



Thermodynamic Parameters and Stability Constants of $\text{UO}_2(\text{II})$ Complexes with Some Hydroxy Acids

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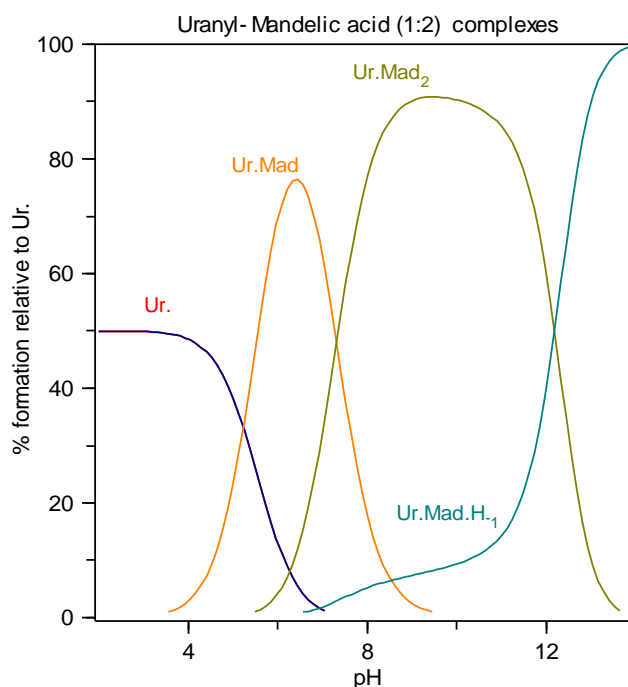
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• Novelty and Highlights:

- 1 – Formation of $\text{UO}_2(\text{II})$ complexes with malic acid, in solution state which is not reported previously.
- 2 – ML and ML_2 type of complexes are formed by coordination of $\text{UO}_2(\text{II})$ ion with selected hydroxy acids.
- 3 – Complexation of $\text{UO}_2(\text{II})$ with hydroxy acids is influenced by pH, ionic strength, temperature, nature of solvent and basicity of the ligand.

• Graphical Abstract:





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Abstract: Formation of complexes of type ML and ML_2 , where $\text{M}=\text{UO}_2(\text{II})$ and L = malic acid, lactic acid, salicylic acid or mandelic acid have been studied by using modified form Bjerrum method in aqueous media at different temperatures and ionic strengths. The resulting formation constants, $\log\beta$ for $\text{UO}_2(\text{II})$ —Hydroxy acid complexes have been calculated by considering BESTFIT model and using Fortran IV program BEST based on least square calculations. Thermodynamic parameters are also evaluated, negative ΔG^0 , ΔH^0 and ΔS^0 values indicate that complex formation is favourable at 303.15K, 313.15K and 323.15K. Using SPEPLOT Fortran IV program, species diffusion curves of complexes are plotted to fantasize about the presence of variegated species in equilibrium. To understand more about this equilibrium, the stability of these complexes is studied in presence of systemic errors which are added as [acid], [alkali], [metal], [ligand] and carbon dioxide concentration changes.

Keywords: Equilibrium, Ionic strength, Bjerrum method, Stability, BEST.

Introduction

Hydroxy acids have innumerable applications in chemical, pharmaceutical and paint industries. For short term therapeutic application, the poly (β -hydroxyacid)-type polyesters like malic acid-based polymers, PMLA and derivatives, and bacterial polyesters are representing quality options [1]. Lactic acid is used in the food industries for the process of adding micronutrients in the food products [2]. In cosmetic products, lactic acid is used for pH regulators and as moisturizers. Moreover, lactic acid has ability for skin lightning, antimicrobial activity and skin hydration [3]. Role of lactic acid in moisturizing effect and skin lighting action is directly related to water retaining capacity of lactate's and reduction of the tyrosinase formation respectively. Lactic acid is also used as an electrolyte for many parenteral/I.V. solutions used to restore the bodily fluids or as an electrolyte for the solution used in typical artificial kidney machines e.g. in dialysis solution, continuous ambulatory peritoneal dialysis solution and in Hartmann's solution. Salicylic acid prevents clogging of pore, causes cells of epidermis to slough off rapidly and helps in growth of new cells. Salicylic acid is useful in treating dandruff and in removing warts. So it is used as an active ingredient in gels and shampoos. [4-6]. Mandelic acid exists in two enantiomers as well as the

