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Received May 13, 1974.

Additivity Relations of Partial Molal Volumes in Carboxylic Acid Series

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It has been shown by a number of workers that the partial molal volumes of electrolytes at infinite dilution are equal to the sum of the ionic components (see Ref. 1). Clearly, as Millero¹ points out, the utility of partial molal volumes to study ion-water interactions lies in the additivity principle.

Only a CH₂-group, with its volume requirements, separates two successive members of a homologous series of carboxylic acids. As early as 1899 Traube² found that the partial molal volume of a CH₂-group in aqueous solution was on the average 16.0 ml mol⁻¹. This has been verified by the data of Sakurai.³ In this paper data at 25 °C obtained by King,⁴ Sakurai,³ and Høiland⁵ have been used to investigate the additivity of the partial molal volumes of the groups comprising the carboxylic acid or the acid anion.

Results. Two requirements must be fulfilled in order to calculate the partial molal volumes of the different groups involved. First, the well documented starting point that the partial molal volume of a CH₂-group is 16.0 ml mol⁻¹. Second, the partial molal volume of the sodium ion is required in order to obtain the partial molal volume of the carboxylate ion. The best value of $\bar{V}^{\circ}(\text{Na}^+)$ is probably found by taking Zana and Yeager's⁶ value for $\bar{V}^{\circ}(\text{H}^+) = -5.4 \pm 0.2$ ml mol⁻¹, and add the experimentally determined difference $\bar{V}^{\circ}(\text{H}^+) - \bar{V}^{\circ}(\text{Na}^+) = -1.2$ ml mol⁻¹. Thus $\bar{V}^{\circ}(\text{Na}^+) = -6.6$ ml mol⁻¹. This was used, and the experimental data are given in Table 2. The value of $\bar{V}^{\circ}(\text{Na}^+)$ does not affect the additivity principle, only

Table 1. Partial molal volumes, infinite dilution, 25 °C, ml mol⁻¹.

-COOH	25.9	
-CH ₃	26.1	
-CH ₂ -	16.0	
-CH ₂ COO ⁻	33.7	(13 + 20.7)

Table 2. Partial molal volumes at infinite dilution, 25 °C, ml mol⁻¹.

<i>n</i>	Exp.	Calc.	Diff.
A; CH ₃ (CH ₂) _{<i>n</i>} COOH			
0	51.9	52.0	-0.1
1	67.9	68.0	-0.1
2	84.6	84.0	0.6
3	100.5	100.0	0.5
4	116.0	116.0	0
B; (CH ₂) _{<i>n</i>} (COOH) ₂			
0	50.2	51.8	-1.6
1	67.2	67.8	-0.6
2	82.9	83.8	-0.9
3	99.1	99.8	-0.7
4	115.7	115.8	-0.1
5	131.9	131.8	0.1
C; CH ₃ (CH ₂) _{<i>n</i>} COO ⁻			
0	45.8		
1	60.3	59.8	0.5
2	75.8	75.8	0
3	91.7	91.8	-0.1
4	107.2	107.8	-0.6
D; COOH(CH ₂) _{<i>n</i>} COO ⁻			
0	45.7	(46.6)	(1.2)
2	75.5	75.6	-0.1
3	91.4	91.6	-0.2
4	107.6	107.6	0
5	123.2	123.6	-0.4
E; (CH ₂) _{<i>n</i>} (COO ⁻) ₂			
0	41.3	(41.4)	(-0.1)
2	67.3	67.4	-0.1
3	83.2	83.4	-0.2
4	99.4	99.4	0
5	115.0	115.4	-0.4

the partial molal volume of the COO⁻ group.

With $\bar{V}^{\circ}(\text{CH}_2) = 16.0$ ml mol⁻¹ average values of the partial molal volume of the COOH group were calculated from series A and B, Table 2, CH₃ group values from A and C. Results are summarized in Table 1. A charged carboxyl group influences the hydration sphere of the nearest neighbouring CH₂ group substantially.⁷ Separation of the partial molal volumes of the COO⁻ group and the nearest CH₂ group will therefore be ambiguous. The partial molal volumes from series C, D, and E (Table 2) are given as $\bar{V}^{\circ}(\text{CH}_2\text{COO}^-)$ in Table

1 with approximate individual values in parenthesis.

