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Complexation of Am(III) by Oxalate in $NaClO_4$ Media

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Abstract

The complexation of Am(III) by oxalate has been investigated in solutions of $NaClO_4$ up to 9.0 M ionic strength at 25°C. The dissociation constants of oxalic acid were determined by potentiometric titration, while the stability constants of the Am(III)-oxalate complexation were measured by the solvent extraction technique. A thermodynamic model was constructed to predict the apparent equilibrium constants at different ionic strengths by applying the Pitzer equation using parameters for the Na^+-HOx^-, Na^+-Ox^-, $AmOx^+$-ClO_4^-, and Na^+-$Am(Ox)_2^-$ interactions obtained by fitting the data.

Keywords. Acid Constants, Stability Constants, Americium, Oxalic Acid, Pitzer Parameters, Solvent Extraction.

Introduction

Some of the organic ligands contained in nuclear wastes have a relatively strong binding ability for actinides and their presence could result in significant increase in the concentration of dissolved actinides released to the surrounding area. Oxalic acid has been identified as one of the organic ligands which may be present in the wastes prepared for disposal in the Waste Isolation Pilot Plant (WIPP) repository [1]. Its presence in actinide wastes is due to its use in separations and in the removal of actinide contamination. These uses reflect the strength of complexation of actinides by oxalate.

In a previous paper [2], we reported on the complexation of oxalate, Ox, with Th(IV) and $U(VI)O_2^{2+}$ in $NaClO_4$ media up to 9.0 M. For the species MOx and $M(Ox)_2$, the stability constants were modeled using the Specific Interaction Theory. In this paper, the stability constants for formation of $AmOx^+$ and $AmOx_2^-$ in $NaClO_4$ ionic media from 0.1 to 9.0 M are reported. The Pitzer equation has been employed to analyze the interactions between Am(III) and oxalate.

Experimental

Reagents

Oxalic acid and sodium perchlorate (Aldrich, A.C.S. reagent grade) were used without purification. Dibenzoylmethane (1,3-diphenyl-1,3-propanedione, HDBM) was purified by vacuum distillation at 125°C [3]. Tributyl phosphate, TBP, was used without further purification. Stock solutions of sodium hydroxide and hydrochloric acid were prepared as 1.00 M standard solutions. All other reagents are of A.C.S. reagent grade.

A stock solution of 0.100 M oxalic acid was prepared by dissolving the required amount of oxalic acid in deionized water. The solutions for potentiometric titration consisted of 0.010 M oxalic acid in $NaClO_4$ media from 0.1 M up to 9.0 M. For the solvent extraction experiments, solutions of different concentrations of oxalate in $NaClO_4$ media were used as the aqueous phases, while the pH was kept constant using 0.01 M hydroxylamine as a buffer. Solutions with a fixed ratio of HDBM to TBP of 1:4 in toluene served as the organic phases. The concentrations of

HDBM varied from 0.010 M to 0.0025 M. The concentration depends on the pcH (-log[H^+] (molar)) of the equilibrated aqueous phases. To avoid photolysis of the extractants, the organic solutions were stored in the dark. ^{241}Am tracer was prepared in 0.001 M $HClO_4$ solution and added to the samples in 10 μL aliquots.

Procedures

Potentiometric Titration. The experimental details have been described previously [3]. The potentiometric titrations at 25.0±0.1°C used 15.0 mL of 0.010 M oxalate solutions titrated with 0.03 M NaOH having the same $NaClO_4$ concentration. The pH measurements were performed using an Orion Corning Semimicro-Combination glass electrode equipped with an Accumet 950 pH/ion Meter. The KCl solution in the reference cell was replaced with saturated NaCl solution to avoid precipitation of $KClO_4$ in the junction. The pH meter readings were converted to pcH using the equation proposed by Irving et al. [4]. The deprotonation constants were determined by plotting dn/ln[H^+] x C_L vs. pcH, where n is the ratio of the concentration of H^+ bound to the ligand and C_L is the total ligand concentration. This method allows for the evaluation of the pK and pK_w values [5].

