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Jana Bocková, Nykola C Jones, Vanessa Leyva, Marc Gaysinski, Søren V Hoffmann, et al.. Concentration and pH effect on the electronic circular dichroism and anisotropy spectra of aqueous solutions of glyceric acid calcium salt. *Chirality*, inPress, CHIRALITY IN FRANCE, 10.1002/chir.23407 . hal-03505484

HAL Id: hal-03505484

<https://hal.science/hal-03505484>

Submitted on 30 Dec 2021

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Concentration and pH effect on the electronic circular dichroism and anisotropy spectra of aqueous solutions of glyceric acid calcium salt

Jana Bocková,^[a] Nykola C. Jones,^[b] Vanessa Leyva,^[a] Marc Gaysinski,^[a] Søren V. Hoffmann,^[b] and Cornelia Meinert*^[a]

Abstract: Electronic circular dichroism (ECD) and anisotropy spectra carry information on differential absorption of left- and right-circularly polarised light (LCPL and RCPL) by optically active compounds. This makes them powerful tools for the rapid determination of enantiomeric excesses (*ee*) in asymmetric synthetic and pharmaceutical chemistry, as well as for predicting the *ee* inducible by UV CPL. The ECD response of a chiral molecule is, however, critically dependent on the properties of the surrounding medium. Here, we report on the first ECD/anisotropy spectra of aqueous solutions of the calcium salt dihydrate of glyceric acid. A systematic study of the effect of the salt concentration and pH on the chiroptical response revealed significant changes and the appearance of a new ECD band of opposite sign. Based on the literature this can be rationalised by the increase in the relative proportion of free glyceric acid/glycerate to Ca²⁺ complexes with glycerate with decreasing salt concentration or pH. Glyceric acid can be readily produced under astrophysical conditions. The anisotropy spectra of the solution containing prevalently the free form of this dihydroxy carboxylic acid resemble the ones of previously investigated aliphatic chain hydroxycarboxylic acids and proteinogenic amino acids. This indicates possible common handedness of stellar CPL-induced asymmetry in the potential co-monomers of primitive proto-peptides.

Keywords: circularly polarised light, chiral hydroxycarboxylic acid, enantiomeric excess, complexation, alkaline earth metal, homochirality, CPL scenario.

Introduction

Differentiation between enantiomers of a chiral species requires a chiral force. Circularly polarised light (CPL) represents a true chiral entity¹ and the origin of biological homochirality – uniformity of handedness of amino acids (L-) and sugars (D-) in the biosphere – remains, up to now, most likely linked to the asymmetric interaction of stellar UV CPL with enantiomers of chiral molecules.^{2,3} The intrinsic response of an optically active molecule to UV CPL is polarisation and wavelength dependent. This dependence is manifested in electronic circular dichroism (ECD) spectroscopy. ECD measures the differential absorption of left- and right-CPL (LCPL and RCPL) as a function of wavelength, $\Delta\varepsilon = \varepsilon_L - \varepsilon_R$, where ε_L and ε_R are extinction coefficients of LCPL and RCPL, respectively. The measure of the effectiveness of an asymmetric photolysis of a racemic mixture by CPL is given by the anisotropy factor $g = \frac{\Delta\varepsilon}{\varepsilon}$, where $\varepsilon = \frac{\varepsilon_L + \varepsilon_R}{2}$ is the extinction coefficient. The magnitude of the *ee* inducible by CPL ($ee_L = \frac{[L] - [D]}{[L] + [D]}$, where [L] and [D] are concentrations of L- and D-enantiomers, respectively) can be approximated as follows^{4,5}

$$|\%ee| \geq \left(1 - (1 - \xi)^{\frac{|g|}{2}}\right) \times 100\% \quad (1)$$

where ξ is the extent of a photochemical reaction and the sign of *%ee* follows the sign of *g*. Apart from elucidating the *ee* inducible by CPL, ECD is widely exploited to discern the enantiopurity of chiral pharmaceuticals, agrochemicals, and specialty chemicals in the fields of asymmetric synthesis and catalysis.^{6–9}

Importantly, electronic circular dichroism is critically dependent on the conformation of the molecule as well as on the properties of the surrounding medium.^{10–12} The effect of pH, temperature and solvent polarizability on the ECD of chiral amino acids in the liquid phase has been well addressed in the literature.^{11,13–17} It should be noted that varying any of the above-mentioned parameters has

been found to only induce shifts in the position and intensity of the UV ECD bands. This implies that although the magnitude of the *ee* inducible by interaction with broadband CPL would depend on the exact conditions, the sign of the *ee* in such cases remains the same.

