

Calcium L-Tartrate Complexes Forming in Neutral and in Hyperalkaline Aqueous Solutions

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ELECTRONIC SUPPLEMENTARY INFORMATION

Scoping experiments Test tube experiments were first performed with solutions containing the metal ion and the ligand in a molar ratio of $\text{Tar}^{2-}:\text{Ca}^{2+} = 2:1$ (the initial analytical concentration of Na_2Tar and CaCl_2 was 0.5 and 0.25 M) and from which some solid $\text{CaTar}_{(s)}$ has already precipitated. Upon addition of a concentrated NaOH solution to the system, the gradual dissolution of the precipitate was observed. A transparent solution was obtained when the $\text{OH}^-:\text{Ca}^{2+}$ ratio reached about 2:1. The important consequence of these experiments is that upon addition of hydroxide ions to the system, the solubility of $\text{CaTar}_{(s)}$ or $\text{Ca(OH)}_{2(s)}$ increases and supposedly some sort of water soluble complex species is formed.

Freezing point depression experiments were also performed. Freezing-point depression of a solution is calculated according to

$$\Delta T_f = K_f \cdot m_B$$

where ΔT_f is the freezing point depression defined as the difference between the freezing point of the solvent and the solution, $T_{f,pure\ solvent} - T_{f,solution}$, K_f is the cryoscopic constant (which is 1.86 °C·kg/mol for water) and m_B is the molality of the solute, expressed as mole of solute particles in 1 kg of solvent. (m_B may be replaced by the practically identical molar concentration

values in case of relatively diluted solutions). If the number of solute particles decreases for, *e.g.*, complex formation, the freezing point depression, being a colligative property, also decreases. Another important outcome of these experiments is the appreciable association between the Na⁺ and Tar²⁻ ($\Delta\Delta T_f = 0.36$ °C increase of the freezing point depression in $[\text{Na}_2\text{Tar}]_T = 0.3$ M solution relative to a solution free of ion-pairs.) To get a further insight in the effect of the sodium ion-pair formation of the tartrate ion, a different set of FPD experiments was performed. Experimental data were obtained for solutions with increasing $[\text{Na}_2\text{Tar}]_T$ (Table S2.) As it is seen from the data of Table S2, the FPD effect caused by the ion-pair formation is well detectable in these solutions and the concentration of the ion-pair increases with increasing salt concentration. (As freezing point depression measurements must be done using solutions with changing ionic strength and temperature, formation constants obtained from such experiments are semi-quantitative.) The stability constant of the ion-pair was estimated by using the PSEQUAD suite of computer programs. The observed values can be represented very well assuming the formation of only the 1:1 ion-pair (Figure S4) and the formation constant of the $\text{NaTar}^-_{(\text{aq})}$ was found to be $\lg K_{1,1} = 0.69 \pm 0.02$ with the average error of 0.01 °C. This constant is valid in the temperature range of 0.25–1.70 °C below zero and agrees reasonably well with those are reported in literature, considering the different temperature and the varying ionic strength. These observations imply, that the species $\text{NaTar}^-_{(\text{aq})}$ may be of some importance under the conditions of the titrations that were performed both in neutral and alkaline media to accurately determine the formation constant and composition of the complex species of Ca²⁺ and Tar²⁻ (see below).

Deduction of variation of the solubility product of CaTar_(s) considering the β_{120}

The solubility product of CaTar_(s) and formation constant of CaTar_{2(aq)} can be defined as (Eq. 1 and 2):

$$L = [\text{Ca}^{2+}] [\text{Tar}^{2-}] \quad (1)$$

$$\beta_{120} = \frac{[\text{CaTar}_2^{2-}]}{[\text{Ca}^{2+}] [\text{Tar}^{2-}]^2} \quad (2)$$

The total concentrations of Ca²⁺ and Tar²⁻ (Eq. 3 and 4):

$$[\text{Ca}^{2+}]_T = [\text{Ca}^{2+}] + [\text{CaTar}^0] + [\text{CaTar}_2^{2-}] \quad (3)$$

$$[\text{Tar}^{2-}]_T = [\text{Tar}^{2-}] + [\text{CaTar}^0] + 2[\text{CaTar}_2^{2-}] \quad (4)$$

