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On the Existence of $NaC_2O_4^-$ Ion Pair Complex

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Synopsis. Existence of $NaCO_4^-$ ion pair complex formation in solutions has been further documented through the solubility measurements of calcium oxalate monohydrate in sodium chloride, magnesium chloride, and mixtures of sodium and magnesium chlorides.

In a recent publication Berland et al.[1] have argued against the existence of alkali metal oxalate ion pair complexes, such as $NaC_2O_4^-$, in urine. However, the evidence for the nonexistence of such ion pairs, presented by them does not seem to be appropriate since using Hammarsten's data[2] of calcium oxalate monohydrate (COM) solubility in sodium chloride, Finlayson et al.[3,4] have computed a value of about 13 $dm^3 mol^{-1}$ as the stability constant of $NaC_2O_4^-$ ion pair. Further, regarding the conductivity measurements on sodium oxalate solutions, indeed 17% of the oxalate will be bound in a 30 $mmol dm^{-3}$ sodium oxalate solution but only 8.5% of the total sodium ion will participate in the complexation. Since $NaC_2O_4^-$ is also charged, the overall decrease in the equivalent conductivity will be 8.5%. The decrease in equivalent conductivity at lower sodium oxalate concentrations, however, would be even smaller and that might be the reason why a substantial change between measured and calculated conductivity values was not observed.

The existence of alkali metal oxalate ion pair complexes in solutions has also been reported in the literature by other workers. For example, Daniele et al.[5] have used potentiometric titration method to determine the stability constants of sodium and potassium oxalate complexes and found a value of about 10 $dm^3 mol^{-1}$ for $NaC_2O_4^-$ and 9 $dm^3 mol^{-1}$ for $KC_2O_4^-$ at 37 °C. An spectral evidence for the existence of $LiC_2O_4^-$, $KC_2O_4^-$, and $CsC_2O_4^-$ ion pairs has been presented by Kanamori et al.[6] after measuring the Raman spectra of aqueous solutions of lithium, potassium, and caesium oxalates.

Because of high concentrations of sodium and potassium ions in urine, correction for $NaC_2O_4^-$ and $KC_2O_4^-$ ion pairs will be important in the computation of urine supersaturation with respect to COM.[7] This reference has further clarified the presence of such ion pairs in urine snd synthetic solutions containing alkali metals and oxalate.

Experimental

Reagent grade calcium chloride dihydrate, magnesium chloride hexahydrate, and sodium chloride (Merck and B. D. H. Chemical companies) were used. Solutions were prepared using doubly distilled, deionized water (Nanopure II) and standardized by analyzing for chloride with Mettler's Memotitrator system (Model DL-40RC). Standard solution of oxalate at 1000 $mg dm^{-3}$ was made from analytical grade oxalic acid purchased from Baker Chemical Co. Calcium oxalate monohydrate used for solubility measurements was received in powdered form from B. D. H. Chemical Co.

Solubility measurements were carried out by equilibrating approximately 20 mg of COM in 20 cm^3 solulion maintained at 37 °C for over 50 h, to ensure complete equilibrium. After that, samples were filtered and diluted immediately to prevent from any precipitation which could result due to the attainment of supersaturation with respect to COM at lower temperature. Diluted solutions were then analyzed for calcium and oxalate using ion chromatography, and solubility was reported as the mean of four determinations.

Ion-chromatographic measurements were made on a Dionex ion chromatograph model 2120i fitted with conductivity detector. The separation of oxalate was achieved on a Dionex AG4 guard column and an AS4 separator. Calcium was analyzed on a Dionex CS1 separator and a CG1 guard column using a mixture of 0.0025 $mol dm^{-3}$ ethylenediamine and 0.005 $mol dm^{-3}$ hydrochloric acid. The eluent for anion chromatography consisted of a mixture of 0.003 $mol dm^{-3}$ sodium hydrogen carbonate and 0.0024 $mol dm^{-3}$ sodium carbonate. The flow rate in both instances was maintained at 2.0 $cm^3 min^{-1}$. Peak heights were integrated on a Dionex 4217 integrator.

The concentrations of different ionic species in the equilibrated COM solutions were calculated from mass balance and electroneutrality expressions.[8] The corrections for $CaC_2O_4^0$ and $NaC_2O_4^-$ ion pairs when needed, were made by using their respective stability constant values of 2746 $dm^3 mol^{-1}$ [3,4] and 13.2 $dm^3 mol^{-1}$.[3,4] Since the Debye-Hückel equation is inaccurate at high ionic strengths, well adopted extended form of the Debye-Hückel equation[9-11] as proposed by Davies,[12] was used to calculate the activity coefficients at high ionic strengths.