racemic mixture, known as paramandelic acid. A vast literature exists in which it is revealed that Mandelic acid and its derivatives showed anti-oxidant [7], urinary antiseptic [8], anti-HIV [9], antitumor [10], antifungal and anti-thrombic effects [11].

Uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2$) are yellow green hexahydrate crystals which are water soluble and are triboluminescent in nature [12]. In analysis of tissue samples, uranyl nitrate and acetate is used as negative stain for viruses in electron microscopy because it stabilizes nucleic acid and cell membrane. In 1950s, Uranyl nitrate was used as feeder fuel in various reactors [13]. In presence of ultraviolet light lower oxidation state of uranium (IV) is obtained by picking of up two electrons and it undergoes reduction. Uranous nitrate is the widely accepted reductant for partitioning now a days. Electrolytic reduction of uranyl nitrate is carried out by using pure titanium as cathode and TSIA (Titanium Substrate Insoluble Anode) as anode.

Many binary and ternary complexes of transition and inner transition metals have been studied pH-metrically [14-23]. It is anticipated that complexes of these selected hydroxyl acids may have some useful applications.

In this study, the formation constants of $\text{UO}_2(\text{II})$ -Hydroxy complexes and their thermodynamic parameters like ΔG^0 , ΔH^0 and ΔS^0 are studied at $303.15 \pm 0.1\text{K}$, $313.15 \pm 0.1\text{K}$, $323.15 \pm 0.1\text{K}$ and at ionic strength $0.2 \text{ mol}\cdot\text{L}^{-1}$ (NaClO_4). The nature and concentration of various formed species at different pH is also established by species distributed curves. Somewhat detailed study is carried to understand more about these formation constants in presence of systemic errors. The change in concentration of carbon dioxide, alkali, acid, metal and ligand were considered as systemic errors.

Experimental

Reagents Four hydroxy acids namely malic acid, lactic acid, salicylic acid or mandelic acid with 99.75% purity were obtained from Chitichem, Vadodara, India and Uranyl nitrate with 99.3% purity was procured from Sigma-Aldrich, USA. All reagents were analytical grade and were used without further purification. Uranyl nitrate was dissolved in water and the solution was standardised gravimetrically [24]. Doubly distilled CO_2 -free water was used for preparation of solutions. Perchloric acid was standardized with standard NaOH (99.0% purity by HPLC, E. Merck Ltd., Mumbai, India). To keep constant ionic strength sodium perchlorate (NaClO_4) (99.0% purity by E. Merck Ltd., Mumbai, India) is used as an inert electrolyte.

Apparatus Systronics μ pH meter 361 having combined glass electrode and temperature probe with readability ± 0.1 °C was used for pH metric titrations. Temperature was maintained with High Precision Water Bath Cat. No. MSW- 274 with readability ± 0.1 °C. Glass cell with specific design and magnetic stirrer in nitrogen atmosphere has been used for titration purpose. The method reported by Bjerrum and Calvin as modified by Irving and Rossotti has been applied here [25].

Titration Sets The following three sets were prepared for titrations:

- (i) Acid [$50 \text{ mmol}\cdot\text{L}^{-1}$]
- (ii) Acid [$50 \text{ mmol}\cdot\text{L}^{-1}$] + Hydroxy acid [$10 \text{ mmol}\cdot\text{L}^{-1}$]
- (iii) Acid [$50 \text{ mmol}\cdot\text{L}^{-1}$] + Hydroxy acid [$10 \text{ mmol}\cdot\text{L}^{-1}$] + Uranyl nitrate [$1 \text{ mmol}\cdot\text{L}^{-1}$].