Solvent Extraction. The solvent extraction experiments were performed following the procedure described in Refs. [2] and [3]. In 5.0 mL of aqueous solutions, 0.0, 10, 20, 30, 40, 50, and 60 μL of 0.10 M oxalic acid stock solution were added to adjust the concentration of oxalate. The borosilicate scintillation vials and the caps were silanized according to the method in Ref [6]. The γ-activity measurements were made using an ISOFLEX automatic gamma counter.

Results and Discussion

Dissociation of Oxalic Acid. Table 1 lists the deprotonation constants of oxalic acid calculated from our potentiometric titration data. At low ionic concentrations the agreement is good for both pK_{a1} and pK_{a2}, within the reported experimental errors of the literature data.

Complexation of Am(III) by Oxalate. The distribution coefficients of Am(III) were measured in the presence of different concentrations of oxalate, from which the apparent stability constants for the complexes of metal to ligand ratios of 1:1 and 1:2 were calculated. Figure 1 shows a typical plot of the experimental values of D_0/D as a function of free oxalate concentration. Tables 2 and 3 summarize the experimental results for the first and the second stability constants of Am(III)-oxalate. The calculation of stability constants from solvent extraction equilibrium data is described in previous papers [2, 3]. To simplify the system, in this study the pcH was chosen to be high enough for complete dissociation of the oxalic acid. As shown in Table 3, no dependence of the apparent stability constants on pcH is observed in the pcH region below 7.0, indicating that only the deprotonated complexes $AmOx^+$ and $Am(Ox)_2^-$ are present. In solutions of higher pcH, the stability constants for both species decrease with increasing pcH, which reflects the competition due to Am(III) hydrolysis [3]. Following the equation derived in Ref. [3], the hydrolysis constants, $^*\beta_{OH}$, of Am(III) for the reaction:

$$Am^{3+} + H_2O \Leftrightarrow Am(OH)^{2+} + H^+ \qquad (1)$$

were estimated. The hydrolysis constants defined by eq. 1 are given in Table 3 for 1.0, 3.0, and 5.0 M ionic strength ($NaClO_4$). The 1.0 M value of -7.78±0.10 at 1.0 M can be compared with earlier reports of -7.03±0.05 [7] and -7.5±0.3 [8] in 1.0 M solutions. Our value agrees within error limits with that of Ref. [9] and also with the value of -7.54±0.20 reported for 0.7 M (NaCl) [3].

Thermodynamic Model Using Pitzer Activity Coefficient Approach. To account for the ionic medium effect on equilibrium constants, a successful approach has involved application of the Pitzer activity coefficient equation [10-12]. We have performed Pitzer modeling to provide some physicochemical understanding of the ionic interactions involved in the Am-oxalate-$NaClO_4$ system, which is of importance for the speciation of Am(III) in brine solutions. The thermodynamic equilibrium model, including activity coefficients, can be expressed as:

$$H_2Ox \Leftrightarrow H^+ + HOx^-, \qquad K_{a1}^T = \frac{m_{H^+}\, m_{HOx^-}}{m_{H_2Ox}} \frac{\gamma_{H^+}\, \gamma_{HOx^-}}{\gamma_{H_2Ox}} \qquad (2)$$

$$\mathrm{HOx^- \Leftrightarrow H^+ + Ox^{2-}}, \qquad K_{a2}^{T} = \frac{m_{H^+}\, m_{Ox^{2-}}}{m_{HOx^-}} \frac{\gamma_{H^+}\, \gamma_{Ox^{2-}}}{\gamma_{HOx^-}} \tag{3}$$

$$\mathrm{Am^{3+} + Ox^{2-} \Leftrightarrow AmOx^+}, \qquad \beta_{101}^{T} = \frac{m_{AmOx^+}}{m_{Am^{3+}}\, m_{Ox^{2-}}} \frac{\gamma_{AmOx^+}}{\gamma_{Am^{3+}}\, \gamma_{Ox^{2-}}} \tag{4}$$

