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Enthalpies of Reaction of Calcium Chloride and Sodium Oxalate in an Aqueous NaCl Solution

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Abstract—The heats of mixing of dilute aqueous solutions of calcium chloride and sodium oxalate with additions of 1–5 wt % NaCl at 298.15 K and the heats of dilution of calcium chloride solutions were measured. Increasing the sodium chloride content in a solution noticeably increases the time of precipitation of calcium oxalate. A fine precipitate of CaC_2O_4 formed in solutions containing 3 and 5 wt % NaCl is difficult to remove from the parts of a calorimeter cell. The enthalpies of precipitation of CaC_2O_4 depend slightly on the content of the "background electrolyte," whereas the enthalpies of dilution, owing to ion association, significantly decrease in magnitude and become positive in a 5% NaCl solution. The "standard" enthalpy of precipitation in water, determined by extrapolation of the experimental values to the zero concentration of the background electrolyte, differs noticeably from the enthalpy of precipitation in water.

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Development of new methods of conservative treatment of urolithiasis calls for comprehensive study of the formation of the major components of uroliths, namely, calcium salts insoluble in water and multicomponent aqueous systems modeling, to an extent, the conditions of in vivo formation of mineral composites. These processes have still been little studied and, although some data on the influence of various factors on the formation of insoluble calcium salts are currently available [1–8], the mechanism of formation of uroliths is still unclear.

Previously [1, 2], we studied the reaction of calcium chloride and sodium oxalate in electrolyte and nonelectrolyte systems partially modeling the biological conditions of formation of uroliths and found that the nature of the additive noticeably influences the precipitation process. In particular, in water and 3% solutions of urea and tetrabutyl- and cetyltrimethylammonium bromides, precipitation is rapid and the nascent flaky precipitate is presumably a crystal hydrate mixture [4, 5]. In 3 wt % Trilon B solutions, there is no precipitation at all because of the endothermic complexation of the calcium cation with the ethylenediaminetetraacetate ion; therefore, Trilon B is used for both inhibiting precipitation and dissolving the already existing concretions [1]. In a sodium chloride solution, the formation of $CaC_2O_{4\,\mathrm{solid}}$ was noticeably hindered, which could be interpreted as partial inhibition of precipitation of calcium oxalate-based concretions. However, the CaC_2O_4 precipitate formed under these conditions is fine and very compact, which made it possible to draw a tentative conclusion that the increased salt level of urine would be favorable for the formation of harder concretions [7, 8].

In the present work, we studied specific features of the formation of $CaC_2O_{4\,\mathrm{solid}}$ in sodium chloride solutions and determined the enthalpy of precipitation as a function of the salt level.

EXPERIMENTAL

The heats of reaction of calcium chloride and sodium oxalate in an aqueous NaCl solution were measured on an isothermal-shell variable-temperature calorimeter with automatic data collection and processing [9]. A calorimeter vessel (~70 cm^3) was equipped with a mercury seal four-bladed stirrer, a heater, and a temperature gage (a thermistor with a resistance of ~7.4 kΩ at 25°C). The stirrer also served as the ampoule holder. The reaction was initiated by brief pressing of the stirrer shaft so that the ampoule was broken against the bottom of the calorimeter vessel. Measurements were taken by a comparative method, the electric calibration time and temperature rise being selected to be as close as possible to those observed in the experiment. The thermistor resistance was measured by a standard temperature measuring instrument. These data were received and processed by a computer. The temperature in the range 10–65°C in a thermostat in the region of location of the calorimeter cell was maintained with an accuracy of no worse than ±0.001°C. The sensitivity of the measuring circuit was 0.00001°C (0.003 J). The cal-

Table 1. Enthalpies of mixing of $Na_2C_2O_4$ and $CaCl_2$ solutions ($\Delta_{mix}H$), enthalpies of dilution of $CaCl_2$ solutions ($\Delta_{dil}H$), and enthalpies of precipitation of CaC_2O_4 ($\Delta_{pr}H$) in aqueous NaCl solutions at 25°C

