Supporting Information

"A ^{195}Pt NMR and MD Simulation Study of the Solvation of $[PtCl_6]^{2-}$ in Water-Methanol and Water-Dimethoxyethane Binary Mixtures"

Leon Engelbrecht,[‡,§,†] Francesca Mocci,[‡,*] Aatto Laaksonen[§,‖] and Klaus R Koch[†,*]

[†]Department of Chemistry and Polymer Science, Stellenbosch University, P Bag X1, Matieland 7602, South Africa
[‡]Department of Chemical and Geological Sciences, University of Cagliari, I-09042 Monserrato, Italy
[§]Division of Physical Chemistry, Department of Materials and Environmental Chemistry, Arrhenius Laboratory, Stockholm University, 10691 Stockholm, Sweden
[‖]Department of Chemistry-Ångström Laboratory, Uppsala University, Box 538, SE-75121 Uppsala, Sweden.
Centre of Advanced Research in Bionanoconjugates and Biopolymers Dept. Petru Poni Institute of Macromolecular Chemistry Aleea Grigore Ghica-Voda, 41A, 700487 Iasi Romania

Mixed Solvent Simulation Details

Simulations of the water-1,2-dimethoxyethane (DME) and water-methanol mixtures, using the classical models used in refs. 1 and 2, were performed (following steepest-descent energy minimization) under NPT conditions, 303 K, 1 atm., with a leap frog integrator, 2 fs time step, and periodic boundary conditions (PBC). Mixed solvent starting configurations were generated by the "gmx insert-molecules" routine of GROMACS 5.0.5.[3,4] Bonds involving hydrogen atoms were constrained to specified equilibrium distances using LINCS[5] (SETTLE[6] for water) and trajectories saved every 1 ps. Other simulation settings were as recommended for use of the CHARMM force field in GROMACS (version 5.0.5), and are summarized in Table S1.[3]

Table S1. Simulation settings

Parameter	Equilibration	Production
Simulation time (ns)	2	40
Temperature coupling method	Berendsen[7]	Nosé-Hoover[8]
Temperature coupl. time constant (ps)	0.1	1.0
Pressure coupling method	Berendsen[7]	Parrinello-Rahman[9]
Pressure coupl. time constant (ps)	0.5	5.0
L-J (vdW) cut-off scheme	Force-switch	Force-switch
L-J (vdW) switching range (Å)	10-12	10-12
Electrostatics treatment	PME	PME
Short range Coulomb cut-off (Å)	12	12

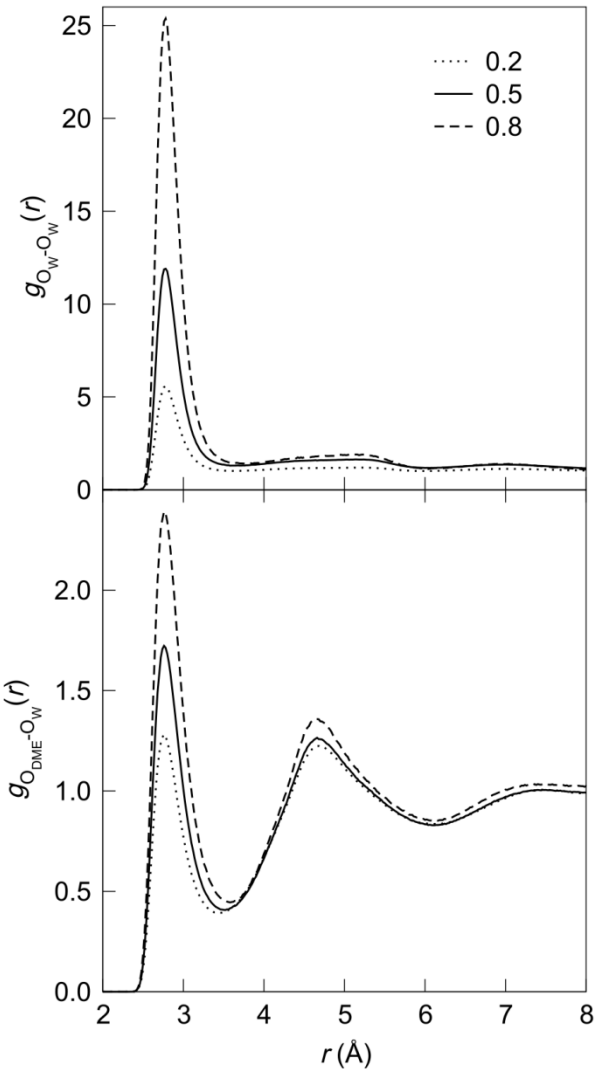

Figure S1. Radial distribution functions (RDFs), $g(r)$, from MD simulations of water-1,2-dimethoxyethane (DME) mixtures (303 K, 1 atm.), computed between water oxygen atoms (O_W, top), and between O_W and DME oxygen (O_{DME}) atom pairs (bottom), where DME mole fraction X_{DME} = 0.2, 0.5 and 0.8.