Expressing total concentrations of Tar²⁻ using Eq. (3) and (4):

$$[\text{Tar}^{2-}]_T = c_{\text{Tar}^{2-}} + [\text{Ca}^{2+}]_T = c_{\text{Tar}^{2-}} + [\text{Ca}^{2+}] + [\text{CaTar}^0] + [\text{CaTar}_2^{2-}] \quad (5)$$

$$[\text{Tar}^{2-}] + [\text{CaTar}^0] + 2[\text{CaTar}_2^{2-}] = c_{\text{Tar}^{2-}} + [\text{Ca}^{2+}] + [\text{CaTar}^0] + [\text{CaTar}_2^{2-}] \quad (6)$$

$$[\text{Tar}^{2-}] + [\text{CaTar}_2^{2-}] = c_{\text{Tar}^{2-}} + [\text{Ca}^{2+}] \quad (7)$$

Expressing the solubility product of $\text{CaTar}_{(s)}$ from Eq. (7) using Eq. (1) and (2):

$$\frac{L}{[\text{Ca}^{2+}]} + \beta_{120} [\text{Ca}^{2+}] [\text{Tar}^{2-}]^2 = c_{\text{Tar}^{2-}} + [\text{Ca}^{2+}] \quad (8)$$

$$\frac{L}{[\text{Ca}^{2+}]} + \beta_{120} [\text{Ca}^{2+}] \frac{L^2}{[\text{Ca}^{2+}]^2} = c_{\text{Tar}^{2-}} + [\text{Ca}^{2+}] \quad (9)$$

$$\frac{L}{[\text{Ca}^{2+}]} + \beta_{120} \frac{L^2}{[\text{Ca}^{2+}]} = c_{\text{Tar}^{2-}} + [\text{Ca}^{2+}] \quad (10)$$

$$L + \beta_{120} L^2 = c_{\text{Tar}^{2-}} [\text{Ca}^{2+}] + [\text{Ca}^{2+}]^2 \quad (11)$$

$$[\text{Ca}^{2+}]^2 + c_{\text{Tar}^{2-}} [\text{Ca}^{2+}] - (L + \beta_{120} L^2) = 0 \quad (12)$$

Solving the Eq. (12) using the quadratic formula:

$$[\text{Ca}^{2+}]_{1,2} = \frac{-c_{\text{Tar}^{2-}} \pm \sqrt{c_{\text{Tar}^{2-}}^2 - 4\alpha}}{2} \quad (13)$$

$$\alpha = L + \beta_{120} L^2 \rightarrow L^2 \beta_{120} + L - \alpha = 0 \quad (14)$$

Solving and the value of the solubility product of $\text{CaTar}_{(s)}$ using Eq. (14) and the quadratic formula

$$L_{1,2} = \frac{-1 \pm \sqrt{1 - 4\beta_{120}\alpha}}{2\beta_{120}}; \beta_{120} = 10^{2,0125} \quad (15)$$

$$L = 1,09 \cdot 10^{-4} \text{M}^2 \quad (16)$$

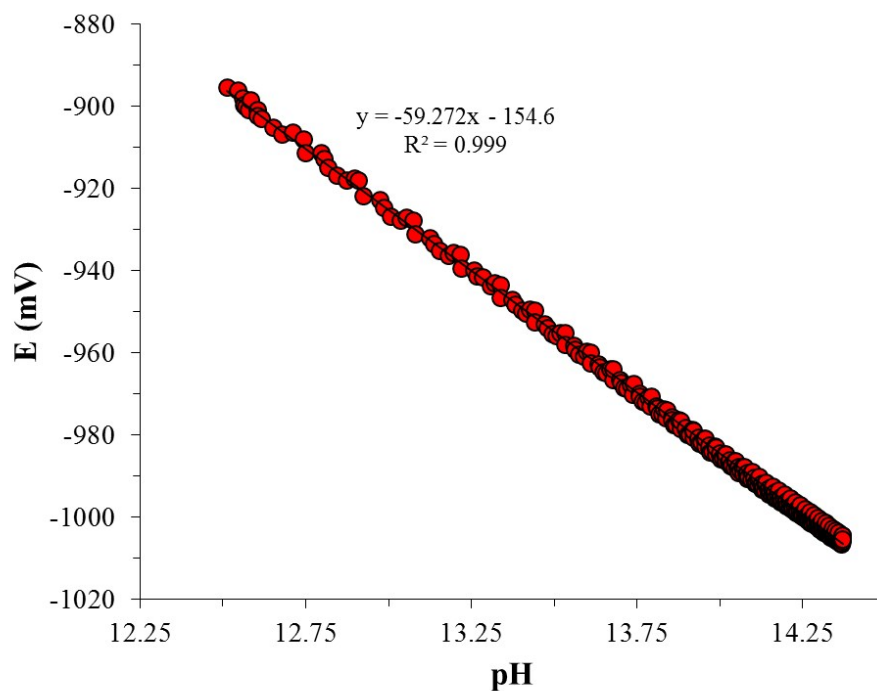


Fig. S1 Calibration curves (three consecutive measurements) of Pt/H₂ electrode in caustic solution at 4 M Na(Cl) ionic strength. $\text{pH} = \text{p}K_w - \lg([\text{OH}^-]/\text{M})$, where $\text{p}K_w = 14.29$. Initial volume: 70 cm³; initial $[\text{NaOH}]_T = 0.01$ M; titrant: $[\text{NaOH}]_T = 4.00$ M; $T = 25$ °C.

