

Supporting Information for Mechanisms of the Viscosity Decrease and Increase of Aqueous CsCl

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This PDF file includes:

Supporting text S1 and S2
Figures S1 to S6
Tables S1 and S2

Supporting Information Text

S1. Details of OHD-OKE Data Processing

The following text contains further details on the processing of the OHD-OKE data. For systems undergoing Markovian relaxations, the OHD-OKE signal can be decomposed using a multi-exponential decay function. The number of exponential terms depends on the number of independent dynamical processes that cause the PPTCF to decay. Therefore, we use a “least-exponential” method for the fits where the model function contains the fewest exponential terms required to converge on the data. For the CsCl solutions studied in this work, three exponential terms were required to fit the OHD-OKE decays. The physical interpretations of these components are discussed in the main text. The fitting function used for the CsCl data is given below.

$$R'_{\text{OKE}}(t) = A_1 e^{-t/t_1} + A_2 e^{-t/t_2} + A_3 e^{-t/t_3} \quad (\text{S1})$$

Since the OHD-OKE experiment provides the time derivative of the PPTCF, it is straightforward to compute it from the fits.

$$R_{\text{OKE}}(t) = A_1 t_1 e^{-t/t_1} + A_2 t_2 e^{-t/t_2} + A_3 t_3 e^{-t/t_3} \quad (\text{S2})$$

From this function, we can derive the normalized correlation coefficients, C_i , which depend on both the decay time and amplitude of each PPTCF component. These coefficients normalize the correlation function and represent the statistical weight of a given dynamical process on the overall decay.

$$\begin{aligned} C_1 &= \frac{A_1 t_1}{A_1 t_1 + A_2 t_2 + A_3 t_3} \\ C_2 &= \frac{A_2 t_2}{A_1 t_1 + A_2 t_2 + A_3 t_3} \\ C_3 &= \frac{A_3 t_3}{A_1 t_1 + A_2 t_2 + A_3 t_3} \end{aligned} \quad (\text{S3})$$

Selected OHD-OKE decays of the CsCl solutions superimposed with the result of fitting to Equation S1 are provided in a log-log plot in Figure S1. OHD-OKE experiments were performed in triplicate or more and the decays were fit individually. Error bounds of the parameters were obtained by calculating the average and standard deviation of each parameter. Table S2 provides the values of all PPTCF parameters from the OHD-OKE experiments, along with their associated error bounds.

S2. Calculation of the Interionic Distance Distribution

At dilute concentrations, we determined that the presence of Cs^+ ions should decrease the viscosity linearly. Each additional Cs^+ ion should result in the same number of weak H-bonds until the ions are close enough together to begin sharing solvation shells. From the DFT calculations, we determined that the 2nd solvation shell extends 6.1 Å from the ion center. Therefore, if two Cs^+ are ≤ 13.2 Å, they will begin to share waters in their 2nd solvation shells and therefore decrease the viscosity sub-linearly since they would make fewer weak H-bonds per ion. To quantify this, we used the fact that interionic distances are described by a Poisson distribution.

$$P(k | r) = \frac{\lambda(r)^k}{k!} e^{-\lambda(r)} \quad (\text{S4})$$

Here, r is the interionic distance, k is the number of ions found in the volume defined by radius r , and $\lambda(r) = \rho \frac{4\pi}{3} r^3$. This expression gives the probability of finding k ions in the volume $4\pi/3 r^3$

weighted by the number density of Cs^+ , $\rho = N/V$. We then calculated the concentration or number density where there would be a 10% chance of an interionic separation ≤ 13.2 Å. The choice of a 10% threshold was arbitrary, but it is where we would expect the prevalence of shared ion 2nd solvation shells to have a non-negligible effect on the viscosity and OHD-OKE signal.

We found that Cs^+ ions have a 10% chance of sharing 2nd solvation shells at a very low concentration of $\sim 2 \times 10^{-2}$ molal. Therefore, ions and their solvation shells are fully isolated only close to the dilute limit. The most probable interionic distance at this concentration is 28 Å (see Figure S6). These results explain why the viscosity of CsCl decreases sub-linearly even at relatively low concentrations.

