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Hydrolysis of dioxouranium(VI): a calorimetric study in $NaCl_{aq}$ and $NaClO_{4\,aq}$, at 25 °C

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Abstract

We report the results of a calorimetric study on the hydrolysis of $UO_2{}^{2+}$ in different ionic media ($NaClO_{4\,aq}$, $NaCl_{aq}$) at 25 °C. Experiments in NaCl were performed at different ionic strength, at $I \le 1\ \text{mol l}^{-1}$. The species considered in both ionic media were $UO_2(OH)^+$, $(UO_2)_2(OH)_2{}^{2+}$ and $(UO_2)_3(OH)_5{}^+$, and in addition $(UO_2)_3(OH)_4{}^{2+}$ and $(UO_2)_3(OH)_7{}^-$ in $NaCl_{aq}$. The dependence on ionic strength of enthalpy changes in $NaCl_{aq}$ was expressed by the simple linear equation $\Delta H_{pq} = \Delta H^\circ_{pq} + aI^{1/2}$ (a, empirical parameter). Comparison with literature findings is given and some recommended values are reported.

Keywords: Calorimetry; Hydrolysis of $UO_2{}^{2+}$; Reaction enthalpy; Ionic strength dependence

1. Introduction

Our research group has been involved for some decades on natural waters and biological fluids speciation studies, and in particular on the sequestering abilities of many organic and inorganic cations and anions. In the last decade our attention has turned to the problems of environmental pollution caused by the presence of heavy metals in the natural fluids [1–9]. The uranyl ion is an elevated source of pollution. As with all heavy metals, uranium has also an elevated chemical toxicity and a great affinity towards biological systems containing phosphoric and sulphuric groups. Hence, it causes serious problems for the normal functionality of the liver, kidney and brain when present in animal and vegetable organisms [10–16].

During the two decades 1950–1970 and in the last decade, research on uranium chemistry has expanded. Despite the extensive data available on the thermodynamic properties of actinides, the information appears often not very clear and contradictory. For this reason new studies on the coordination chemistry of uranium in solution, that can help to get models of chemical behaviour of $UO_2{}^{2+}$ in the various environmental sectors, are needed. Moreover, the information on actinides speciation is fundamental to solve problems such as the migration of dangerous substances from the deposits of nuclear discards and to improve the technologies of treatment of such wastes, with the purpose of limiting their environmental impact.

Our group has undertaken a systematic study on the complexing abilities of $UO_2{}^{2+}$ towards different classes of ligands, and some results have been published [17–19]. A correct speciation model cannot neglect the hydrolysed species that a metal ion such as uranyl can form. The hydrolysis constants of $UO_2{}^{2+}$ at different ionic strengths and in different ionic media, have been published [19], and the aim of this work is to determine other thermodynamic parameters such as the reaction enthalpies and entropies, in an ionic medium such as $NaCl_{aq}$ that is known to be a major constituent of natural and biological fluids and in $NaClO_4$ which is considered a non-interactive ionic medium.

An analysis of hydrolysis enthalpies reported in [20–28] has shown that many of these results are not obtained by direct experimental measurements of reaction heat, but are calculated from hydrolysis constant values determined at different temperatures, or by extrapolation of literature data obtained at different temperatures.

The existence of several hydrolytic polynuclear species of $UO_2{}^{2+}$ is confirmed in many investigations, among this

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species the $(UO_2)_3(OH)_4{}^{2+}$ and the $(UO_2)_3(OH)_7{}^{-}$ proposed in our speciation model have been already reported by Sutton [28] in 1949, and recently by Lemire and Tremaine [29]; nevertheless for few of these species the enthalpies of hydrolysis have been calculated.

The results obtained allowed us to determine the dependence of enthalpies of hydrolysis on ionic strength for the measurements performed in $NaCl_{aq}$, and to compare the difference of thermodynamic parameters obtained for both ionic media. A comparison with literature data is reported.