All the titration sets were maintained at 0.10, 0.20, 0.30, 0.40 $\text{mol}\cdot\text{L}^{-1}$ [NaClO_4] ionic strength and at $303.15 \pm 0.1\text{K}$, $323.15\text{K} \pm 0.1\text{K}$, $323.15 \pm 0.1\text{K}$ temperature by keeping total volume 50 ml. Mixtures were titrated with carbonate free standardized $0.20 \text{ mol}\cdot\text{L}^{-1}$ NaOH solution.

Modelling strategy internal consistency and a good sigma fit are rather easy to be achieved because the curve

fitting algorithm is set up to do just that. Internal accuracy means that reproducibility is possible and that the equipment is in apparently good shape, but does not guarantee absolute accuracy. A poor or incorrect model is either incomplete or an incorrect statement of species present. Therefore, once it is ascertained that the data are accurate, the model may be modified one item at a time in accordance with sound principles of coordination chemistry until a satisfactory refinement (low S_{\min} to experimental data) is obtained.

A Bjerrum analysis is performed [26] in selected model. The function $\bar{n}L$ and $\bar{n}H$ are given by the equations

$$\bar{n}L = [L - \{H - (h - oh)\} \sqrt{\bar{n}H}] / M \quad (1)$$

$$\bar{n}H = \frac{\sum_{j=1}^3 j\beta_{0j}h^j}{1 + \sum_{j=1}^3 j\beta_{0j}h^j} \quad (2)$$

The free ligand concentration is derived,

$$pL = - \frac{(L - \bar{n}LM)}{1 + \sum_{j=1}^3 j\beta_{0j}h^j} \quad (3)$$

In equations 1-3, $\bar{n}L$ is average number of ligands bound to per metal ion, L is total concentration of ligand, H is total concentration of excess hydrogen, h is the free hydrogen ion concentration, oh is the free hydroxide ion concentration, $\bar{n}H$ is average no. of protons associated with ligand, M is total metal ion concentration, β_j is cumulative formation constants of j^{th} associated species. The values of β_n were calculated with BEST program [27-28] run on personal computer using BESTFIT model from data obtained by titration of mixtures from sets (i), (ii) and (iii). Determination of set of β_n values was considered with weighted least squares treatment and making the function,

$$U = \sum_{n=0}^N (y - x - nz) \beta_n x^n \quad (4)$$

nearest to zero by minimizing the function 's'

$$S_{\min} = \sum_{i=1}^I U^2 (x_i y_i z_i) \quad (5)$$

Where, y = total concentration of ligand, x = total concentration of unbound ligand, z = total concentration of metal ion and β_n = Stability constants.

S_{\min} values for the different metal complexes is calculated and reported in Table 2. S_{\min} can be equated to χ^2 . S_{\min} is the similar statistical distribution as χ^2 with K degrees of freedom as reported by Powell [29].

Calculations

Dissociation constant Dissociation constant values for hydroxyl acids like malic acid, lactic acid, salicylic acid and mandelic acid are available in the literature [30, 32]. The



values are recalculated with Fortran IV programs PKAS [31], BEST [27-28] and point wise calculation method to check the selected BESTFIT model.

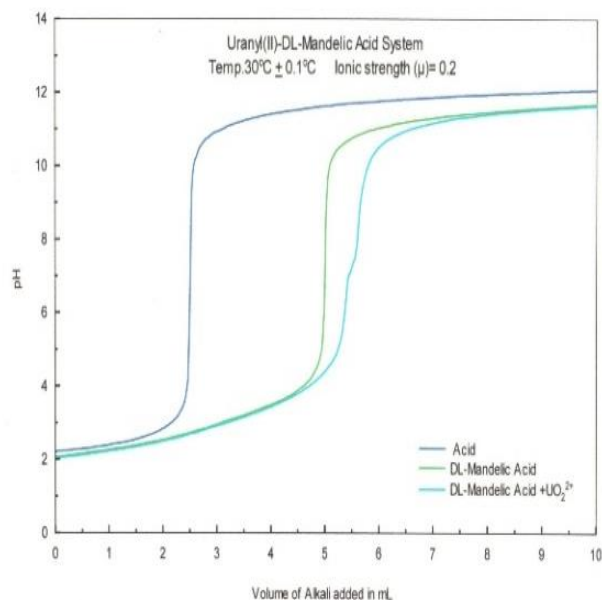


Figure 1: pH metric titration curves for the $\text{UO}_2(\text{II})$ -DL Mandelic acid binary system.

