and 3-phenylpropionate protonation. However, we note that the pK_a values for benzoic and phenylacetic acids are very close which would seem to disagree with the prediction that the basicity of benzoate ion is weaker than that of phenylacetate.

Table 3 is an example of the calorimetric titration data. The net heat changes (Q(corr)) were obtained by subtracting the dilution heat and the protonation heat from the observed heat.

The values of the stability constants and of the enthalpy changes obtained are listed in Table 4. The values for the formation of the second complex, LnA_2^+, from both the potentiometric and the calorimetric data are uncertain for the 3-phenylpropionate and salicylate systems since only a small amount of the second complex was formed. Neither the potentiometric nor the calorimetric data gave evidence of the formation of the second complex with phenylacetate ion. (As seen in Table 3, the observed heat coincides with the heat calculated without the second complex over all the range studied.) The thermodynamic parameters calculated on the basis of the data in Table 4 are compared to those with benzoic acid in Fig. 1.

Table 4-a. Stability Constants of Complexation of Lanthanoids by Phenylacetate and 3-Phenylpropionate (I=0.10 M ($NaClO_4$); T=298 K)

	Phenylacetate	3-Phenylpropionate	
Ln^{III}	$\log\beta_{101}\pm\delta$[a]	$\log\beta_{101}\pm\delta$	$\log\beta_{102}\pm\delta$
La	1.74±0.04		
Pr	2.04±0.01	2.08±0.02	3.60±0.17
Nd	2.09±0.06	2.16±0.01	3.67±0.09
Sm	2.13±0.01	2.19±0.00	3.75±0.10
Eu	2.06±0.02	2.18±0.02	3.77±0.11
Gd	1.96±0.06		
Tb	1.82±0.08		
Dy	1.77±0.03	1.96±0.03	3.62±0.24
Ho	1.77±0.02		
Er	1.70±0.01	1.89±0.03	3.40±0.06
Tm	1.73±0.06	1.91±0.01	3.45±0.11
Yb	1.80±0.02	1.98±0.03	3.58±0.08
Lu	1.82±0.09		

a) δ donotes error limits based on the agreement in repetitive titrations.

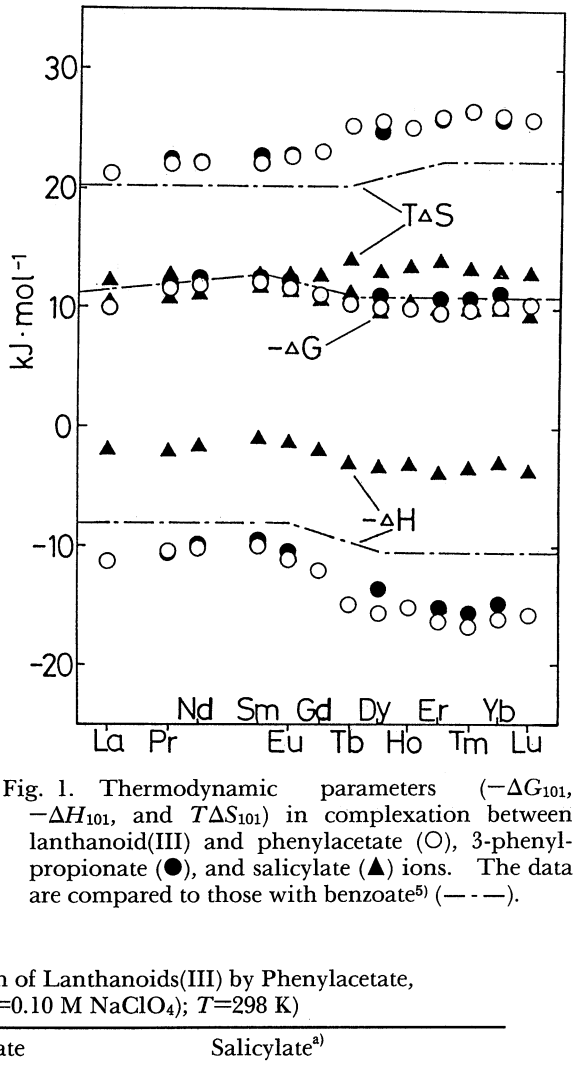

Fig. 1. Thermodynamic parameters ($-\Delta G_{101}$, $-\Delta H_{101}$, and $T\Delta S_{101}$) in complexation between lanthanoid(III) and phenylacetate (○), 3-phenylpropionate (●), and salicylate (▲) ions. The data are compared to those with benzoate[5] (— - —).