Significant changes in the ECD spectra of amino^{18–22} and hydroxycarboxylic acid (HCA)²³ solutions were observed in the presence of transition metal ions as a result of complexation. In addition to structural changes (chelate ring formation), coordination of an optically active molecule (ligand) to a transition metal ion induces rotational strength into its d-d electronic transitions which gives rise to new ECD signals.^{18–22} This phenomenon has been recently exploited in a novel chiroptical *ee* sensing technique which is based on the detection of induced visible ECD bands by complexation of transition metal ions with chiral organic analytes.^{24,25} In addition to transition metal ions, it has also been shown that alkali (Li⁺, Na⁺, K⁺) and alkaline earth metal ions (Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺)^{26–33} have a tendency to form complexes with hydroxycarboxylates. Their presence in solutions of HCAs was shown to induce changes in the intensity and

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Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

position of the ECD bands extrema corresponding to the $n\pi^*$ transition of the carbonyl chromophore.²⁹ The differences in the ECD signal were found to be critically dependent on (1) the nature of the ionic medium^{29,34} confirming the formation of complexes,²⁹ (2) the type of the ligand which was ascribed to the extent of conformational modification of anions upon complexation,²⁹ and (3) the ionic strength, where the higher ionic strength was linked to the higher extent of complexation.²⁹ In addition to the change of the relative intensity of the negative ECD band of L-tartaric acid in aqueous solution at around 210–215 nm, Hoffmann et al.³⁴ reported a gradual increase of a newly appearing negative ECD band at around 193 nm upon addition of NaOH. Based on density functional theory (DFT) calculations, this effect was assigned to the change in the preferred structural symmetry between fully protonated tartaric acid and completely ionised tartrate in the presence of metal ions.³⁴

Interestingly, our recent study³⁵ has shown that the ECD/anisotropy spectra of aqueous solutions of aliphatic chain HCAs resemble those of proteinogenic amino acids, suggesting that broadband stellar CPL has the potential to induce a net ee of the same handedness in the two families of chiral molecules. This has strong implications in the origin-of-life research, since these species have been discussed as the most likely monomers of primitive proto-peptides preceding contemporary peptides.^{36–38} However, some enantiomerically pure standards of prebiotically relevant species are commercially available only in the form of salts of alkali/alkaline earth metal ions (e.g. glyceric acid, gluconic acid, glycerol-1/3-phosphate) due to their low stability in the solid-phase.³⁹ Here we report on the first ECD/anisotropy spectroscopy experiments on aqueous solutions of the calcium salt of glyceric acid, which is a chiral dihydroxy carboxylic acid (**Figure 1 a**). Glyceric acid was found in UV-irradiated interstellar/cometary ice analogues (1:1 mixture of $\text{CH}_3\text{OH}:\text{NH}_3$, 80 K)⁴⁰ as well as in meteoritic samples.^{41,42} This suggests the molecule was very likely present on the early Earth and could have been involved in co-building proto-peptides.^{36–38} The present ECD/anisotropy spectra of the aqueous solutions of glyceric acid calcium salt dihydrate revealed significant changes as a function of concentration and pH, notably the appearance of a new band of opposite sign as well as changes in the intensity and position of the extrema of the bands. The present study, therefore, highlights the importance of carefully monitoring the equilibrium concentration and acidity of solutions of alkaline earth metal salts in ECD/anisotropy studies aimed at investigating enantiopurity, as well as elucidating CPL inducible enantiomeric excesses of astrochemically relevant chiral molecules in their free form, in which they would most likely be found in interstellar environments. Comparison of the anisotropy spectrum of the free acid with those of previously investigated proteinogenic amino acids^{11,13} and HCAs³⁵ brings additional insights into potential common CPL inducible ee in candidate ancestral co-building blocks of proto-peptides.