Formation constant Formation constant values are calculated using BEST FIT models using program BEST [27].

Thermodynamic Parameters

Various thermodynamic parameters like Gibb's free energy (ΔG^0), Enthalpy (ΔH^0) and the Entropy (ΔS^0) are calculated by following Eq. 6 to 8

$$\Delta G = -2.303RT \log K \quad (6)$$

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

$$\frac{d \log\left(\frac{K_1}{K_2}\right)}{d\left(\frac{1}{T}\right)} = \frac{-\Delta H}{4.57} \quad (8)$$

Where, R = ideal gas constant, T = Temperature in kelvin, K = equilibrium constant, ΔH = change in enthalpy, ΔS = change in entropy.

Results and discussion

Stability Constants A representative titration graph for $\text{UO}_2(\text{III})$ -Mandelic acid binary system is given in Figure 1. From the figure of curves of solution (I), (II) and (III), the values of $\log\beta$ were calculated with BEST program run on personal computer using BESTFIT model.

BESTFIT model was developed considering $S_{\min} < 1$ and repeating each titration three times and considering 50-60 titration data points between pH ranges 2-10. The dissociation constants are calculated by PKAS, BEST and Point wise are presented in Table 1. The results for three methods are in good agreement. The formation of the constants for binary complexes formed due to interaction of divalent uranyl ion with hydroxyl acids like Malic acid, Lactic acid, Salicylic acid and Mandelic acid were calculated and are given in Table 2.

According to Lewis acid-base theory, a complex formation is an acid base reaction in which a ligand donates electron pair and a metal accepts an electron pair. The stability of complexes is influenced by nature of metal, ligand and other constraints like temperature, pressure, kinetic effect, and thermodynamic effect. The most stable oxidation state of $\text{UO}_2(\text{II})$ is M^{2+} . In inner transition metals ions all outer electrons reside in the 4f and 6s electron; the 5d shell may be partially occupied. In aqueous medium, hydration shell of water molecules surrounds the metal ions. The exact hydration number for different metal ions is a matter of controversy. In aqueous medium water act as ligand and added ligands experience competition and face difficulty in replacing water molecules from coordination sphere of metal ions. The binary formation constant in case of $\text{UO}_2(\text{II})$ complexes with Hydroxy acid are explained on the basis

- (1) Basicity of ligand
- (2) Steric hinderence
- (3) Size and charge of metal ion or charge/size ratio.

Besides these factors, changes in thermodynamic functions are also operative in determining the value of formation constants. The order of stability of binary complexes is given as under: malic acid > lactic acid > salicylic acid > mandelic acid. The four hydroxyl acids selected are biologically important. Out of these, two of them have aromatic ring and one (salicylic acid) is having acidic -OH (phenolic) group. All the remaining three have aliphatic hydroxy group which is not acidic in character. The two aliphatic acids are highly soluble in water. All the three optically active acids are racemates. Salicylic acid has lowest basicity but the stability of its binary complexes with salicylic acid is more than mandelic acid in these complexes. It may be due to the ring structure of salicylic acid which has led to ring stabilization with $\text{UO}_2(\text{II})$. DL- lactic acid has highest value for dissociation constant (pK_1^{H}) than DL- malic acid but $\log K_2$ value for binary complexes of DL- malic acid is higher than DL- lactic acid. DL- malic acid is a tridentate ligand with one -OH group and two -COOH groups. Two stability constants ($\log\beta_1$ and $\log\beta_2$) are observed in case of DL- malic acid showing the precipitation of both -COOH groups in formation of binary complexes.