2. Experimental

2.1. Reagents

Standard $UO_2(NO_3)_2{\cdot}6H_2O$ solutions of analytical grade (puriss. > 99.5%) were prepared from Fluka product without further purification and standardized by the gravimetric determination of uranium after ignition to the oxide U_3O_8. Standard NaOH, HCl and $HClO_4$ solutions were prepared by diluting Fluka concentrate products and standardized against potassium biphthalate (Fluka puriss.) and sodium carbonate (Fluka puriss.), respectively. NaCl (Fluka puriss.) was prepared by weighing the pure salt after drying in an oven at 140 °C. $NaClO_4{\cdot}H_2O$ solutions (Fluka puriss. $\geq$ 99.5%) were prepared from the corresponding solid product, which had previously been vacuum-dried. All solutions were prepared using grade A glassware and ultrapure water (conductivity $< 0.1\,\mu S$).

2.2. Calorimetric measurements

Calorimetric measurements were performed at 25.000 ± 0.001 °C by a Tronac isoperibol titration calorimeter model 450 coupled with a Keithley 196 system Dmm digital multimeter. The titration of 25 or 50 ml of solution containing $UO_2{}^{2+}$ in variable concentrations (for experimental conditions, see Table 1), NaCl or $NaClO_4$ and NaOH in order to have the pre-established value of ionic strength and pH, were performed with HCl or $HClO_4$. The pH of each solution was the limit immediately before the precipitation (generally pH $\leq$ 5, in $NaClO_4$, and pH $\leq$ 6, in NaCl).

The titrants (see Table 1) were prepared at different concentrations of HCl or $HClO_4$ respectively, when NaCl or $NaClO_4$ were utilized as ionic medium. The titrant was delivered by a 2.5 ml capacity Hamilton syringe, model 1002TLL. For each experimental condition were performed two measurements.

A computer program was used for the acquisition of the calorimetric data. The accuracy was checked by titrating a Tris (tris-(hydroxymethyl)amino-methane) buffer with HCl. The enthalpy of dilution was measured before each experiment under the same ionic strength. The accuracy of calorimetric apparatus Q was ±0.008 J and the accuracy of the titrant volume was $\pm 0.001\,cm^3$.

Table 1
Experimental conditions[a] for the calorimetric measurements at 25 °C

I (mol l^{-1})	Vessel		Titrant
	C_{UO_2} (mol l^{-1})	C_H[b] (mol l^{-1})	C_H (mol l^{-1})
NaCl			
<0.05	0.0085	−0.0126	0.4018
<0.05	0.0104	−0.0162	0.4018
<0.05	0.0152	−0.0228	0.4018
0.1	0.0081	−0.0121	0.4018
0.1	0.0126	−0.0186	0.4018
0.1	0.0151	−0.0227	0.4018
0.5	0.0081	−0.0121	0.4018
0.5	0.0149	−0.0224	0.5783
0.5	0.0126	−0.0186	0.5783
1	0.0081	−0.0121	0.4018
1	0.0126	−0.0186	0.4018
1	0.0151	−0.0227	0.4018
$NaClO_4$			
1	0.0080	−0.0121	0.5183
1	0.0040	−0.0061	0.5183
1	0.0110	−0.0165	0.5183

[a] Two or three titrations for each experimental condition.
[b] Negative values indicate an excess of NaOH.

2.3. Calculations

Calorimetric data were analysed by the computer program ES5CM [30]. The different functions for the dependence of thermodynamic parameters on ionic strength were analysed by the general linear and non-linear least squares computer program LIANA [31]. In Fig. 1 we show, as an example, a calorimetric titration ($I = 1$ mol l^{-1}, $NaClO_4$). The equilibrium constants and the reaction enthalpies reported in this work, are referred to the reaction:

$$p\mathrm{UO_2}^{2+} + q\mathrm{H_2O} = (\mathrm{UO_2})_p(\mathrm{OH})_q{}^{2p-q} + q\mathrm{H}^+$$