Materials and Methods

Enantiopure standards of D- and L-enantiomers of glyceric acid calcium salt dihydrate (**Figure 1 a**) were purchased from Sigma-Aldrich (purity 99% and $\geq 97\%$, respectively) and were used without further purification. The aqueous solutions for the ECD/anisotropy spectroscopy measurements were prepared in deionised, filtered, and UV-irradiated ultrapure water at

concentrations of 100, 20, and 5 g L^{-1} . Their pH was measured using a pH meter (InoLab pH 730). The acidic solutions at pH 2 to 3.8 were adjusted by adding a 6 M hydrochloric acid solution (diluted from a 37% – 12 M – solution of HCl, Sigma-Aldrich). The rather low volumes of the acidic sample solutions prevented using a pH meter and their pH was determined with MColorpHast pH indicator strips (non-bleeding, range 2–9).

For ECD/anisotropy spectroscopy experiments on free glyceric acid/glycerate, 1.444 g of glyceric acid calcium salt was dissolved in 12 ml of D_2O and passed, sequentially, through two cation exchange columns each containing 5 g of BT AG 50W-X8 (100–200 mesh) resin. The columns had been equilibrated and washed with four bed volumes (BV) of 1 M HCl, followed by four BV of MilliQ® water, and 1.5 BV of D_2O . The eluted solution from the first column, employing four BV of D_2O , was pre-concentrated to 15 ml and passed through the second column using four BV of D_2O . Finally, the second solution was pre-concentrated to a final volume of 12 ml. The approximate concentration of glyceric acid in the purified solution, as determined by $^1\text{H NMR}$, was 0.75 M. The pH of the solution was determined to be 1–1.5 with MQuant pH indicator strips (non-bleeding, range 0–6).

Electronic circular dichroism and anisotropy spectra of D- and L-enantiomers of glyceric acid calcium salt dihydrate were recorded in the 170–280 nm wavelength range using the synchrotron radiation electronic circular dichroism spectrophotometer on the AU-CD beamline at the ASTRID2 synchrotron storage ring facility, Aarhus University, Denmark. The technique described in detail in Evans et al.⁴³ allowed the simultaneous measurement of extinction (ϵ) and differential extinction ($\Delta\epsilon$) coefficients. The spectra of the aqueous sample solutions were measured at 24.2 ± 0.5 °C using quartz cells with nominal path lengths of 2, 10, 100 and 500 μm . All spectra were recorded with a 2 s dwell time per point, 1 nm steps and multiple accumulations for each sample. The ECD spectra were mildly smoothed with a 7-point Savitzky-Golay filter.

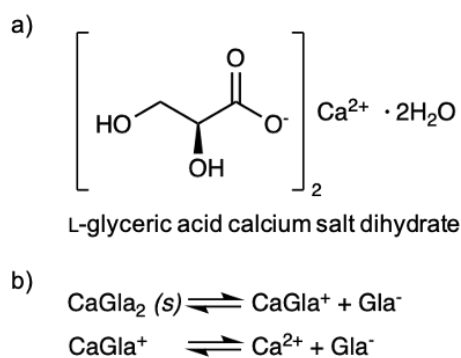


FIGURE 1 a) Chemical formula of the L-enantiomer of glyceric acid calcium salt dihydrate and **b)** schematic of stepwise dissolution of calcium salt of glyceric acid $\text{CaGla}_2 (s)$, where CaGla^+ is 1:1 complex of glycerate Gla^- and calcium ion Ca^{2+} .