Supporting Information Figures

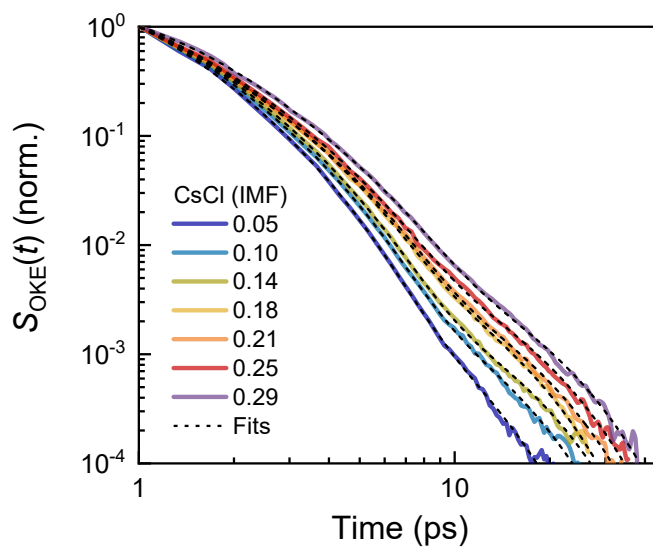


Fig. S1. Selected OHD-OKE decays of aqueous CsCl solutions of various concentrations with fits to Eqn. S1 superimposed (black dashed lines).

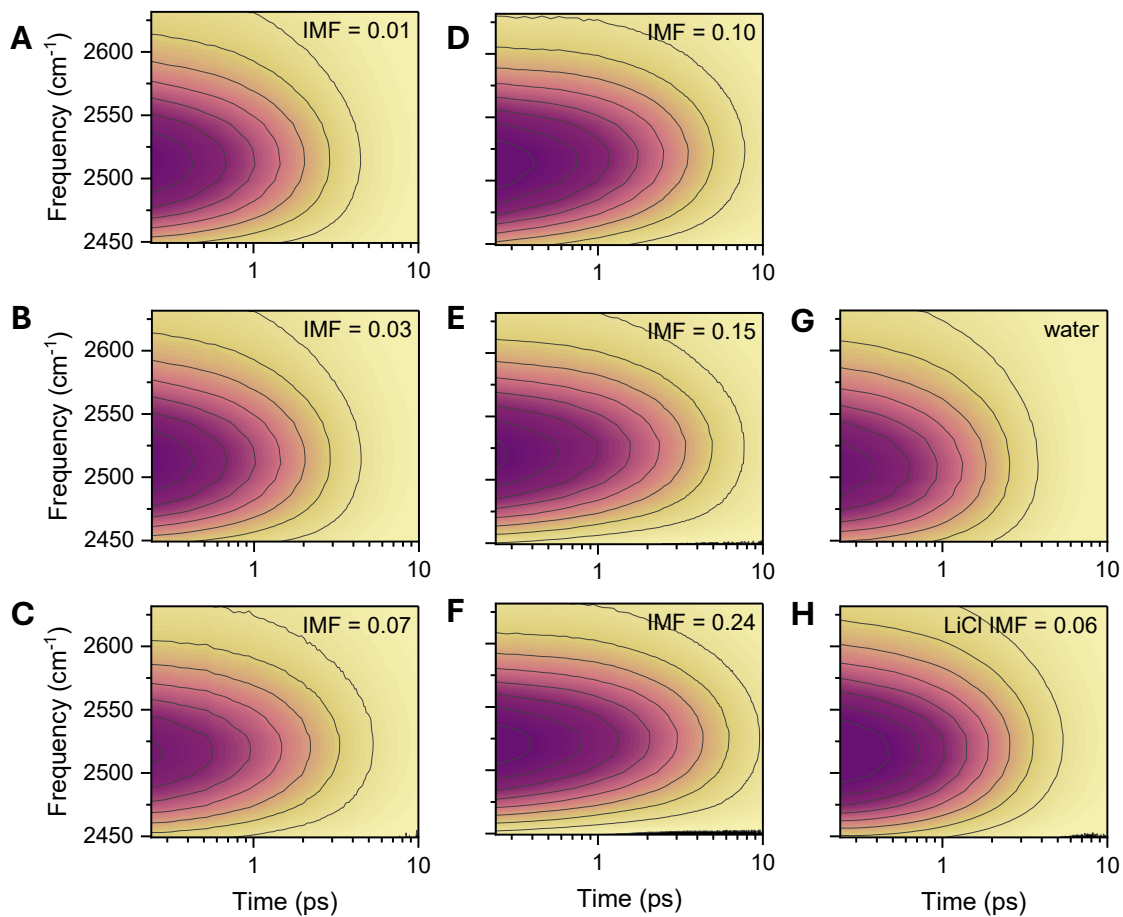


Fig. S2. Frequency-dependent vibrational excited state population decays for **A-F**. CsCl solutions; **G**. pure water; and **H**. mildly concentrated LiCl.