Effect of systemic error on the BESTFIT model An investigation is made on pessimistic errors so as to evaluate critical stability constants in present set of experimental



conditions using BESTFIT model. The changes in concentration of dissolved carbon dioxide, alkali, acid, ligand and metal content are used in calculation as pessimistic errors. The changes in formation constants due to change in systematic errors (in %) are given in Table 4. The order of effect of systematic errors on formation constants are: dissolved carbon dioxide > alkali > acid > ligand > metal. When the error is higher, the % of species ML & ML₂ get changed and hydroxy species becomes predominant.

Effect of Temperature From Table 2, it is clear that the with increase in temperature the values of formation constants decrease along with the pK_H values. The increase in temperature does not favor the stability of these complexes.

Effect of ionic strength The ionic strength influences all selected complexes and the values of formation constants (logβ) decrease with increase in ionic strength. The values of dissociation constant also decrease with increase of ionic strength of medium. Thermodynamic stability constant (logβ₀) is obtained by theorize the linear plot of logβ vs √μ to zero ionic strength and values are given in Table 3.

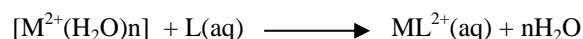
Solvent Effect It is known that two major features influence the basicity and acidity of a molecule namely structure and solvent effects. A number of investigations have been done on protonation constants of amines in aqueous medium but a very little information is available on dissociation constants of hydroxyl acids and their corresponding metal complexes in water-organic solvent (v/v) mixtures. Comparison of dissociation constants of hydroxyl acids and the formation constant of UO₂(II) complexes obtained in ethanol-water mixtures (10-40% V/V) with values in aqueous media, show that values in water are greater than those in ethanol-water mixtures (Table 4).

It is clear that pK_H values of hydroxyl acids decrease with increase in content of ethanol in organic – aqueous mixtures. Increase in ethanol content decreases the dielectric constant of medium, hydrogen bonding and increase in proton solvation. In general, stability of complexes decreases due to decrease in dielectric constant of bulk solution. As dielectric constant decreases, the ion-ion interaction involving proton (or metal ion) and the ligand decreases to a greater extent because dissociation of protons decrease in mixed equilibrium.

Thermodynamic Parameters Equilibrium involving the formation of metal complexes is dependent on temperature. Determination of formation constants at different temperatures has been used in the estimation of thermodynamic parameters accompanying the formation of metal complex. The enthalpy (ΔH) changes reflect the energy changes with the intramolecular bonding whereas free energy factor (ΔG) gives the magnitude of stability of a particular equilibrium.

The enthalpy (ΔH) changes have been calculated from linear plots of logK vs 1/T according to equation of isobaric reaction. The representative plot for salicylic acid is given in Figure 2. The values of general change in the free energy (ΔG), enthalpy (ΔH) and the entropy (ΔS) for the complexation reaction of metal ions and hydroxyl acids are presented in the Table 2. The data indicate that with increase in temperature the dissociation constant of the ligands and their formation constants with metal ions decrease indicating that formation equilibria are exothermic in nature. This is also evident from negative values of the enthalpy (ΔH). The negative values of free energy (ΔG) and the negative values of entropy (ΔS) indicate that these factors are major propulsive force for the spontaneity of binary complexes. The enthalpy changes accompanying the complexation in solution state is the characteristic property and it is the measure of energy difference between metal ligand (ML) and the metal water [M-H₂O] coordination bonds. The obtained results suggest that the metal-ligand bonds are reasonably strong as illustrated by the negative changes in enthalpy.

The entropy changes accompanying the formation of metal complexes can be related to number of reacting species in the system and changes in solvation of the reactant and product species. During the formation of metal complexes in the solution, the ligand species get coordinated to the solvated metal ions by displacing the water molecules from the aquo complex [M(H₂O)_n]⁴⁺ as shown by the following equation.