Results and Discussion

The electronic circular dichroism spectra of aqueous solutions of D- and L-enantiomers of glyceric acid calcium salt dihydrate measured at 24.2 ± 0.5 °C at three different concentrations are shown in **Figure 2 a to c** along with their corresponding anisotropy spectra in **Figure 2 d to f**. The ECD spectra significantly differ from each other, which suggests that different structures

contribute to the ECD signals in **Figure 2 a to c**. The reliability of the recorded data is confirmed by the mirror symmetry of the ECD signal of the two enantiomers at each concentration (nearly equal magnitude and position of extrema). Given the uncertainties induced by low absorbance and ECD signals above ~ 240 – 250 nm, the values of the anisotropy factor g are less reliable in this wavelength range as indicated by dashed line in **Figure 2 d to f**.

Dissolution of calcium salt of glyceric acid in water is a two-step equilibrium process and it is schematically shown in **Figure 1 b**.^{31,44} Calcium salts of hydroxycarboxylic acids were found to be unusually weak electrolytes.⁴⁵ In a 0.27 M (58 g L⁻¹) solution of calcium lactate and 0.08 M (32.7 g L⁻¹) solution of calcium gluconate at 20 °C only about 21% and 30% of calcium, respectively, is present in the free form.³¹ Glyceric acid is an aliphatic polyhydroxy carboxylic acid with two hydroxyl groups on the C _{α} - and C _{β} - atoms (**Figure 1 a**). Several experimental studies have confirmed that the carboxylate group (COO⁻) is capable of coordinating to alkali (Li⁺, Na⁺, K⁺)/alkaline earth metal ions (Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺).^{26–33} Moreover, ¹³C NMR experiments,^{27,28,30} ¹H–⁴³Ca NMR experiments^{32,33} as well DFT and Hartree-Fock *ab initio* calculations^{31,32,33} showed that in addition to the carboxylate group, a hydroxyl group can be involved in such coordination in the presence of a negatively charged group nearby (e.g. COO⁻). Pallagi et al.³² reported that gluconate – another aliphatic polyhydroxy carboxylic acid – acts as a multidentate ligand in aqueous solution with Ca²⁺, with the binding sites being the oxygens of the carboxylate and hydroxyl groups on the C _{α} , C _{β} , and C _{ϵ} . On the other hand, Vavrusova et al.³¹ reported a coexistence of two conformers in a solution of calcium gluconate: (1) the conformation with Ca²⁺ bound to two carboxylate oxygens and the oxygen of the hydroxyl group on the C _{β} , as well as (2) the conformation where Ca²⁺ binds to only one oxygen of the carboxylate group and to the oxygens of the hydroxyl groups on the C _{α} and C _{β} . Based on the strong precedent in the literature for the interaction of Ca²⁺ with the carboxylate^{26–33} and hydroxyl^{27,28,30–33} groups of hydroxycarboxylates, we therefore

attribute part of the spectral changes in our ECD data to such ion-selective pairing. The precise conformations have yet to be determined with the help of theoretical calculations and/or ¹H–⁴³Ca NMR spectroscopy experiments.

With decreasing glyceric acid calcium salt dihydrate concentration, we expect a decrease in the extent of complexation, i.e. lower relative abundance of complexes of glycerate and Ca²⁺ to free glyceric acid/glycerate (at constant K_a). This could explain the gradual shift of the negative ECD band to shorter wavelengths in the solution of L-glyceric acid calcium salt dihydrate from 100 g L⁻¹ to 5 g L⁻¹ which is at least partly driven by the gradual appearance of a positive band at slightly longer wavelength (**Figure 2 a to c** and **Figure 3 a to c**). It should be noted that the pH of the three solutions (100 , 20 , and 5 g L⁻¹) did not vary significantly (**Figure 3 a to c**). This picture is in line with the ECD spectra of L-glyceric acid calcium salt dihydrate (**Figure 3 b and d to f**) showing further increase in the intensity of the longer wavelength positive ECD band upon addition of 6 M HCl. HCl is a strong acid, addition of which results in the dissociation of ion complexes and protonation of glycerate. In addition, some formation of ion pairs such as CaCl⁺ can be expected⁴⁶. At pH ~ 2 – 2.5 we expect the majority of glyceric acid to be present in its free form (**Figure 3 f**), i.e. without bound Ca²⁺. The anisotropy spectra of 5 , 20 and 100 g L⁻¹, with the pH adjusted using 6 M HCl to ~ 2 – 2.5 , all show a positive band with the maximum at around 210 nm (**Figure 4**). Moreover, they resemble well the anisotropy spectrum of the L-glyceric acid calcium salt dihydrate solution after the removal of Ca²⁺ by cation exchange chromatography (**Figure 4**). Hence the anisotropy band at around 210 nm can be undoubtedly ascribed to pure glyceric acid/glycerate. The intensity of this band in the solutions at pH ~ 2 – 2.5 is slightly lower at 100 g L⁻¹ compared to the two lower concentrations. This could be explained by a slightly higher net pH of this solution that was not measurable within the uncertainty of the pH indicator strips. However, it is clearly visible in **Figure 3 j to l** that with decreasing pH the intensity of this anisotropy band increases.