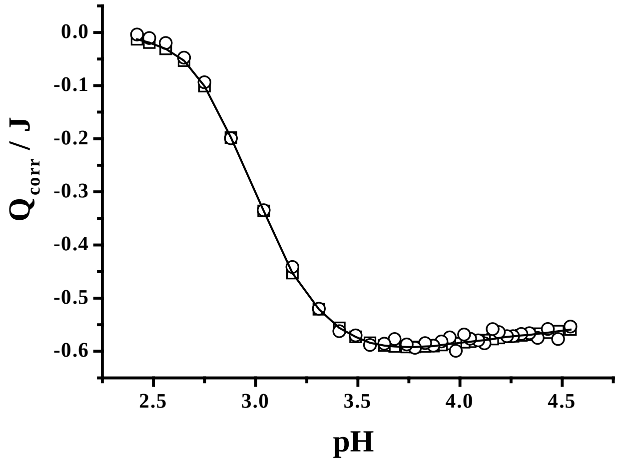

Fig. 1. Q_{corr} (J) vs. pH for the calorimetric titration of $UO_2{}^{2+}$ in 1 mol l^{-1} $NaClO_4$; experimental conditions: $C_{UO_2}{}^{2+} = 0.0110$ mol l^{-1}; $C_H = -0.0165$ mol l^{-1}; titrant: $HClO_4 = 0.5183$ mol l^{-1} ((□) calculated values; (○) experimental values).

The enthalpy changes for the ionization of water at different ionic strengths used in the calculations were taken from De Stefano et al. [32]. In all the tables errors are expressed as standard deviation.

3. Results and discussion

In a previous work [17] we reported the results of a potentiometric investigation on the hydrolysis constants of $UO_2{}^{2+}$ in NaCl and $NaNO_3$ at different ionic strengths. The values obtained in NaCl medium, expressed on the molar scale, are reported in Table 2. In this work, we report the results of calorimetric investigation on the hydrolytic species of $UO_2{}^{2+}$ in NaCl and in $NaClO_4$ at different ionic strengths and $t = 25\,^\circ C$. The hydrolysis enthalpies calculated for each ionic strength, together with other thermodynamic parameters (ΔG_{pq} and $T\Delta S_{pq}$) for measurements performed in NaCl in the ionic strength range $0\,\mathrm{mol}\,kg^{-1} \le I \le 1.02\,\mathrm{mol\,kg^{-1}}$, are given in Table 3. The thermodynamic parameters for the hydrolytic species of $UO_2{}^{2+}$ in $NaClO_4$ at $I = 1\,\mathrm{mol\,kg^{-1}}$ are reported in Table 4.

Table 2
Equilibrium constants[a] for the hydrolysis of dioxouranium(VI) in $NaCl_{aq}$, at $t = 25\,^\circ C$

p, q	$-\log \beta_{pq}$			
	$I = 0\,\mathrm{mol\,l^{-1}}$	$I = 0.1\,\mathrm{mol\,l^{-1}}$	$I = 0.5\,\mathrm{mol\,l^{-1}}$	$I = 1\,\mathrm{mol\,l^{-1}}$
1, 1	5.19	5.45	5.72	5.96
2, 2	5.76	5.98	6.14	6.24
3, 4	11.82	12.22	12.38	12.41
3, 5	15.89	16.55	16.93	17.13
3, 7	29.26	29.68	29.79	29.80

[a] Ref. [17].

Table 3
Molal thermodynamic parameters for the hydrolysis of dioxouranium(VI) in $NaCl_{aq}$, at $t = 25\,^\circ C$

p, q	I ($\mathrm{mol\,kg^{-1}}$)	ΔG_{pq} ($\mathrm{kJ\,mol^{-1}}$)	ΔH_{pq} ($\mathrm{kJ\,mol^{-1}}$)	$T\Delta S_{pq}$ ($\mathrm{kJ\,mol^{-1}}$)
1, 1	0	29.6 ± 0.3	40.7 ± 2.9	11 ± 3
2, 2	0	32.9 ± 0.3	47.8 ± 1.3	15 ± 2
3, 4	0	67.5 ± 0.5	98.9 ± 0.5	31 ± 1
3, 5	0	90.7 ± 0.4	119.5 ± 2.0	29 ± 3
3, 7	0	167 ± 0.7	177 ± 7.0	10 ± 8
1, 1	0.1	31.1 ± 0.2	42.7 ± 2.3	12 ± 3
2, 2	0.1	34.1 ± 0.2	47.2 ± 0.5	13 ± 1
3, 4	0.1	69.7 ± 0.3	97.9 ± 0.5	28 ± 1
3, 5	0.1	94.4 ± 0.3	118.8 ± 0.6	24 ± 1
3, 7	0.1	169.4 ± 0.6	176 ± 6.0	7 ± 7
1, 1	0.51	32.6 ± 0.1	40.2 ± 0.5	8 ± 1
2, 2	0.51	35 ± 0.1	43.9 ± 1.9	9 ± 2
3, 4	0.51	70.6 ± 0.3	93 ± 1	22 ± 2
3, 5	0.51	96.6 ± 0.2	112.1 ± 1.7	16 ± 2
3, 7	0.51	169.9 ± 0.5	166 ± 6.0	−4 ± 7
1, 1	1.02	34 ± 0.2	35 ± 5.0	1 ± 6
2, 2	1.02	35.6 ± 0.1	43.8 ± 1.5	8 ± 2
3, 4	1.02	70.7 ± 0.3	89.5 ± 0.6	19 ± 1
3, 5	1.02	97.6 ± 0.2	108.5 ± 0.5	11 ± 1
3, 7	1.02	169.8 ± 0.5	158 ± 6.0	−12 ± 7