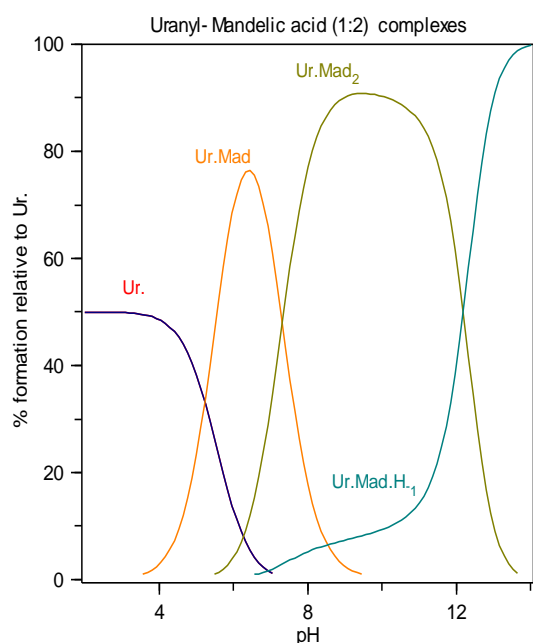
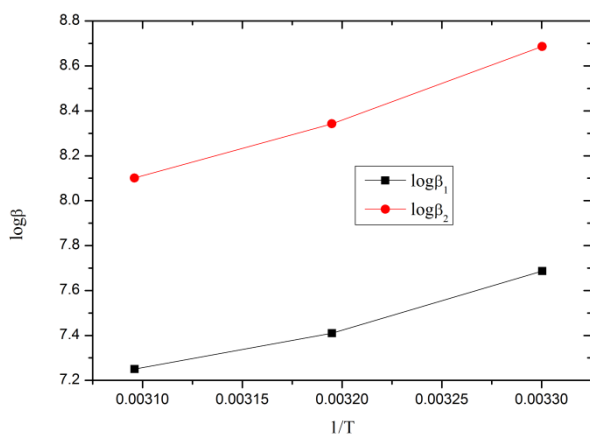


It is under stable that the logK increases as ΔG becomes more negative. Thus equilibrium constant is defined by the changes in entropy during the reaction and measure of heat released in the reaction.

For all the binary complexes studied, the negative ΔH and the Positive ΔS negative ΔH values obtained for all the binary complexes studied shows that the complex formation is favored by both enthalpy and entropy factors.

Species Distribution Constant For evolution of species distribution plots, the data were knock off for various expected stoichiometric species like HL, H₂L, ML, ML₂ and MLH₁ and for different set of models.

Inspection of species diagram revealed that ML₂ species lie in between 92-97% between pH range 0-12.0 and 75-80% ML species are formed between the pH of 5.5-6.8. Formation constant values and species distribution diagrams revealed that ML₂ is the most stable type of species formed. Using the SPEPLOT program species distribution curves were plotted [28] and representative species distribution plot for binary UO₂(II) Mandelic systems has been presented in Figure 3.

Figure 2: The representative plot of $\log\beta$ vs $1/T$ for Salicylic acidFigure 3: Species distribution curves as a function of pH for binary $\text{UO}_2(\text{II})$ -DL Mandelic acid systems in ratio of 1:10 at $303.15\text{K} \pm 0.1\text{K}$, $\mu = 0.20 \text{ mol}\cdot\text{L}^{-1}$ (NaClO_4). $\text{Ur.Mad}=\text{ML}$, $\text{Ur.Mad}_2=\text{ML}_2$, $\text{Ur.Mad.H}_1=\text{ML}(\text{OH})$.