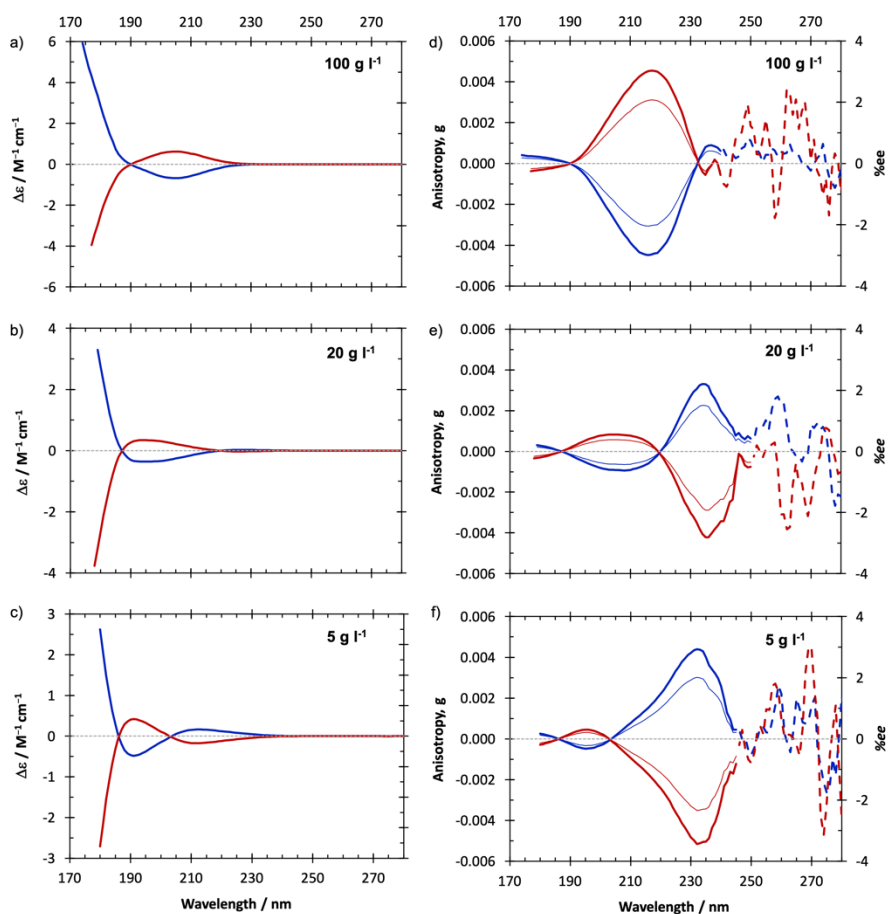


FIGURE 2 a) to c) ECD and d) to g) anisotropy spectra (thick lines) of aqueous solutions of D- (*R*-, red) and L-enantiomers (*S*-, blue) of glyceric acid calcium salt dihydrate at concentrations of 100, 20 and 5 g L⁻¹, respectively. Thin lines in d) to g) represent the lower limit of the enantiomeric excess (%ee) inducible by either left- or right-circularly polarised light as a function of wavelength at the extent of reaction $\xi = 0.9999$ calculated based on relation (1)⁵.