Table 4-b. Enthalpy Changes of Complexation of Lanthanoids(III) by Phenylacetate, 3-Phenylpropionate and Salicylate (I=0.10 M $NaClO_4$); T=298 K)

	Phenylacetate	3-Phenylpropionate		Salicylate[a]	
Ln^{III}	$\Delta H_{101}\pm\delta$	$\Delta H_{101}\pm\delta$	$\Delta H_{102}\pm\delta$	$\Delta H_{101}\pm\delta$	$\Delta H_{102}\pm\delta$
	kJ mol^{-1}	kJ mol^{-1}		kJ mol^{-1}	
La	11.30±0.17			2.01±0.34	5.07±4.91
Pr	10.43±0.33	10.65±0.08	5.47±5.91	2.07±0.07	3.63±1.15
Nd	10.21±0.04	9.82±0.64	17.56±3.48	1.66±0.20	5.94±0.76
Sm	9.99±0.22	9.47±0.23	18.16±13.2	0.98±0.01	3.91±0.02
Eu	11.05±0.37	10.36±0.54	13.83±9.80	1.29±0.34	5.71±2.45
Gd	12.01±0.50			1.93±0.31	5.92±0.78
Tb	14.86±0.07			3.02±0.01	4.43±0.10
Dy	15.57±0.44	13.60±0.26	17.48±6.40	3.32±0.00	8.77±1.63
Ho	15.08±0.11			3.05±0.03	7.30±0.42
Er	16.34±0.03	15.15±0.40	16.82±11.5	3.81±0.11	6.31±3.09
Tm	16.73±0.05	15.60±0.66	14.24±9.28	3.34±0.36	6.97±2.43
Yb	16.10±0.01	14.82±0.63	22.98±12.8	2.98±0.07	18.58±0.56
Lu	15.76±0.07			3.61±0.22	9.46±2.04

a) Using the stability constants taken from Ref. 3.

In Fig. 1 the patterns of the variation with lanthanoid atomic number are similar for the different ligands. All the curves can be resolved in an initial group (the lighter lanthanoids), an intermediate group (Sm–Dy) and a final group (the heavier ones). The trends observed in the enthalpy changes as a function of the atomic number may be explained in terms of the different hydration number of the lighter and the heavier lanthanoid ions.[6] The values of ΔH_{101} (the complexation heat of the reaction, $Ln^{3+}+A^{-}\rightarrow LnA^{2+}$) of the heavier lanthanoid(III) complexes are more endothermic as more dehydration occurs for these cations when they are complexed.

Figure 1 also shows that the enthalpy changes in the complexation with the carboxylates having methylene group(s) between carboxyl and phenyl groups are more endothermic than those by the carboxylates joining directly to these groups, that is, the enthalpy changes of the phenylacetates and 3-phenylpropionates are more endothermic than those of benzoates. The difference in ΔH_{101} between benzoate and phenylacetate could be related to difference in the dehydration of the ligands when they are complexed as the difference in ΔH_{101} is about the same as in protonation heat(ΔH_{011}), e.g., the difference of ΔH_{011} is 2.6 kJ mol^{-1} and that of ΔH_{101} for neodymium(III) is 2.2 kJ mol^{-1}. This is also reflected in the entropy changes where $T\Delta S_{101}$ is about 2 kJ mol^{-1} more positive for Nd(phenylacetate)$^{2+}$ than for Nd(benzoate)$^{2+}$ formation and $T\Delta S_{011}$ is about 2 kJ mol^{-1} more positive for phenylacetic acid compared to benzoic acid. If the difference with these two ligands would mainly be caused by the difference of the hydration of the ligand anions, the difference should be similar regardless of lanthanoids. However, the difference of the enthalpy changes with the phenylacetates between the lighter and the heavier lanthanoids is larger than that of the benzoates (the difference for the phenylacetates, ca. 6 kJ mol^{-1} and for the benzoates, ca. 3—4 kJ mol^{-1}). Some effects caused by the direct combination of carboxyl and phenyl groups, i.e., the resonance[7] as well as the inductive effect of benzoate ions, would influence the complexation of lanthanoids. This is also seen in the values of enthalpy changes and entropy changes of the 3-phenylpropionates which are very similar to those of the phenylacetates and in the similarity in the patterns in the benzoates and the salicylates. It apparently suggests that such a difference would be attributable to the direct combination of carboxyl and phenyl groups.

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