$$\mathrm{AmOx^+ + Ox^{2-} \Leftrightarrow Am(Ox)_2^-}, \quad \beta_{102}^{T} = \frac{m_{Am(Ox)_2^-}}{m_{AmOX^+}\, m_{Ox^{2-}}} \frac{\gamma_{Am(Ox)_2^-}}{\gamma_{AmOx^+}\, \gamma_{Ox^{2-}}} \tag{5}$$

where m_x denotes the concentration in molality and γ_x is the corresponding activity coefficient. $K_{a1}{}^{T}$ and $K_{a2}{}^{T}$ are the respective thermodynamic dissociation constants of H_2Ox and HOx^-, and $\beta_{101}{}^{T}$ and $\beta_{102}{}^{T}$ are the thermodynamic stability constants for $AmOx^+$ and $Am(Ox)_2^-$, respectively.

The activity coefficients of the species were calculated by employing the Pitzer equations for trace cation (c) and anion (a) [9, 13, 14]:

$$\ln\gamma_c = Z_c^2 f^{\gamma} + 2(B_{cClO_4} + EC_{cClO_4})m + Z_c(Z_c B'_{NaClO_4} + C_{NaClO_4})m^2 + (2\phi_{cNa} + m\psi_{cNaClO_4})m \tag{6}$$

$$\ln\gamma_a = Z_a^2 f^{\gamma} + 2(B_{Naa} + EC_{Naa})m + |Z_a|(|Z_a|B'_{NaClO_4} + C_{NaClO_4})m^2 + (2\phi_{ClO_4a} + m\psi_{NaClO_4a})m \tag{7}$$

where Z_c and Z_a are the charge of the cation and the anion, respectively, and $E=1/2\sum m_i|Z_i|$. ϕ is the two-body interaction term from binary mixing, $\phi = \theta + \theta^E(I)$, where θ^E is an ionic strength dependent term for asymmetric mixing which can be calculated from the numerical approach proposed by Pitzer [14]. Other terms are defined as:

$$f^{\gamma} = A_{\phi}\left[\frac{\sqrt{I}}{1+b\sqrt{I}} + \frac{2}{b}\ln(1+b\sqrt{I})\right] \tag{8}$$

with A_ϕ=-0.392 at 25°C, b=1.2 $Kg^{1/2}\ mol^{-1/2}$, and α=2.0 $mol^{-1/2}$:

$$B_{MX} = \beta_{MX}^{0} + 2\beta_{MX}^{1} \frac{1-(1+\alpha\sqrt{I})\exp(-\alpha\sqrt{I})}{\alpha^2 I} \tag{9}$$

$$B'_{MX} = -2\beta^1_{MX} \frac{1-(1+\alpha\sqrt{I}+\alpha^2 I/2)\exp(-\alpha\sqrt{I})}{\alpha^2 I^2} \quad (10)$$

$$C_{MX} = 3C^{\phi}_{MX}/2 \quad (11)$$

where $\beta^0{}_{MX}$, $\beta^1{}_{MX}$, and $C^{\phi}{}_{MX}$ are parameters independent of the ionic strength. (N.B. These parameters are not to be confused with the stability constants which are also denoted by β, see eq. (4) and (5).) For neutral species, the Pitzer equation is reduced to:

$$\ln\gamma_{HOx} = 2m_{Na}\lambda_{Na,HOx} + 2m_{Cl}\lambda_{Cl,HOx} \quad (12)$$

where $\lambda_{Na,n}$ and $\lambda_{Cl,n}$ are the parameters for ion-neutral interactions.

The Pitzer parameters for protons are available from Ref. [14]. For the Am^{3+}-ClO_4^- interaction, Felmy et al. [15], in their Am(III) solubility model, used $Nd(ClO_4)_3$ as an analog to $Am(ClO_4)_3$ and obtained the parameters from osmotic pressure data of $Nd(ClO_4)_3$. Rai et al. [16] used the data given by Pitzer [14] for $Nd(ClO_4)_3$. In this work, we used the Pitzer parameters for $Am(ClO_4)_3$ from Rosta [17].