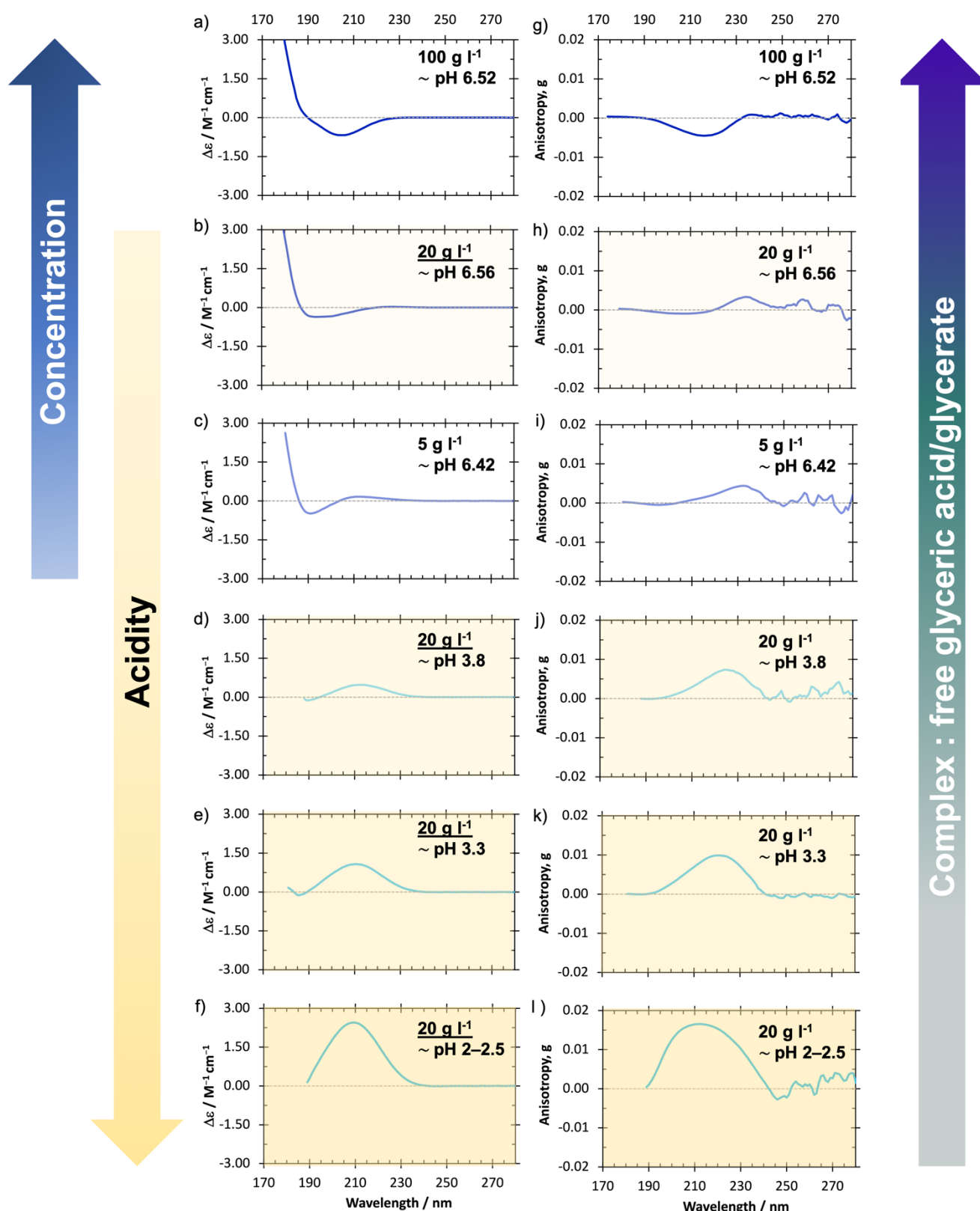


FIGURE 3 a) to c) ECD and g) to i) anisotropy spectra of aqueous solutions of L-glyceric acid calcium salt dihydrate at concentrations 100 g L⁻¹ (~pH 6.52), 20 g L⁻¹ (~pH 6.56) and 5 g L⁻¹ (~pH 6.42), respectively. d) to f) ECD and j) to l) anisotropy spectra of aqueous solutions of L-glyceric acid calcium salt dihydrate at 20 g L⁻¹ with pH adjusted by 6 M HCl to ~3.8, ~3.3 and ~2–2.5, respectively. The blue arrow indicates increase in the concentration for solutions at similar pH. The yellow arrow indicates increase in the acidity of the solutions with concentration 20 g L⁻¹ (corresponding spectra with yellow gradient). The arrow on the right indicates expected increase in the extent of complexation.

The dominant anisotropy spectral band of free L-glyceric acid in the 170–280 nm wavelength range is of the same sign as those of previously investigated L-HCAs³⁵ (aliphatic chain, malic, and mandelic acid) and proteinogenic L-amino acids^{11,13}. This suggests that CPL acting in this wavelength range, which is the dominant UV emission wavelength range of the majority of normal stars,^{35,47,48} can induce an enantiomeric excess of the same handedness in these molecular species, which were likely present on the early Earth^{40–42} and thought to be involved in co-building primitive proto-peptides.