Table 4
Calculation of ΔH values for the hydrolysis of $UO_2{}^{2+}$ by keeping constant hydrolysis constants and by refining simultaneously ΔH_{pq} and $\log \beta_{pq}$ values; $I = 1\,\mathrm{mol\,kg^{-1}}$ ($NaClO_4$) and $t = 25\,^\circ C$

p, q	Calorimetric data		Potentiometric and calorimetric data	
	$-\log \beta_{pq}$[a]	ΔH°_{pq} ($\mathrm{kJ\,mol^{-1}}$)	$-\log \beta_{pq}$[a,b]	ΔH°_{pq} ($\mathrm{kJ\,mol^{-1}}$)
1, 1	5.2 ± 0.2	42 ± 6	4.92	31 ± 7
2, 2	5.95 ± 0.05	43.8 ± 0.9	5.72	45.0 ± 1.2
3, 5	16.2 ± 0.1	106.4 ± 0.6	16.10	107.1 ± 0.6

[a] Molal scale.
[b] Vasca (pers. commun.).

The enthalpies of hydrolysis at $I = 0\,\mathrm{mol\,kg^{-1}}$ reported in Table 3 are not extrapolated values, but are semi-empirical values obtained by measurements at low ionic strengths. To extrapolate the ΔH values to zero ionic strength we used a method already described [33].

The analysis of the data obtained for both supporting electrolytes leads to the following conclusions:

(a) The different ionic medium has a low influence on the enthalpies of reaction in the ionic strength range investigated. The ΔH_{pq} of hydrolysis calculated for the common species (UO_2OH^+, $(UO_2)_2(OH)_2{}^{2+}$, $(UO_2)_3(OH)_5{}^+$) at $I = 1\,\mathrm{mol\,kg^{-1}}$ in both ionic medium are comparable.
(b) The small difference of ΔH_{pq} of hydrolysis obtained in the two ionic media investigated can be interpreted in terms of the different binding of chloride and perchlorate anions to $UO_2{}^{2+}$ [27]. The perchlorate anion does not form ion-pairs of significant strength with $UO_2{}^{2+}$.
(c) The species $(UO_2)_3(OH)_4{}^{2+}$ is formed appreciably only in chloride medium and the relative ΔH_{pq} value was determined only in NaCl solutions.
(d) As expected, all ΔH_{pq} values for the hydrolysis are a decreasing function of ionic strength.

The dependence on ionic strength of ΔH_{pq} of hydrolysis (in NaCl) can be expressed by the simple equation:

$$\Delta H_{pq} = \Delta H^\circ_{pq} + aI^{1/2} \tag{1}$$

and the experimental data from Table 3 can be expressed by the following relationships:

$$\Delta H_{11}(\pm 1.8) = 42.5 - 5.6I^{1/2},$$
$$\Delta H_{22}(\pm 0.6) = 47.9 - 4.2I^{1/2},$$
$$\Delta H_{34}(\pm 0.8) = 99.7 - 9.7I^{1/2},$$
$$\Delta H_{35}(\pm 1.1) = 120.4 - 11.7I^{1/2},$$
$$\Delta H_{37}(\pm 2.0) = 179.2 - 19.5I^{1/2}$$

in which ΔH°_{pq} is the thermodynamic hydrolysis enthalpy (at infinite dilution), and a is the parameter for the