Conclusion. Calculations of partial molal volumes by adding the partial molal volumes of the groups comprising the molecule or ion, agree well with the experimental values for the carboxyl series, Table 2. The additivity relations thus established make possible a simplified treatment of solute solvent interactions, reducing the effective number of systems. It would mean that investigations of microscopic relations in solution may be concentrated to one or two of the groups of the molecule. The search for realistic models for statistical simulation calculations would also be simplified.

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Received June 6, 1974.

Aqueous Chemistry of Protactinium(IV). 4. Complex Formation between Pa(IV) and EDTA

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In studying the aqueous chemistry of Pa(IV) it was concluded¹ that Pa(IV) exists as a doubly charged cation PaO^{2+} (or $\text{Pa}(\text{OH})_2^{2+}$). To obtain further information on this species, complex formation with ethylenediaminetetraacetic acid (EDTA) was investigated. To study the complexation with EDTA, the liquid-liquid distribution system $^{233}\text{Pa}(\text{IV})$ -acetylacetonone in benzene-1 M $(\text{Na},\text{H})\text{ClO}_4$ was chosen since this system had been used previously.² The influence of EDTA (added to the aqueous phase

of the extraction system) on the distribution of Pa(IV) will then provide information on Pa(IV)-EDTA complexes.

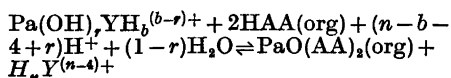
Experimental. The extraction technique and the preparation of most chemicals have been previously described.^{2,3} The distribution system, 2.16 M acetylacetonone in benzene-1 M $(\text{Na},\text{H}, 0.01 \text{ Cr}^{3+})\text{ClO}_4$ was reduced electrolytically in an atmosphere of argon gas before addition of ^{233}Pa and EDTA (EDTA was always added after the ^{233}Pa). EDTA (Merck, *p.a.*) was added as a 10^{-2} M solution in 1 M NaClO_4 . The system was stirred during electrolysis until the D -values ($D = [\text{Pa}]_{\text{org}}/[\text{Pa}]$) were constant, which usually occurred within 15 min.

The extraction system was found to be independent of the Cr^{2+} concentration for concentrations up to at least 0.02 M, at pH ($= -\log [\text{H}^+]$) = 1. Moreover, the degree of complexation between Cr^{2+} and EDTA was calculated using literature data⁴ and was found negligible for the pH range examined.

Evaluation of the species involved in the extraction. In order to derive the ionic forms of the complexes formed in the reactions between Pa(IV) and EDTA the following general reaction is considered: $\text{PaO}^{2+} + \text{H}_n\text{Y}^{(n-4)+} \rightleftharpoons \text{Pa}(\text{OH})_r\text{YH}_b^{(b-r)+} + (n-b-2+r)\text{H}^+ + (1-r)\text{H}_2\text{O}$; $b = 0, 1, 2$; $n = 0, 1, \dots, 6$.

Here Pa(IV) is denoted with PaO^{2+} but a similar reaction may be set up with $\text{Pa}(\text{OH})_2^{2+}$. Since EDTA, denoted by H_nY , is expected to have a maximum of 6 chelate positions, of which at least 4 are assumed to be occupied by Pa(IV) in the complex $\text{Pa}(\text{OH})_r\text{YH}_b^{(b-r)+}$, b can have the values 0, 1 or 2. In the above equation provision is made for a change in the extent of hydrolysis of the central atom.

The number of protons participating in the reaction may be derived from the experimentally determined pH dependence of the extraction reaction. The extraction reaction formula is obtained by combination of the above reaction formula and the extraction reaction formula valid for Pa(IV) in the absence of EDTA: $\text{PaO}^{2+} + 2\text{HAA}(\text{org}) \rightleftharpoons \text{PaO}(\text{AA})_2(\text{org}) + 2\text{H}^+$, (HAA = acetylacetonone); equilibrium constant K_D . The following overall extraction reaction is thus obtained:



This reaction mechanism was studied experimentally under conditions where the Pa-EDTA complex was the dominating protactinium species. The observed dependence of the distribution ratio on the concentrations of HAA ($\partial \log D / \partial \log [\text{HAA}] = 2$) and EDTA ($\partial \log D / \partial \log [\text{EDTA}] = -1$) verifies the proposed extraction mechanism.

From the limiting pH -dependence $\partial \log D / \partial \log \text{pH} = -2$ (see Fig. 1), one concludes that the average number of protons ($n-b-4+r$)