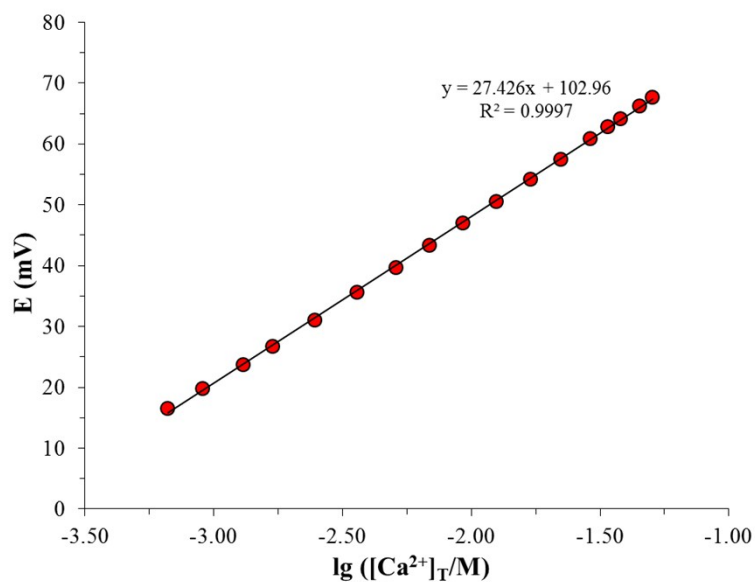


Fig. S2 Calibration curve of Ca-ionselective electrode in neutral solution at 4 M (Na)Cl ionic strength. Initial volume: 25 cm³; initial $[\text{CaCl}_2]_T = 10^{-3.18}$ M; titrant: $[\text{CaCl}_2]_T = 1.00$ M; $I = 4$ M (TMA)Cl, $T = 25$ °C.