Table 5
Molal thermodynamic parameters for the hydrolysis of dioxouranium(VI) in $NaClO_4$ at $I = 1\,mol\,kg^{-1}$ and $t = 25\,°C$

p, q	ΔG_{pq} ($kJ\,mol^{-1}$)	ΔH_{pq} ($kJ\,mol^{-1}$)	$T\Delta S_{pq}$ ($kJ\,mol^{-1}$)
1, 1	28.6 ± 0.5	37 ± 7	8 ± 8
2, 2	33.2 ± 0.4	44.2 ± 1	11 ± 2
3, 5	92.0 ± 0.5	106.6 ± 0.5	15 ± 1

$pM^{2+} + qH_2O = Mp(OH)_q{}^{2p-q} + qH^+$.

dependence on ionic strength; in parenthesis the standard deviations in the fit of Eq. (1) for each hydrolytic species are reported. Fig. 2 reports the dependence of ΔH_{pq} on ionic strength (molal scale). As can be seen, the dependence of ΔH_{pq} values on ionic strength (NaCl) is very low for the hydrolytic species UO_2OH^+, $(UO_2)_2(OH)_2{}^{2+}$ and $(UO_2)_3(OH)_4{}^{2+}$, and the maximum variation observed for $(UO_2)_3(OH)_7{}^-$ is about $20\,kJ\,mol^{-1}$ in the ionic strength range $0\,mol\,kg^{-1} \leq I \leq 1.02\,mol\,kg^{-1}$; see Table 3.

Table 4 reports the hydrolysis constants of $UO_2{}^{2+}$, in $NaClO_4$ for the species UO_2OH^+, $(UO_2)_2(OH)_2{}^{2+}$, $(UO_2)_3(OH)_5{}^+$ (Vasca, pers. commun.), together with enthalpies of hydrolysis at $I = 1\,mol\,kg^{-1}$ (in this work). For these thermodynamic parameters, two different sets of values for ΔH_{pq} and $\log \beta_{pq}$ are reported. In the first set we refined simultaneously both $\log \beta_{pq}$ and ΔH_{pq} values using calorimetric data; in the second set we refined only ΔH_{pq} values by maintaining constant β_{pq}: as can be seen results of the two procedures are in quite good agreement. This can be considered as an internal check for the reliability of results. The large error associated to UO_2OH^+ is due to its low percentage of formation in our experimental conditions. In Table 5 we report the mean values of the thermodynamic parameters of hydrolysis for $UO_2{}^{2+}$ in $NaClO_4$ at $I = 1\,mol\,kg^{-1}$ and 25 °C, obtained from data given in Table 4.

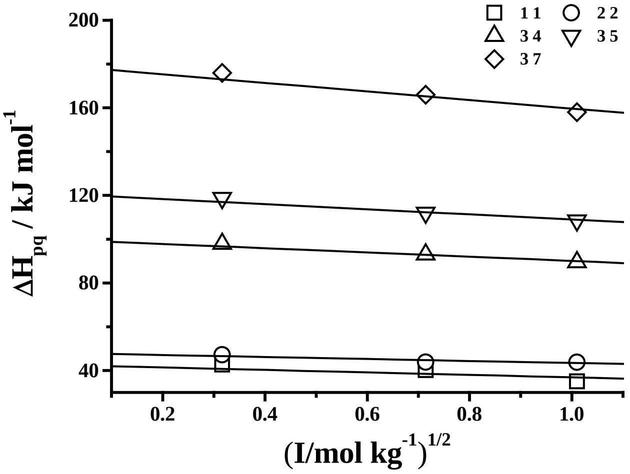

Fig. 2. ΔH_{pq} values vs. $(I,\ mol\,kg^{-1})^{1/2}$ for the hydrolytic species of $UO_2{}^{2+}$ in NaCl and $t = 25\,°C$.

3.1. Literature comparison

Few literature data are available on the ΔH_{pq} of hydrolysis of $UO_2{}^{2+}$ derived by direct calorimetric measurements, and no systematic study at different ionic strengths has been reported.