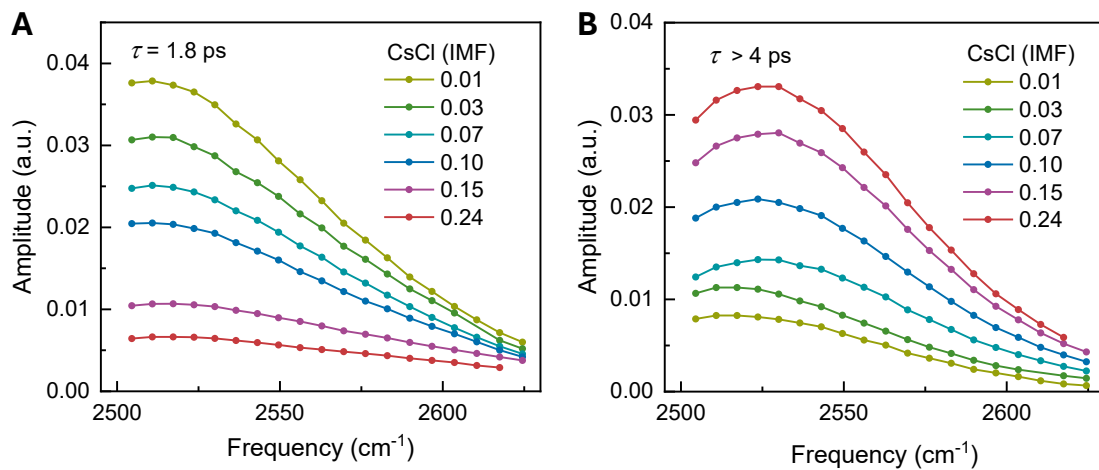


Fig. S3. Unnormalized lifetime amplitude spectra showing strong concentration-dependence for both the frequency and amplitude of the decay components. (A.) Water-water-associated lifetime component. (B.) Water-anion-associated lifetime component.

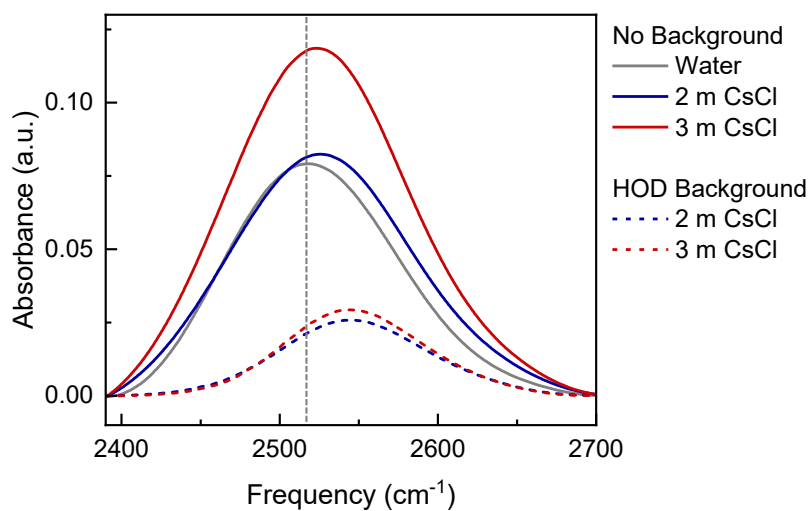


Fig. S4. Linear FTIR spectra of aqueous CsCl solutions. The 2 m and 3 m spectra are blue-shifted with respect to the pure water spectrum, but it is not possible to attribute this shift to a particular structure from these steady-state experiments.