$n(Na_2C_2O_4)^a \times 10^4$, mol	$n(NaCl) \times 10^4$, mol	$m(CaCl_2)_{fin}$, mol/kg	$-\Delta_{mix}H$, kJ/mol	$-\Delta_{mix}H$, kJ/mol	$-\Delta_{dil}H$, kJ/mol
1 wt % NaCl					
3.398	1.484	0.00211	23.82	1.42	22.40
3.460	1.220	0.00171	23.73	1.46	22.27
3.381	1.456	0.00206	23.35	1.43	21.92
				$\Delta_{pr}H$ (av.) = –22.0 ± 0.28[b]	
2 wt % NaCl					
3.469	1.292	0.00182	23.06	1.07	21.99
3.903	1.338	0.00191	23.30	1.07	22.23
3.962	1.357	0.00190	22.96	1.07	21.89
				$\Delta_{pr}H$ (av.) = –22.04 ± 0.21	
3 wt % NaCl[c]					
3.393	1.004	0.00142	22.61	0.71	21.90
3.470	1.329	0.00189	22.46	0.68	21.78
3.547	1.419	0.00198	22.15	0.67	21.48
3.848	1.589	0.00225	22.47	0.65	21.82
				$\Delta_{pr}H$ (av.) = –21.75 ± 0.18	
5 wt % NaCl					
3.612	1.177	0.00166	20.57	–0.14	20.71
3.624	0.7296	0.00102	20.00	–0.08	20.08
3.955	1.256	0.00176	20.22	–0.15	20.37
3.927	1.148	0.00161	20.45	–0.13	20.58
				$\Delta_{pr}H$ (av.) = –20.44 ± 0.27	

Notes: [a] The first and second columns, respectively, list the number of sodium oxalate and calcium chloride moles in the solution before mixing. [b] Errors are expressed as the doubled standard mean deviation. [c] Taken from [1]. Note. The enthalpies of dilution were found by linear extrapolation of the data in Table 2. The enthalpy of precipitation in water is –20.37 ± 0.11 and –20.56 ± 0.08 kJ/mol according to {1, 2], respectively.

orimeter performance was checked by measuring the enthalpies of solution of potassium chloride and 1-propanol in water at 25°C. The results demonstrated complete agreement between our data and the most reliable literature data [9].

Calcium chloride (pharmacopeial grade, from Reakhim) was recrystallized from absolute methanol and vacuum dried at 250°C to constant weight. Sodium oxalate and chloride (chemically pure, Reakhim) were not additionally purified and only vacuum dried at 90°C to constant weight. Solutions were prepared by introducing exact weights (the error of weighing was $\pm 1 \times 10^{-4}$ g) of the dried compounds into a specified water volume.

The experiments were carried out as follows. A portion of ~0.1–0.3 mL of an aqueous $CaCl_2$ solution (m = 0.51967 mol/kg) was poured into a thin-walled glass ampoule. The ampoule was placed into the calorimeter cell filled with a solution containing 1–5% sodium chloride and $Na_2C_2O_4$ ($m \approx 0.005$ mol/kg solvent). Then, the calorimeter was assembled and placed into a thermostat where it was kept for 30–50 min at the experiment temperature. The specific heat of the calorimeter was determined by means of electric calibration immediately before the experiment was started. Then, the initial period was recorded, the ampoule was broken against the bottom of the calorimeter vessel, and the main and final periods of the process were recorded. The time of the mixing reaction was 3–15 min, depending on the content of the background electrolyte; therefore, to determine the change in temperature corrected for heat exchange, the modified Dickinson method was used, in which the linear segments of the temperature versus time curve are extrapolated to the mean temperature of the main period so that the areas cut off by the vertical line under and over the experimental curve are equal.

RESULTS AND DISCUSSION

The enthalpies of mixing of solutions of sodium oxalate and calcium chloride are presented in Table 1. As in [1, 2], all measurements were taken from dilute solutions in order the systems under consideration were studied under conditions similar to the in vivo ones, on the one hand, and the solubility product of calcium oxalate was achieved and the enthalpy of precipitation could be determined experimentally, on the other hand.

It follow from Table 1 that the enthalpies of mixing $\Delta_{mix}H$ are negative and decrease in magnitude with increasing the content of sodium chlorine in a solution. This decrease in the enthalpy constitutes ~20% in going from 1% to 5% NaCl solution. Changes in the enthalpy of dilution of calcium chloride are more significant (here, an NaCl solution is treated as an individual sol-

Table 2. Enthalpies of dilution of $CaCl_2$ solutions from 0.51697 mol/kg to $m(CaCl_2)_{fin}$ in NaCl solutions of various concentration at 25°C