Many data are obtained from hydrolysis constants at different temperature; therefore the values of enthalpies can be affected by high errors, associated to the errors in the hydrolysis constants. For example, Baes and Meyer [20] report ΔH_{pq} of hydrolysis in KNO_3 $0.5\,mol\,kg^{-1}$, but these values are calculated by hydrolysis constants obtained at different temperatures for the species $UO_2(OH)^+$; $(UO_2)_2(OH)_2{}^{2+}$ and for $(UO_2)_3(OH)_5{}^+$ (see Table 6), while the values reported by Nikitin et al. [24] for $UO_2(OH)_2$ are obtained by dissolution of $\beta UO_3 \cdot H_2O$.

Table 6
Some literature data of ΔH_{pq} and $T\Delta S_{pq}$ for the hydrolysis of $UO_2{}^{2+}$

Species	t (°C)	Medium	Method[a]	I	ΔH_{pq} ($kJ\ mol^{-1}$)	$T\Delta S_{pq}$ ($kJ\,mol^{-1}\,K^{-1}$)	Reference
$UO_2(OH)^+$	25	KNO_3	T	$0.5\,mol\,kg^{-1}$	46	13.7	[20]
	25–125		T	0	53	22.7	[23]
	25–125		T	0	58	28.0	[24]
$(UO_2)_2(OH)_2{}^{2+}$	25	KNO_3	T	$0.5\,mol\,kg^{-1}$	42.6	8.7	[20]
	25	$NaClO_4$	Cal	$3.0\,mol\,l^{-1}$	39.7	5.4	[21]
	25	$NaClO_4$	Cal	$1\,mol\,l^{-1}$	44.4	10.9	[22]
	100–150		T	0	37	6.0	[25]
	150–200		T	0	28	−6.0	[26]
	25–125		T	0	54	21.8	[24]
	25–125		T	0	40	7.7	[23]
$(UO_2)_3(OH)_5{}^+$	25	KNO_3	T	$0.5\,mol\,kg^{-1}$	104.9	12.5	[20]
	25	$NaClO_4$	Cal	$3.0\,mol\,l^{-1}$	102.0	7.5	[21]
$UO_2(OH)_2$	100–150		T	0	122	69.3	[23]
	50–4200		T	0	20	−18.8	[24]

[a] Cal: calorimetric measurements; T: temperature gradient.

Table 7
Recommended (or tentative) ΔH_{pq} values for the hydrolysis of UO_2^{2+} at $t = 25\,^{\circ}C$

p, q	I (mol kg^{-1})	ΔH_{pq} (kJ mol^{-1})	
1, 1	0	50 ± 8	T[a]
2, 2	0	48 ± 5	R[b]
3, 5	0	123 ± 5	R[b]
2, 2	1[c]	44.1 ± 2	R[b]
3, 5	1[c]	112 ± 6	R[b]

[a] T: tentative.
[b] R: recommended.
[c] Ionic medium $NaClO_{4\,aq}$.

Only the data reported by Arnek and Schlyter [21], and by Rizkalla et al. [22] have been obtained by experimental measurements of reaction heats.

Our enthalpy data are in agreement with those reported in the literature. For example, Rizkalla et al. [22] report for $(UO_2)_2(OH)_2^{2+}$ at $1\,mol\,l^{-1}$ in $NaClO_4$ and $t = 25\,^{\circ}C$, $\Delta H_{22} = 44.4\,kJ\,mol^{-1}$; this value is close to $\Delta H_{22} = 44.2 \pm 1\,kJ\,mol^{-1}$ obtained in this work. Also the other thermodynamic data reported in this work are in agreement with literature data reported in Table 6. No further information is available for the hydrolysis enthalpies of $(UO_2)_3(OH)_4^{2+}$ and $(UO_2)_3(OH)_7^{-}$ and for hydrolysis ΔH_{pq} values obtained by direct calorimetric measurements in $NaCl_{aq}$, despite its importance in the pH range of interest for natural fluids. By considering altogether our and literature findings we calculated some recommended (or tentative) values, that are reported in Table 7. Moreover, by analysing some literature data at different temperatures [27,29], we obtained rough thermodynamic data for the species $UO_2(OH)_2$ (that cannot be studied calorimetrically owing their low solubility): $\log\beta_{12} = -12.8 \pm 0.4$; $\Delta H_{12} = 100 \pm 20\,kJ\,mol^{-1}$, at $I = 0\,mol\,l^{-1}$ and $t = 25\,^{\circ}C$.

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