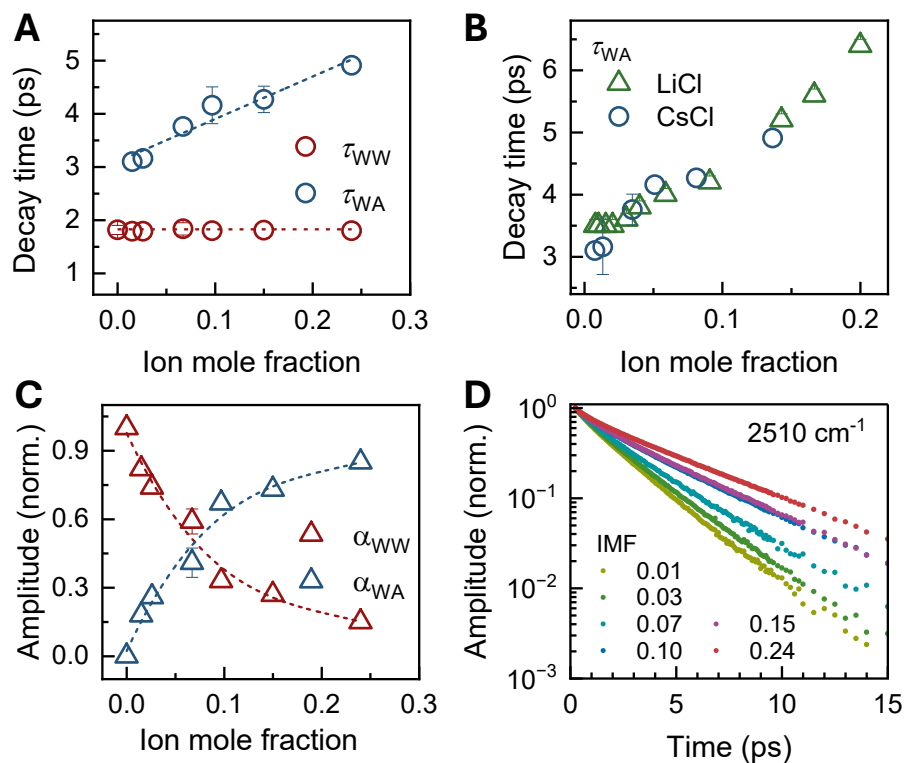


Fig. S5. Excited state population relaxation dynamics of ν_{OD} in CsCl solutions of various concentrations. **A.** Vibrational lifetimes show two distinct sub-ensembles with different relaxation times: a bulk water-associated (WW) and an anion-associated component. A detailed discussion of this assignment is given in the text. **B.** Comparison of the slow lifetime component of CsCl and LiCl solutions. **C.** Frequency-independent amplitudes of each lifetime component showing the typical concentration trend seen in other salts such as LiCl. **D.** Population decays at 2510 cm^{-1} for each CsCl solution, demonstrating the concentration dependence of the vibrational lifetime.