$m(CaCl_2)_{fin}$, mol/kg	$-\Delta_{dil}H$, kJ/mol	$m(CaCl_2)_{fin}$, mol/kg	$-\Delta_{dil}H$, kJ/mol	$m(CaCl_2)_{fin}$, mol/kg	$-\Delta_{dil}H$, kJ/mol
1 wt % NaCl		2 wt % NaCl		5 wt % NaCl	
0.001905	1.44	0.00144	1.10	0.00101	–0.07
0.004156	1.24	0.00357	0.93	0.00297	–0.27
				0.0047	–0.47

vent). Their values (Table 2) not only decrease in magnitude but also change their sign. Dilution of a calcium chloride solution with water is accompanied by heat release (~–3 kJ/mol [1]), whereas dilution with a 5% NaCl solution leads to heat absorption (0.1–0.2 kJ/mol). It is evidently due to the appearance in the aqueous solution of an electrolyte with common anion, namely, chloride ion. As the concentration of the latter increases, the competition between the ions for the solvent and the tendency for association of Ca^{2+} and Cl^- ions become stronger. These processes are presumably responsible for the change of the sign at $\Delta_{dil}H$.

To calculate the change in enthalpy in the course of precipitation of $Ca_2C_2O_4$ ($\Delta_{pr}H$), the enthalpy of dilution of a calcium chloride solution from 0.51697 mol/kg to the final concentration $m(CaCl_2)_{fin}$ should be subtracted from $\Delta_{mix}H$:

$$\Delta_{pr}H = \Delta_{mix}H - \Delta_{dil}H.$$

These values determined experimentally are listed in Table 2. The enthalpies of mixing and dilution (Tables 1 and 2) decrease in magnitude with an increase in the NaCl content in water; however, the rates of these changes are different. In a 1% NaCl solution, the decrease in $\Delta_{dil}H$ as compared to that in pure water is ~1.5 kJ/mol. The $\Delta_{mix}H$ values in water and the salt solution are nearly the same (see data in Table 1 and in [1]). This leads to an increase in the exothermic character of precipitation in solutions with low NaCl contents. A further increase in the concentration of the background electrolyte brings about a decrease in heat release in the course of mixing and dilution. However, $\Delta_{dil}H$ decreases at a slower rate, which leads to that the $\Delta_{pr}H$ values in a 5% NaCl solution and in water become the same. This, however, in no way means that the mechanism of precipitation in these systems is identical. Figure 1 shows the temperature versus time curves of mixing of calcium chloride and sodium oxalate in water and in aqueous NaCl solutions. In water and in a 1% NaCl solution, precipitation is rapid. The resulting flaky precipitate is presumably a mixture of the $CaC_2O_4 \cdot H_2O$ and $CaC_2O_4 \cdot 2H_2O$ crystal hydrates, which constitute the major part of oxalate calculi [4]. As follows from Fig. 1, a further increase in the background electrolyte concentration significantly increases the reaction time. This can be associated with some increase in the solubility of calcium oxalate owing to a decrease in activity coefficients, as well as with the appearance of a considerable amount of background electrolyte ions so that, in the reaction zone, the Ca^{2+} and $C_2O_4^{2-}$ ions turn out to be separated by sodium and, especially, chloride ions. The fine precipitate that slowly forms in these systems is tightly adsorbed on the cell surface and is very difficult to remove mechanically from the latter. It is likely that, in solutions of sodium chloride with a concentration of 3 wt % or higher, the CaC_2O_4 precipitate is not a crystal hydrate. Inasmuch as Na^+ and Cl^- ions constitute a major part of the mineral content of urine