Results and Discussion

The results of solubility of COM in water and different concentrations of sodium chloride are summarized in Table 1. The mean solubility product, $(3.347\pm0.18)\times10^{-9}$ $mol^2 dm^{-6}$, obtained from the solu-

Table 1. Results of Solubility Determinations of COM in Water and Sodium Chloride Solutions at 37 °C

NaCl / $mol dm^{-3}$	Solubility $Ca^{2+}=C_2O_4^{2-}$ / $10^{-4} mol dm^{-3}$	K_{sp}[a] / $10^{-9} mol^2 dm^{-6}$	K_{so}[b] / $10^{-9} mol^2 dm^{-6}$
0.00	0.564±0.010	2.18	2.18
0.05	1.364±0.015	3.39	2.20
0.10	1.610±0.020	3.15	2.18
0.15	1.890±0.025	3.50	2.18

a) K_{sp}=Solubility product of COM corrected for ionic strength and $CaC_2O_4^0$ ion pair. b) K_{so}=Thermodynamic solubility product of COM corrected for ionic strength and, $NaC_2O_4^-$ and $CaC_2O_4^0$ ion pairs.

bility values at three different sodium chloride concentrations after $CaC_2O_4^0$ ion pair and ionic strength correction is in good agreement with the value, $(3.289\pm0.03)\times10^{-9}$ mol^2 dm^{-6}, computed by Berland et al.[1] from Hammarsten's data. However, as can be seen from the last column of Table 1, both of the above values are about 50% higher than the corresponding thermodynamic solubility product, K_{so}. The K_{so} was calculated from the solubility of COM in water and sodium chloride solutions following the corrections of both $CaC_2O_4^0$ and $NaC_2O_4^-$ ion pairs, and ionic strength. The marked difference in K_{sp} and K_{so} values (the latter is a constant at a given temperature) clearly emphasizes the importance of taking into account $NaC_2O_4^-$ ion pair correction when calculating the thermodynamic solubilily product from COM solubility in sodium chloride solutions. The mean K_{so}, $(2.185\pm0.01)\times10^{-9}$ mol^2 dm^{-6}, thus obtained from the solubility results in Table 1, compared well with 2.244×10^{-9} mol^2 dm^{-6}, the value computed by Finlayson and co-workers from Hammarsten's data of COM solubility in water.[3,4]

Table 2 contains the results of COM solubility in different magnesium chloride solutions, and in the mixtures of magnesium chloride and 0.15 mol dm^{-3} sodium chloride. Magnesium concentrations were kept the same in both instances. The stability constants of $MgC_2O_4^0$ ion pair were calculated from different solubility values and reported in the last two columns of the Table 2. Closely similar values of stability constants (K_1) were obtained from the solubilities of COM in pure magnesium chloride solutions with a mean value of 4037 ± 138 dm^3 mol^{-1}, following $CaC_2O_4^0$ ion pair and ionic strength correction. The mean value of K_1 at 2446 ± 129 dm^3 mol^{-1} obtained from the COM solubilities in the mixtures of magnesium and sodium chlorides after ionic strength and, only $CaC_2O_4^0$ ion pair correction, was found to be approximately 40% lower then the above mentioned value. However, after additional correction of $NaC_2O_4^-$ ion pair, the mean K_1 at 2446 ± 129 dm^3 mol^{-1} changed to 4001 ± 189 dm^3 mol^{-1} (reported as K_2 in the last column of Table 2) and compared excellently well ($p>0.25$) with 4037 ± 138 dm^3 mol^{-1}. A value of approximately 4000 dm^3 mol^{-1} for the stability constant of $MgC_2O_4^0$ ion pair has also been reported by other workers using different methods.[13,14]

In conclusion, the existence of $NaC_2O_4^-$ ion pair in solulion containing sodium and oxalate ions (Tables 1 and 2) has been further confirmed from the results of COM solubility measurements. Direct observations, obtained from Raman spectroscopy by Kanamori et al.,[6] together with the results of potentiometry[5] and COM solubility measurements in different media, all indicated the existence of $NaC_2O_4^-$ or $KC_2O_4^-$ ion pairs in urine or synthetic solutions containing sodium/potassium and oxalate ions. In the light of above it is, therefore, suggested that the correction for these ion pairs should be made when calculating the supersaturation of calcium oxalate phases in synthetic solutions, containing alkali metal and oxalate ions, and urine.

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Table 2. Results of Solubility Determinations of COM in Magnesium Chloride and in the Mixtures of Magnesium Chloride and 0.15 mol dm^{-3} Sodium Chloride at 37 °C

NaCl	$MgCl_2$	Solubility $Ca^{2+}=C_2O_4^{2-}$	γ_2	K'	K_1	K_2
mol dm^{-3}	mmol dm^{-3}	mmol dm^{-3}				
0.0	1.0	0.119	0.7936	2658	4220	—
0.0	2.0	0.154	0.7114	2054	4058	—
0.0	4.0	0.207	0.6312	1582	3970	—
0.0	8.0	0.285	0.5416	1144	3900	—
Mean					4037	
SD					138	
0.15	1.0	0.208	0.3193	237	2325	3825
0.15	2.0	0.233	0.3182	241	2380	3901
0.15	3.0	0.276	0.3160	245	2458	4019
0.15	4.0	0.349	0.3119	255	2621	4257
Mean					2446	4001
SD					129	189

K'=conditional stability constant of MgC_2O^0 ion pair. K_1=stability constant of $MgC_2O_4^0$ ion pair corrected for $CaC_2O_4^0$ ion pair and ionic strength. K_2=stability constant of $MgC_2O_4^0$ corrected for both $CaC_2O_4^0$ and $NaC_2O_4^-$ ion pairs, and ionic strength. γ_2=activity coefficient for bivalent ion.

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