Conclusions

BESTFIT models based on pH-metric studies are used to study interaction of $\text{UO}_2(\text{II})$ with Hydroxy acids namely lactic acid, malic acid, salicylic acid and mandelic acid. Species distribution curves show that ML_1 and ML_2 type of binary complexes are formed in different pH ranges, with dominance of ML_2 type of complexes. The order of all the analogous complexes is malic acid > lactic acid > salicylic acid > mandelic acid. This order is explained on the basis of dissociation constants, charge on metal ion and stabilization after chelation. Thermodynamic studies reveal that these complexation reactions are accommodate by enthalpy

change and are exothermic. The effect of systematic error on stability of complexes is studied by considering the changes in percentage of ligand, metal, acid, alkali and dissolved carbon dioxide. Comparison of formation constant values obtained in ethanol – water mixtures (10 - 40 % V/V) with aqueous medium show that the values in aqueous medium are higher than the mixtures. The possible reason for higher formation constant values in aqueous medium are due to increase in proton solvation by organic solvent, hydrogen bonding and decrease in dielectric constant of medium.

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Table 1: Dissociation constants of Hydroxy acids 303.15K \pm 0.1K [μ = 0.20 mol·L⁻¹ (NaClO₄)]

Hydroxy acids	PKAS			BEST			Point wise calculation method		
	pK_1^H	pK_2^H	pK_3^H	pK_1^H	pK_2^H	pK_3^H	pK_1^H	pK_2^H	pK_3^H
Malic acid	11.7001	4.7801	3.2100	11.6599	4.7208	3.1978	11.6608	4.7107	3.0861
Lactic acid	11.4100	3.8300	--	11.3287	3.7991	--	11.2938	3.7334	--
Salicylic acid	11.8000	2.9300	--	11.6987	2.8384	--	11.6849	2.5998	--
Mandelic acid	11.6000	3.1800	--	11.5384	3.1191	--	11.4489	3.0994	--

Table 2: Formation constants and thermodynamic parameters UO₂(II)- Hydroxy acid complexes.

Hydroxy acids		Formation Constant			$\Delta G \text{ kcal.mol}^{-1}$			$\Delta H \text{ kcal.mol}^{-1}$		$\Delta S \text{ kcal.mol}^{-1}$	
		303.15K	313.15K	323.15K	303.15K	313.15K	323.15K	313.15K	323.15K	313.15K	323.15K
Malic acid	$\log\beta_1$	20.6619	20.4101	20.1137	-28.65	-29.19	-29.69	-10.91	-13.69	-0.0331	-0.0409
	$\log\beta_2$	33.0812	32.9112	32.6140	-45.87	-47.08	-48.14	-7.37	-13.73	-0.0197	-0.0392
	S_{min}	0.7821	0.7001	0.6832	--	--	--	--	--	--	--
Lactic acid	$\log\beta_1$	10.1119	10.0001	9.9712	-14.02	-14.3	-14.72	-4.85	-1.34	-0.0146	-0.0029
	$\log\beta_2$	12.5312	12.4309	12.3114	-17.38	-17.78	-18.17	-4.35	-5.52	-0.0126	-0.0159
	S_{min}	0.5596	0.01321	0.5844	--	--	--	--	--	--	--
Salicylic acid	$\log\beta_1$	7.6865	7.41013	7.2499	-10.66	-10.6	-10.7	-11.98	-7.4	-0.0385	-0.0226
	$\log\beta_2$	8.6865	8.3425	8.1009	-12.04	-11.93	-11.96	-14.91	-11.16	-0.0480	-0.0345
	S_{min}	0.4190	0.1109	0.7321	--	--	--	--	--	--	--
Mandelic acid	$\log\beta_1$	3.3257	3.1207	2.9117	-4.61	-4.46	-4.3	-8.88	-9.66	-0.0289	-0.0304
	$\log\beta_2$	6.7450	6.5312	6.4117	-9.35	-9.34	-9.46	-9.27	-5.52	-0.0296	-0.0167
	S_{min}	0.8424	0.9134	0.7311	--	--	--	--	--	--	--

Table 3: Binary formation constants of UO₂(II)-Hydroxy acids at different ionic strength Temperature 303.15K $\pm 0.1K$.