The remaining Pitzer parameters required in the calculation are those for the binary interactions (Na^+-HOx^-, Na^+-Ox^{2-}, HOx^--ClO_4^-, Ox^{2-}-ClO_4^-), ternary interactions (Na^+-ClO_4^--HOx^-, Na^+-ClO_4^--Ox^{2-}), and neutral-ion interactions (H_2Ox-Na^+ and H_2Ox-ClO_4^-). As the experimental data are not sufficient to determine all of these parameters, in our calculation only the cation-anion binary interactions were retained as model parameters. They were obtained together with the thermodynamic equilibrium constants by fitting the model calculation result to the experimental data using the program MacNONLIN 2.0 [18, 19].[a] The results are summarized in Table 4. Both values of β^1 for Na^+-Ox^{2-} and Na^+-HOx^- interactions are positive and comparable to those given by Pitzer [14] for the salts of the same type, indicating that our assumptions may be reasonable. The β^1 values for the complexes $AmOx^+$ and $Am(Ox)_2^-$ are respectively 0.3159 and

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[a] MacNONLIN 2.0 is the Macintosh version of NONLIN. NONLIN was developed by A. R. Felmy and uses the MINPACK nonlinear least squares programs combined with a chemical equilibrium program based on a Gibbs free-energy minimization procedure.[18]

-0.2516, which are in the same level of magnitude with those of univalent electrolytes. This implies that our proposed model is of a reasonable physicochemical basis.

In Figures 2 and 3, the equilibrium constants calculated from the proposed model are compared with the experimental points. The first dissociation constant at zero ionic strength, pK_{a1}^{T}=1.423, is a little higher than those given in Refs. [19] and [20] (see Table 1), while the second constant, pK_{a2}^{T}=4.264, is in good agreement with the literature data. The thermodynamic stability constants were calculated to be: $\log\beta^{T}_{101}$=6.557, $\log\beta^{T}_{102}$ =9.450. No comparison can be made for these two constants due to the lack of suitable data. Above ca. 0.1 M, the agreement between data and calculation is quite satisfactory; in other words, the model is accurate for predicting the equilibrium quotient in the concentration region of 0.1 to 5 m. It should be noted that the Pitzer parameters for Na^+-ClO_4^- and H^+-ClO_4^- interactions are valid only at concentrations below 6.0 m. For the concentration of the brine in the salt beds in the WIPP repository area, application of the Pitzer model to obtain information on the effect of the brines on actinide solubility seems justified.

Acknowledgments

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Table 1. Stoichiometric dissociation constants of oxalic acid in $NaClO_4$ media at 25°C

$NaClO_4$		pK_{a1}		pK_{a2}	
M	m	p. w.	Lit.	p. w.	Lit.
0.00	0.00		1.252 [20]		4.224 [20]
0.00	0.00		1.299 [20]		4.300 [20]
0.00	0.00		1.271[20]		4.275 [20]
0.100	0.103			3.97±0.01	
0.100	0.103		1.37 [21]		3.81 [21]
0.150	0.156		1.33 [21]		3.94 [21]
0.300	0.315			3.73±0.01	
0.500	0.529	1.28±0.03		3.65±0.01	
0.500	0.529		1.20 [22]		3.67 [22]
1.000	1.073	1.331±0.04		3.60±0.01	
1.000	1.073		1.08 [23]		3.554 [23]
3.000	3.483	1.49±0.02		3.84±0.01	
5.000	6.535	1.42±0.04		4.23±0.01	
7.000	10.563	1.75±0.01		4.71±0.01	
9.000	14.061	2.13±0.04		5.11±0.04	

Table 2. Stoichiometric stability constants of Am(III)-oxalate complexation in $NaClO_4$ media at 25°C