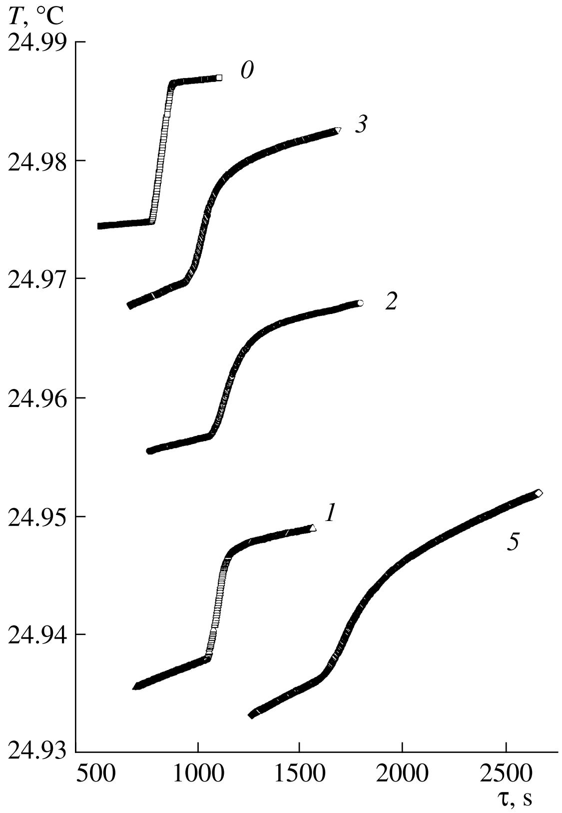

Fig. 1. Temperature vs. time curves of mixing of an aqueous $CaCl_2$ solution with an $Na_2C_2O_4$ solution in water and in aqueous NaCl solutions of various concentrations at 25°C: (*0*) water, (*1*) 1% NaCl, etc. For clarity the curves are shown with a shift along the ordinate axis; their linear portions refer to the initial and final periods of the process.

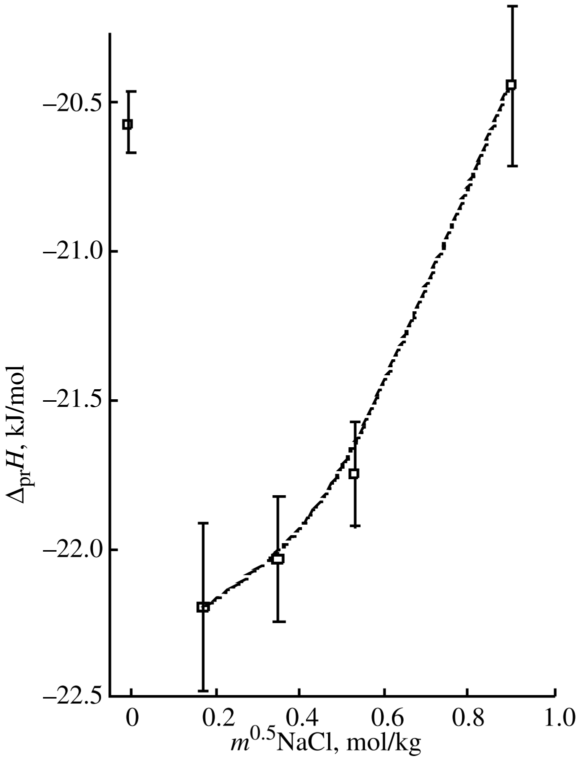

Fig. 2. Enthalpy of precipitation of calcium oxalate vs. square root of the NaCl molality at 25°C, ⌶ enthalpy of precipitation in water [2]. Errors are expressed as the doubled standard deviation. The dashed line is shown for clearness.

(up to 0.5 mol per day [3], or more than 50%), we can state that, other conditions being equal, the increased salt level will be favorable for relatively slow but persistent precipitation of hard uroliths.

Our findings allow us to draw another important conclusion. As is known, extrapolation methods based on the Debye–Hückel theory are used for determining standard thermodynamic quantities characterizing the processes of dissolution, acid–base interactions, complex formation, etc., which occur in electrolyte solutions [10]. However, in our case, such an approach appears to give incorrect results. First, the enthalpy of precipitation is an essentially nonlinear function of the background electrolyte molality (Fig. 2).The use of a routine approach [10], where the Debye term proportional to $\sqrt{m}$, is subtracted from the heat of the process, also gives no way of obtaining a linear dependence since its variation is rather small in this temperature range. Second, even if a linear dependence were obtained, the use of equations from [10] shifts the curve in Fig. 2 down. Hence, the extrapolated value of the enthalpy of precipitation will be 3–4 kJ/mol lower than $\Delta_{pr}H$ in water [1, 2], which is also shown in Fig. 2. In our opinion, a major reason for the phenomena observed is that sodium chloride, in this case, is not an indifferent electrolyte with respect to the process. It has an effect on the association of Ca^{2+} and Cl^- ions, thus significantly changing the enthalpies of dilution and mixing, and changes the time of precipitation and the form of the nascent precipitate. A crystal hydrate is mainly deposited in water, whereas calcium oxalate precipitating in an NaCl solution is presumably not a crystal hydrate. Hence, the $\Delta_{pr}H$ values in water and aqueous NaCl solutions can hardly be compared.

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