Hydroxy acids	Dissociation/ Formation Constant	Ionic Strength ($\text{mol}\cdot\text{L}^{-1}$)				$\log\beta_0$
		0.10	0.20	0.30	0.40	
Malic acid	pK_1^H	11.8200	11.7001	11.6301	11.5234	12.1198
	pK_2^H	4.8311	4.7801	4.6311	4.5301	5.1685
	$\log\beta_1$	20.8143	20.6619	20.3841	20.0912	21.5951
	$\log\beta_2$	33.1421	33.0812	32.8431	32.5824	33.7692
	S_{min}	0.3121	0.7821	0.7001	0.6832	----
Lactic acid	pK_1^H	11.5901	11.4100	11.3321	11.2234	11.9372
	pK_2^H	3.9602	3.8300	3.7871	3.6453	4.2586
	$\log\beta_1$	10.4121	10.1119	9.9863	9.7841	11.0067
	$\log\beta_2$	12.7290	12.5312	12.3981	12.2918	13.1595
	S_{min}	0.6595	0.5595	0.0233	0.6844	----
Salicylic acid	pK_1^H	11.9563	11.8000	11.6523	11.5219	12.3988

	pK_2^H	3.0110	2.9300	2.8734	2.7292	3.2939
	$\log\beta_1$	7.8143	7.6865	7.3941	7.1432	8.5531
	$\log\beta_2$	8.9141	8.6865	8.2843	7.9873	9.9187
	S_{\min}	0.5180	0.4190	0.2109	0.7321	-----
Mandelic acid	pK_1^H	11.7321	11.6000	11.4796	11.3812	12.0895
	pK_2^H	3.2934	3.1800	3.011	2.8900	3.8979
	$\log\beta_1$	3.4813	3.3257	3.2291	2.7841	4.1819
	$\log\beta_2$	6.8412	6.7450	6.4931	6.3878	7.3532
	S_{\min}	0.6425	0.8424	0.4134	0.7311	-----

Table 4: Effect of Ethanol – Water (V/V) mixtures on Binary formation constants of $UO_2(II)$ -Hydroxy acids at 0.20 mol·L⁻¹ ionic strength and Temperature 303.15K ±0.1K

Hydroxy acids	Dissociation/ Formation Constant	Ethanol – Water (%V/V) mixture				
		0%	10%	20%	30%	40%
Malic acid	pK_1^H	11.7001	11.6423	11.5110	11.3230	11.2001
	pK_2^H	4.7801	4.71098	4.6234	4.5090	5.4234
	$\log\beta_1$	20.6619	20.5432	20.3312	20.2890	20.2001
	$\log\beta_2$	33.0812	32.9870	32.8431	32.7600	32.6598
	S_{\min}	0.7821	0.7821	0.7001	0.6832	0.5678
Lactic acid	pK_1^H	11.4100	11.3456	11.3287	11.2255	11.1978
	pK_2^H	3.8300	3.6798	3.5643	3.4321	4.2590
	$\log\beta_1$	10.1119	10.0879	9.0163	8.8841	8.8067
	$\log\beta_2$	12.5312	12.4310	12.3081	12.2618	12.1145
	S_{\min}	0.5595	0.5595	0.0233	0.6844	0.3423
Salicylic acid	pK_1^H	11.8000	11.6543	11.5234	11.4321	12.2911
	pK_2^H	2.9300	2.7812	2.5911	2.4325	3.2939
	$\log\beta_1$	7.6865	7.5432	7.4211	7.2780	7.1234
	$\log\beta_2$	8.6865	8.5312	8.3215	8.0299	7.9876
	S_{\min}	0.4190	0.4190	0.2109	0.7321	45630
Mandelic acid	pK_1^H	11.6000	11.4567	11.3786	11.2234	12.1134
	pK_2^H	3.1800	3.0987	2.9868	2.8901	2.7645
	$\log\beta_1$	3.3257	3.2250	3.1292	2.9841	2.7654
	$\log\beta_2$	6.7450	6.6459	6.4955	6.3975	6.2980
	S_{\min}	0.8424	0.8424	0.4134	0.7311	0.5678