$NaClO_4$		$\log\beta_{101}$		$\log\beta_{102}$	
M	m	p. w.	Lit.	p. w.	Lit.
0.100	0.103		5.25 [24]		8.85 [24]
0.500	0.529		4.82 [25]		8.60 [25]
0.700	0.750		4.58 [3]		7.91 [3]
1.000	1.073	4.61±0.06		8.39±0.12	
1.000	1.073		4.63 [26]		8.35 [26]
3.000	3.483	4.65±0.04		8.67±0.13	
5.000	6.535	4.83±0.06		9.24±0.09	
7.000	10.563	4.93±0.11		9.42±0.06	
9.000	14.061	4.54±0.06		8.77±0.05	

Table 3. Stability constants of oxalate complexation and hydrolysis of Am(III) in NaClO$_4$ media at 25°C

	1.0 M		3.0 M		5.0 M	
pcH	logβ_{101}	logβ_{102}	logβ_{101}	logβ_{102}	logβ_{101}	logβ_{102}
6.32	4.41±0.13	8.39±0.12				
6.42	4.51±0.07	8.47±0.07				
6.46	4.69±0.03	8.36±0.04				
6.52			4.65±0.04	8.67±0.13		
6.77	4.65±0.03	8.41±0.05				
6.78					4.83±0.06	9.24±0.09
6.91			4.62±0.06	8.46±0.12		
6.97	4.68±0.03	8.29±0.03				
7.07			4.60±0.04	8.38±0.07		
7.10	4.49±0.24	8.29±0.12				
7.14			4.60±0.08	8.73±0.07		
7.16	4.57±0.13	8.33±0.19				
7.24	4.60±0.08	8.34±0.07				
7.28					4.80±0.06	9.10±0.10
7.29			4.40±0.04	8.33±0.05		
7.31		8.27±0.20				
7.36					4.94±0.09	9.24±0.12
7.39			4.53±0.03	8.43±0.03		
7.44					4.85±0.08	9.03±0.05
7.45			4.06±0.03	8.44±0.03		
7.52			3.95±0.31	8.50±0.03		
7.55	4.52±0.09	8.13±0.15				
7.59			3.85±0.10	8.23±0.05		
7.63	4.48±0.06	8.18±0.14				
7.64					4.69±0.17	9.15±0.03
7.70			3.70±0.14	8.01±0.11		
7.75			3.30±0.20	7.92±0.12		
7.80	4.56±0.10	8.09±0.08				
7.85					4.48±0.07	9.06±0.03
7.94					4.59±0.04	8.59±0.15
8.06					4.60±0.04	8.63±0.11
8.13					4.52±0.03	8.40±0.21
8.27					4.30±0.05	8.22±0.08
			log$^*\beta_{OH}$			
	-7.78±0.10 (1.0 M)		-7.83±0.10 (3.0 M)		-8.00±0.12 (5.0 M)	