^{36–38} Cooper and Rios⁴² reported racemic or near racemic glyceric acid concentrations in carbonaceous chondrites. However, some of the analyses were accompanied by poor enantioseparation, potential contamination could not be fully excluded, and the analytical uncertainties were not stated. Based on the anisotropy spectra in **Figure 5** and relation (1) the maximum enantiomeric excess of $\geq 7.6\%$ could be induced by an asymmetric photolysis by RCPL at 210 nm at the extent of reaction $\xi = 0.9999$. It should be noted that in the present-day biosphere, glyceric acid is primarily found in the D-form⁴⁹ mainly as an end product of metabolic pathways.⁵⁰ This, however, does not necessarily reflect on its preferential handedness on the early Earth. Instead, enantioselective analyses of meteoritic samples will be invaluable for shedding light on the relevance and conditions of the CPL scenario.

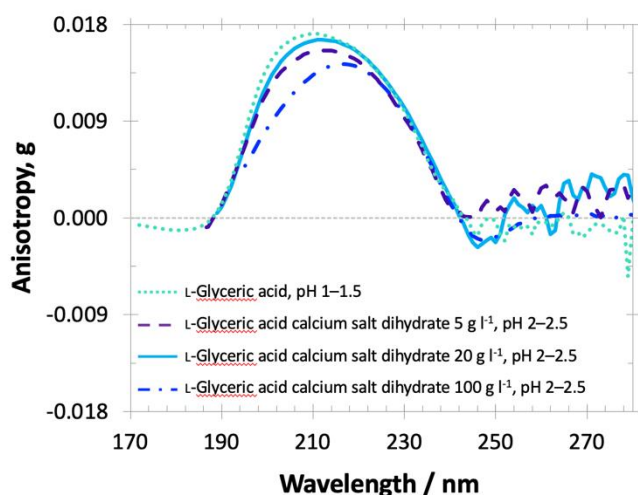


FIGURE 4 Comparison of the anisotropy spectra of aqueous solutions of L-glyceric acid calcium salt dihydrate at concentrations 5, 20 and 100 g L⁻¹ with pH adjusted by 6 M HCl to ~2–2.5 with the anisotropy spectrum of free L-glyceric acid (D₂O solution of L-glyceric acid calcium salt dihydrate after purification from Ca²⁺).