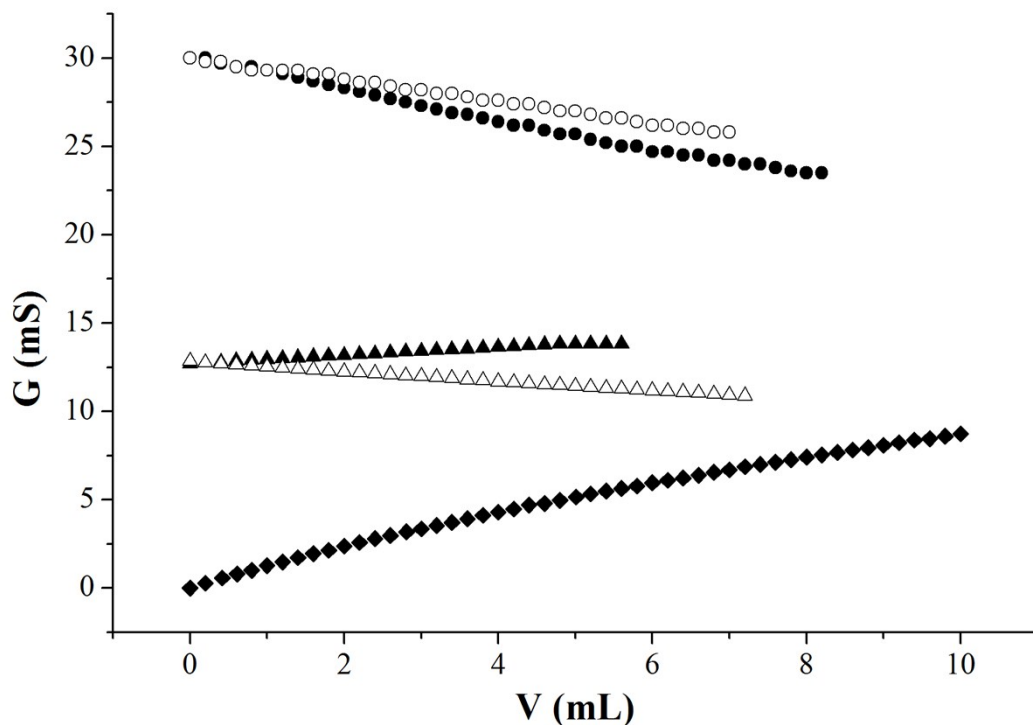


Fig. S3 Conductometric titration curves: 35 cm³ solution with an initial $[\text{Na}_2\text{Tar}]_{\text{T}} = 0.057 \text{ M}$ titrated with distilled water (empty symbols) and with a $[\text{CaCl}_2]_{\text{T}} = 0.15 \text{ M}$ solution (full symbols) in presence (o,●) and in absence (\square , \blacktriangle) of NaOH (initial $[\text{NaOH}]_{\text{T}} = 0.057 \text{ M}$). $T = 25 \text{ }^\circ\text{C}$, ionic strength was not maintained. As blank titration, distilled water titrated with CaCl_2 (\blacklozenge) is also shown.

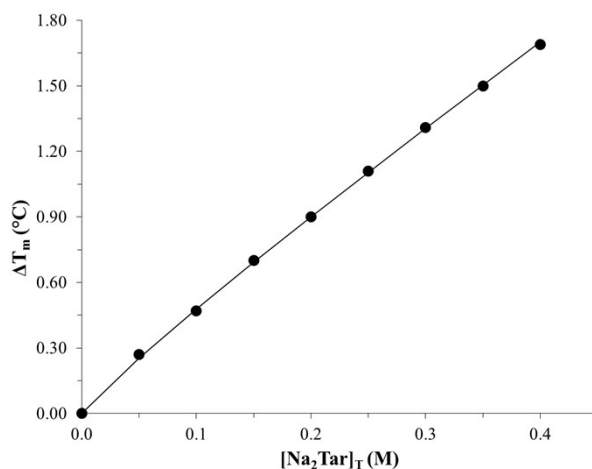


Fig. S4 Observed (full circles) and calculated (solid line) freezing point depression values obtained for $[\text{Na}_2\text{Tar}]_{\text{T}} = 0\text{--}0.4 \text{ M}$ solutions. The solid line was calculated *via* assuming a formation constant of $\lg K_{1,1} = 0.69$ for the $\text{NaTar}_{(\text{aq})}^-$ ion-pair.

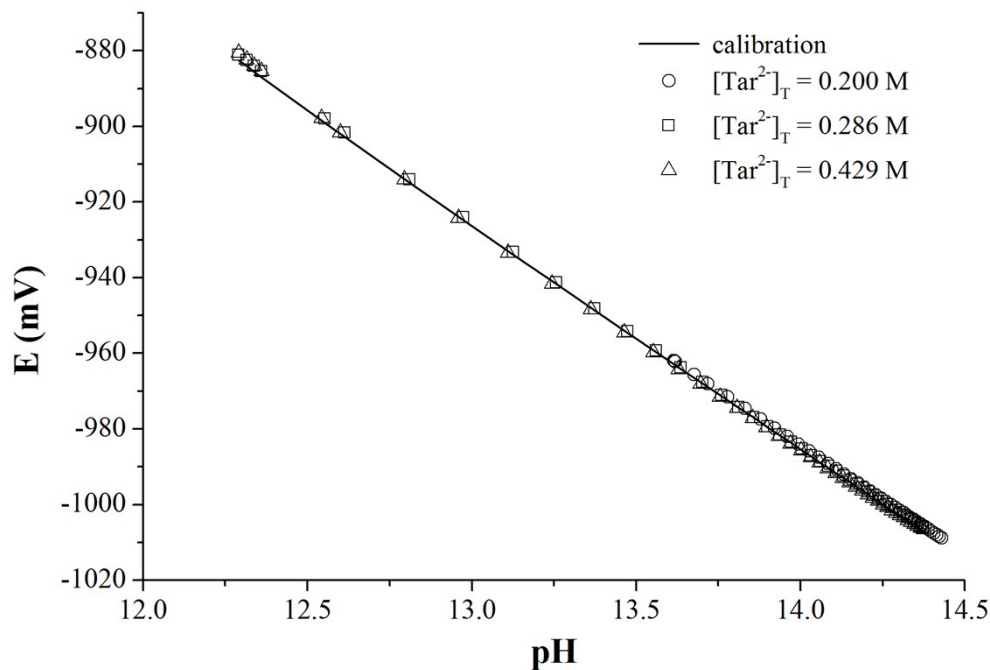


Fig. S5 H₂/Pt electrode potentiometric titration curves of alkaline solutions containing Tar²⁻ at constant ionic strength (4 M NaCl)). Initial compositions of the solutions are shown on the figure. $\text{pH} = \text{p}K_w - \lg([\text{OH}^-]/\text{M})$, where $\text{p}K_w = 14.29$, and the solid line was obtained for tartrate free solution. Initial volume: 70 cm³; initial $[\text{NaOH}]_T = 0.20$ M; titrant: $[\text{NaOH}]_T = 4.00$ M; T = 25 °C.