Table 4. The Pitzer parameters for the Am-H-Na-ClO_4-Ox system

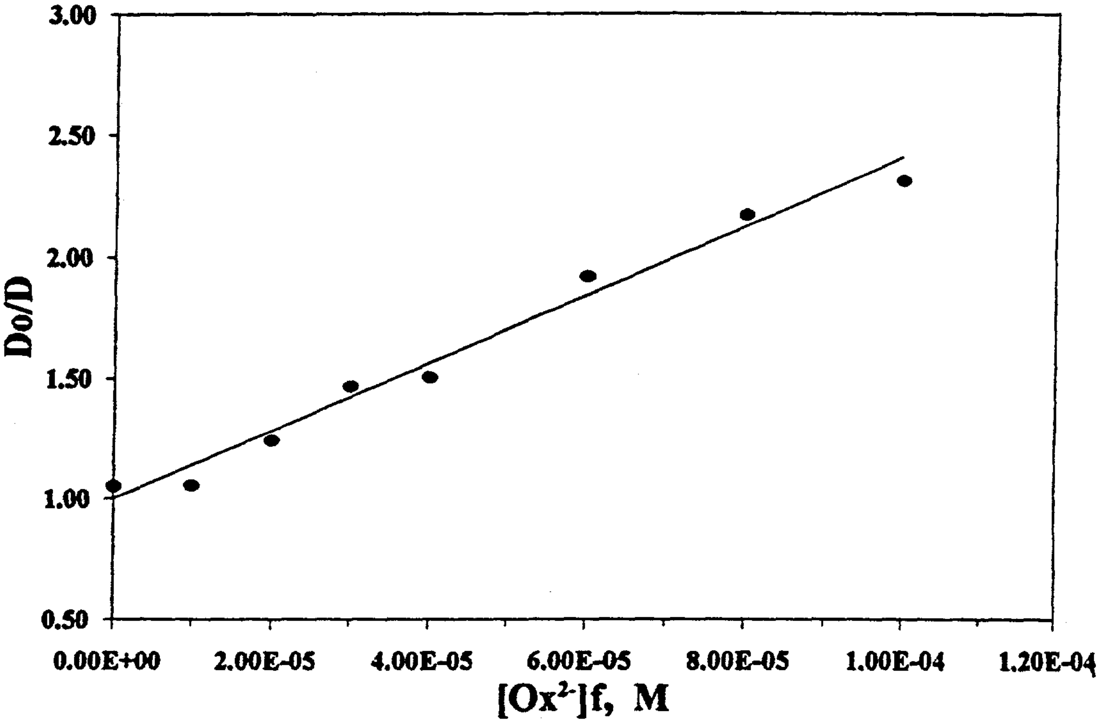
Cation	Anion	β^0	β^1	C^ϕ	References
H^+	ClO_4^-	0.1747	0.2931	0.00819	[14]
Na^+	ClO_4^-	0.0554	0.2755	-0.00118	[14]
Na^+	Ox^{2-}	0.0055	2.1396	-0.03338	p.w.
Na^+	HOx^-	-0.1256	0.7540	-0.00319	p.w.
Na^+	$Am(Ox)_2^-$	0.1139	-0.2516	-0.2356	p.w.
Am^{3+}	ClO_4^-	1.5922	4.6434	-0.1665	p.w.
$AmOx^+$	ClO_4^-	0.7269	0.3159	-0.1323	p.w.
H^+	Na^+	θ=0.036			p.w.

Figure Captions

Fig. 1. Representative plot of D_0/D vs. free oxalate concentration. Aqueous phase: 1.0 M $NaClO_4$, pcH 6.42. Organic phase: 0.010 M HDBM + 0.040 M TBP in toluene.

Fig. 2 The stoichiometric first dissociation constants, pK_{a1} and pK_{a2}, of oxalic acid as a function of $NaClO_4$ concentration. The solid line is calculated from Pitzer modeling.