The comparison of the anisotropy spectrum of free L-glyceric acid (D₂O solution of L-glyceric acid calcium salt dihydrate after purification from Ca²⁺) with those of L-lactic acid (a representative of aliphatic chain HCAs) and L-glyceric acid's amino acid analogue L-serine is shown in **Figure 5**. It is reasonable to assume that the positive ECD band with the maximum at around 210 nm is associated with the $n\pi^*$ transition of the carboxyl chromophore of free glyceric acid/glycerate. On the contrary, the negative band in **Figure 3 a** to **c** is then most likely linked to the formation of 1:1 complexes of glycerate and Ca²⁺. The presence and hence contribution of 2:1 complexes cannot be ruled out, however, it is expected to be negligible.^{31,32} Theoretical calculations and/or ¹H-⁴³Ca NMR spectroscopy experiments will be necessary to confirm the contributing molecular conformations and determine the electronic excited states involved. Moreover, complexometric titration in combination with electrochemical measurement of

calcium ion activity can be used to elucidate association constants for complex formation.³¹

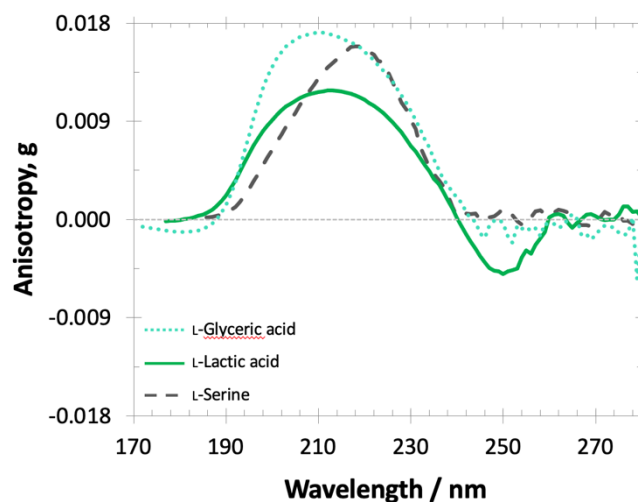


FIGURE 5 Comparison of the anisotropy spectra of aqueous solutions of the L-enantiomers of glyceric acid (D₂O solution of L-glyceric acid calcium salt dihydrate after purification to remove Ca²⁺), the HCA lactic acid³⁵ and the glyceric acids' amino acid analogue serine¹¹ in the dominant UV emission wavelength range of the majority of normal stars^{35,47,48} indicating the same handedness of stellar CPL-inducible enantiomeric excess.

Conclusion

The present paper highlights the effects of concentration and pH on the electronic circular dichroism and anisotropy spectra of aqueous solutions of the calcium salt of glyceric acid. Based on previous studies these can be ascribed to the changes in the extent of complexation of Ca²⁺ and glycerate. Concentration and acidity must therefore be carefully considered in any ECD/anisotropy spectroscopy studies aimed at investigating enantiomeric excesses inducible by CPL or the enantiopurity of a mixture. On the other hand, ECD spectroscopy can be exploited for determination of association constants.

Adjusting the pH of the aqueous solutions of L-glyceric acid calcium salt dihydrate to ~2–2.5 was shown to reduce the complex formation. The corresponding ECD/anisotropy spectra resemble well the anisotropy spectrum of the free L-glyceric acid derived from a L-glyceric acid calcium salt dihydrate solution after the removal of Ca²⁺ ions by ion exchange chromatography. The anisotropy spectrum of pure L-glyceric acid indicates the same handedness of a broadband UV (170–280nm) CPL inducible enantiomeric excess as in the previously investigated hydroxycarboxylic acids and proteinogenic amino acids, which could have been common constituents of ancestral proto-peptides.

Acknowledgements

This research has received funding from the European Research Council under the European Union's Horizon 2020 research and innovation programme [grant agreement 804144]. Further funding was provided by the French government through the UCA^{JEDI} Investments in the Future project managed by the National

Research Agency (ANR) with the reference number ANR-15-IDEX-01 as well as by the project CALIPSOplus under the Grant Agreement 730872 from the EU Framework Programme for Research and Innovation HORIZON 2020.

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Graphical Abstract

The pH and salt concentration induce significant changes in the chiroptical response of aqueous solutions of the calcium salt of glyceric acid. These are rationalised by changes in the relative proportion of free glyceric acid/glycerate to Ca^{2+} complexes. The anisotropy spectra of free glyceric acid resemble the ones of previously investigated potential co-monomers of proto-peptides and indicate common handedness of circularly polarised light inducible enantiomeric excess across molecular families.