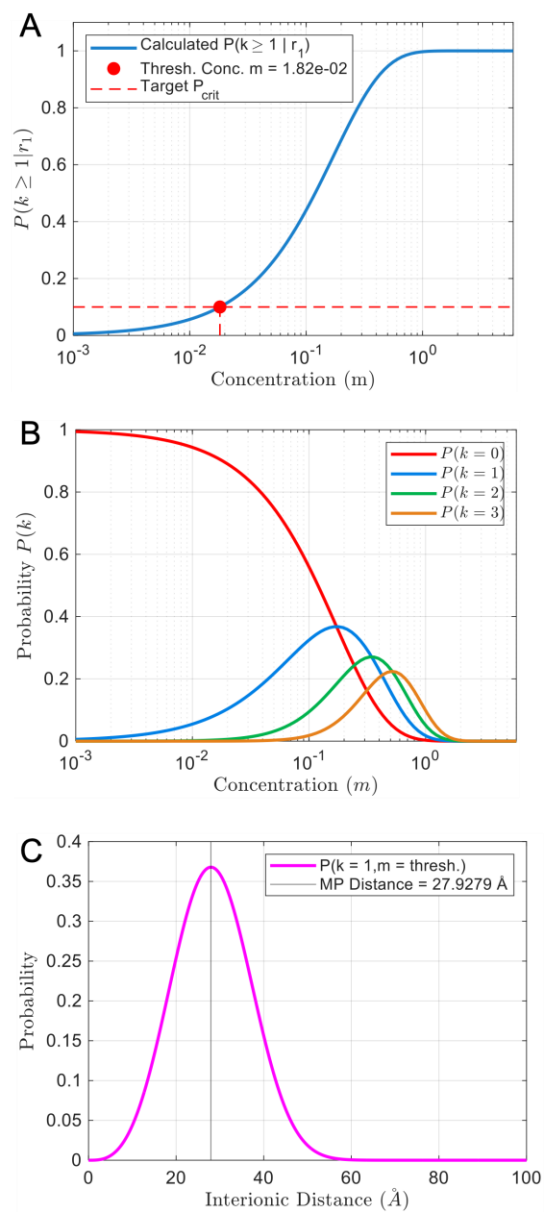


Fig. S6 Results of Poisson distribution calculations to find the concentration where there is a 10% chance of finding a pair of Cs^+ ions at an interionic separation of $r_1 \leq 13.2 \text{ \AA}$, the minimum distance for the ions to have complete 2nd solvation shells. **A.** Calculation of threshold concentration, which is $c_{\text{thresh}} \sim 2 \times 10^{-2}$ molal, indicates that Cs^+ ions begin to share solvation shells even at low concentrations. Above this concentration, the viscosity decreases sub-linearly. **B.** Poisson probability distributions for finding k Cs^+ ions within $r_1 \leq 13.2 \text{ \AA}$. **C.** Distribution of interionic distances at c_{thresh} with the most probable distance indicated with the black line.

Supporting Information Tables

Table S1. Concentrations of CsCl used in the OHD-OKE experiments in units of ion mole fraction, molal, and water molecules per ion, as well as the dynamic viscosities obtained from the literature (ref. 9).

IMF	Molal (m)	Waters per ion	Dynamic viscosity (cP)
0	0	--	0.891
0.035	1.0	29	0.851
0.05	1.4	20	0.833
0.1	2.9	10	0.826
0.14	4.2	7	0.866
0.18	5.5	5.5	0.963
0.21	6.5	4.7	1.138
0.25	7.9	4	1.403
0.29	9.2	3.5	1.768

Table S2. PPTCF parameters obtained from OHD-OKE experiments on CsCl solutions of various concentrations.

IMF	t_1 (ps)	t_2 (ps)	t_3 (ps)	C_1	C_2	C_3
0	0.52	1.29	--	0.66	0.34	--
0.035	0.57 $\pm$ 0.03	1.25 $\pm$ 0.06	3.56 $\pm$ 0.68	0.673 $\pm$ 0.032	0.318 $\pm$ 0.034	0.00907 $\pm$ 0.0065
0.05	0.61 $\pm$ 0.02	1.29 $\pm$ 0.08	3.98 $\pm$ 0.16	0.685 $\pm$ 0.043	0.304 $\pm$ 0.042	0.0105 $\pm$ 0.0012
0.1	0.63 $\pm$ 0.02	1.35 $\pm$ 0.08	4.84 $\pm$ 0.96	0.639 $\pm$ 0.037	0.345 $\pm$ 0.033	0.016 $\pm$ 0.004
0.14	0.6 $\pm$ 0.03	1.31 $\pm$ 0.1	5.32 $\pm$ 0.72	0.557 $\pm$ 0.04	0.423 $\pm$ 0.039	0.0194 $\pm$ 0.002
0.18	0.64 $\pm$ 0.06	1.45 $\pm$ 0.03	6.63 $\pm$ 0.58	0.601 $\pm$ 0.054	0.376 $\pm$ 0.052	0.0229 $\pm$ 0.003
0.21	0.65 $\pm$ 0.03	1.58 $\pm$ 0.06	6.5 $\pm$ 0.42	0.591 $\pm$ 0.025	0.383 $\pm$ 0.02	0.0256 $\pm$ 0.006
0.25	0.74 $\pm$ 0.11	1.77 $\pm$ 0.11	7.16 $\pm$ 0.47	0.602 $\pm$ 0.005	0.371 $\pm$ 0.01	0.027 $\pm$ 0.003
0.29	0.75 $\pm$ 0.08	1.96 $\pm$ 0.11	7.6 $\pm$ 0.65	0.576 $\pm$ 0.029	0.396 $\pm$ 0.027	0.027 $\pm$ 0.004