Fig. 3 The stoichiometric stability constants, $\log\beta_{101}$ and β_{102}, of Am^{3+}-Ox^{2-} complexation as a function of $NaClO_4$ concentration. The solid line is calculated from the Pitzer modeling.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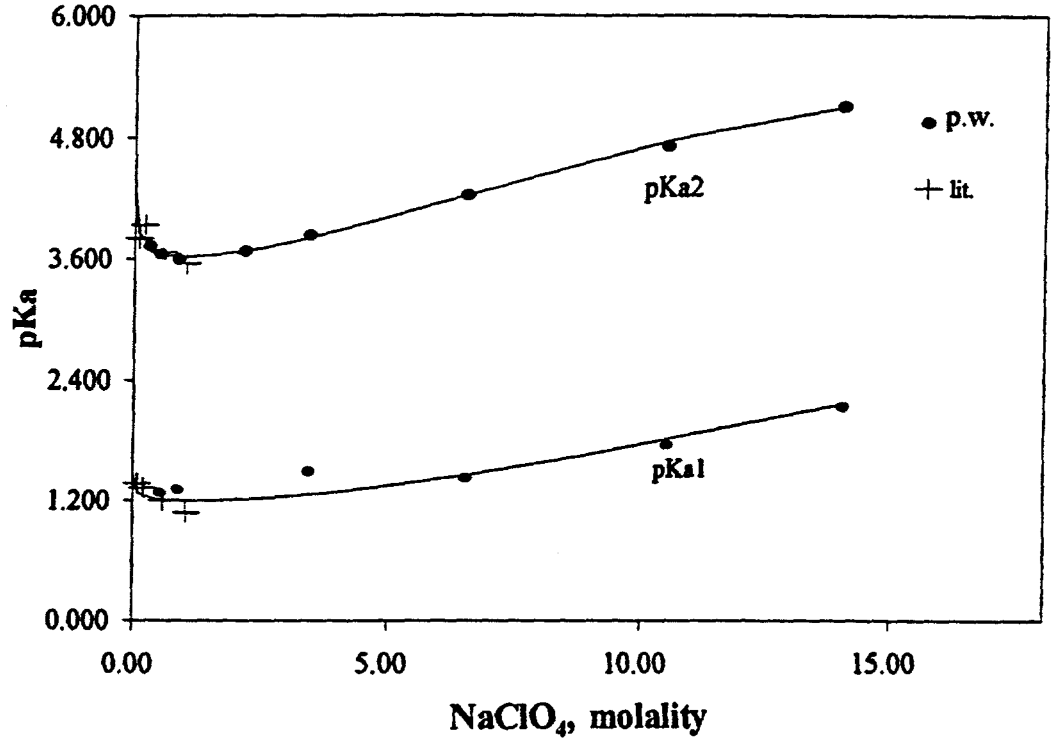
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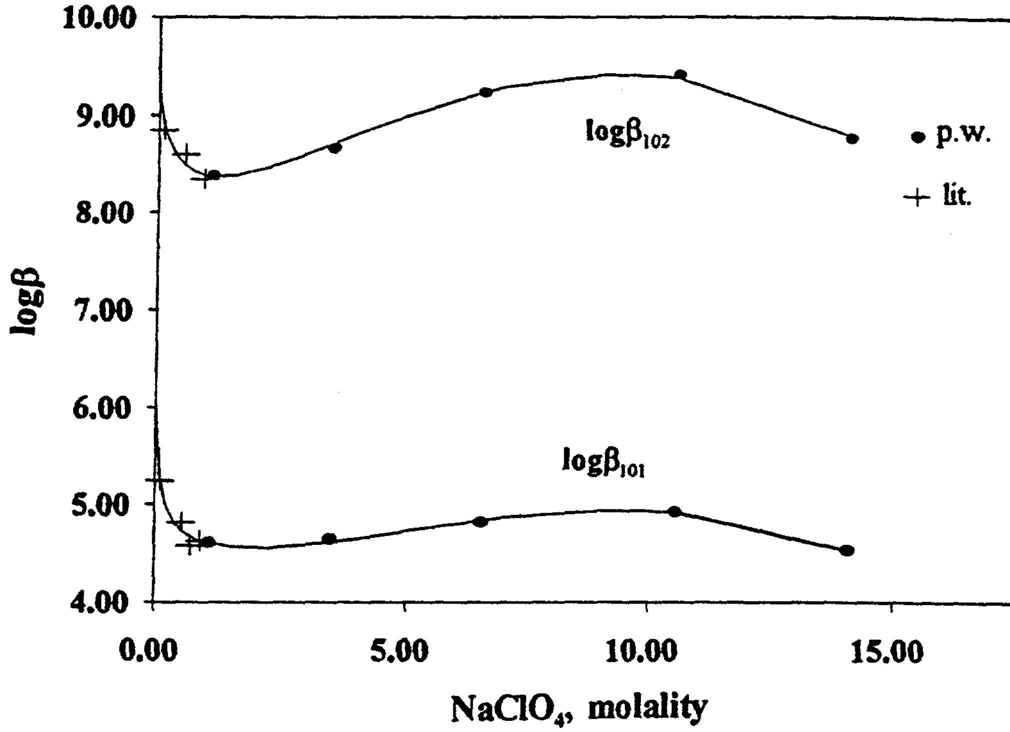
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