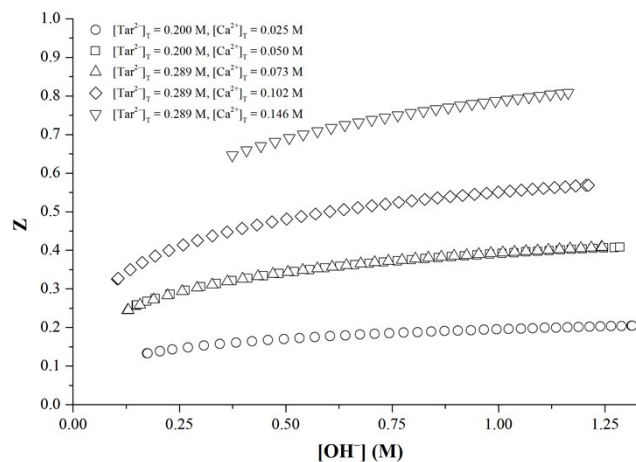


Fig. S6. The average number of OH⁻ ions reacted per Tar²⁻, Z, obtained from H₂/Pt potentiometric titrations. Initial compositions of the solutions are shown on the figures.

Table S1. Results of the freezing point depression measurements in solutions containing Ca^{2+} , Tar^{2-} and OH^- . $\Delta T_{f,theo}$ is the freezing point depression calculated on the basis of the assumption, that all the solute molecules are completely dissociated to ions; $\Delta T_{f,meas}$ is the observed freezing point depression; $\Delta\Delta T_f = \Delta T_{f,theo} - \Delta T_{f,meas}$.

$[\text{NaOH}]_T$ (M)	$[\text{Na}_2\text{Tar}]_T$ (M)	$[\text{CaCl}_2]_T$ (M)	$\Delta T_{f,theo}$ (°C)	$\Delta T_{f,meas}$ (°C)	$\Delta\Delta T_f$ (°C)
0.30	0	0	1.11	1.09	0.02
0	0.30	0	1.67	1.31	0.36
0	0	0.05	0.28	0.29	0.01
0	0	0.10	0.56	0.55	0.01
0	0	0.15	0.84	0.81	0.03
0.30	0.30	0.05	3.07	2.32	0.75
0.30	0.30	0.10	3.34	2.35	0.99
0.30	0.30	0.15	3.62	2.47	1.15

Table S2. Results of the freezing point depression measurements for solutions containing Na_2Tar . $\Delta T_{f,theo}$ is the freezing point depression calculated on the basis of the assumption, that all the solute molecules are completely dissociated to ions; $\Delta T_{f,meas}$ is the observed freezing point depression; $\Delta\Delta T_f = \Delta T_{f,theo} - \Delta T_{f,meas}$.

$[\text{Na}_2\text{Tar}]_T$ (M)	$\Delta T_{f,theo}$ (°C)	$\Delta T_{f,meas}$ (°C)	$\Delta\Delta T_f$ (°C)
0.05	0.28	0.27	0.01
0.10	0.56	0.47	0.09
0.15	0.84	0.70	0.14
0.20	1.12	0.90	0.22
0.25	1.40	1.11	0.29
0.30	1.67	1.31	0.36
0.35	1.95	1.50	0.45
0.40	2.23	1.69	0.54

Table S3. Calculated Ca–O distances using high theoretical level (HF/6–31 G**) quantum chemical calculations for the assumed configuration of the forming Ca²⁺ and Tar²⁻ containing complexes in highly caustic solutions

Complex	Ca–O distances (Å)				
	Ca– carboxylate O (bonding)	Ca– carboxylate O (non-bonding)	Ca– alcoholate O	Ca– hydroxyl O	Ca–OH
CaTarH ₋₁ ⁻ (aq) A-type	2.41-2.43	-	2.20	2.53	-
CaTarH ₋₁ ⁻ (aq) B-type	2.28, 2.42, 2.45	4.28	-	-	2.12
CaTarH ₋₂ ⁻² (aq) A-type	2.32	-	2.26	-	-
CaTarH ₋₂ ⁻² (aq) B-type	2.36	-	-	2.25	-