The average densities of these mixed solvent systems (Table S2) compare favourably with experimental measurements and the results of classical MD simulation performed at temperatures 298 and 318 K.[1,2,10,11] The water oxygen (O_W-O_W) and DME-water oxygen (O_{DME}-O_W) radial distribution functions (RDFs) computed from the MD trajectories are shown in Figure S1, with corresponding RDF data and coordination numbers collected in Table S2.

Table S2. Selected RDF parameters, including the position of the first maximum (r_{max}) and the integration radii (r_{int}) used in the computation of hydration numbers (N_W), for water-DME mixtures.

X_{DME}	ρ (kg/m^3)	O_W-O_W			O_{DME}-O_W		
		r_{max} (Å)	r_{int} (Å)	N_W	r_{max} (Å)	r_{int} (Å)	N_W
0.2	959	2.78	3.70	4.0	2.76	3.40	1.1
0.5	903	2.78	3.70	2.7	2.76	3.50	0.5
0.8	874	2.78	3.70	1.4	2.76	3.60	0.2

Simulated solution system details

The detailed final system compositions and sizes for $(H_3O)_2[PtCl_6]$ solutions, each containing 12 $[PtCl_6]^{2-}$ and 24 H_3O^+ ions, are summarized in Table S3. These were used to perform the 40 ns NVT production simulations, the results of which are discussed in the main manuscript.

Table S3. Simulation system compositions and sizes as pertaining to the 40 ns NVT production simulations. All systems contained, in addition to the numbers of water, W, and co-solvent, A, molecules, 12 $[PtCl_6]^{2-}$ and 24 H_3O^+ ions.

Co-solvent A	X_A	N_A	N_W	$N_{(A+W)}$	Box size (Å)*
–	0.0	0	6783	6783	58.8907
Methanol	0.2	1103	4414	5517	59.2865
Methanol	0.5	2040	2040	4080	58.7277
Methanol	0.8	2701	675	3376	59.2448
Methanol	1.0	2943	0	2943	58.9232
DME	0.2	682	2889	3571	59.0370
DME	0.5	940	940	1880	57.8544
DME	0.8	1085	279	1364	58.5949
DME	1.0	1178	0	1178	59.5451

*****Cubic simulation box side length (Å)

Simulations of $(H_3O)_2[PtCl_6]$ in water-DME mixtures using full ionic charges

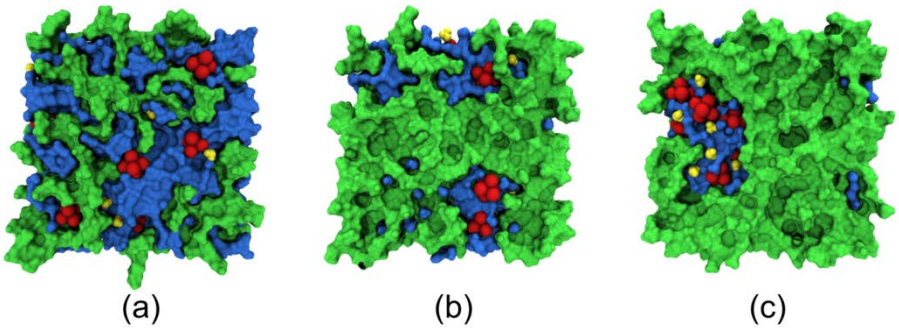

Figure S2. Representations of final configurations (15 Å-thick slices) from classical MD simulations of $(H_3O)_2[PtCl_6]$ in water-1,2-dimethoxyethane (DME) mixtures, *using original full ionic charges*:[13,14] X_{DME} = 0.2 (a), 0.5 (b), 0.8 (c). Color scheme: water, blue surfaces; DME, green surfaces; $[PtCl_6]^{2-}$, red; H_3O^+, yellow.

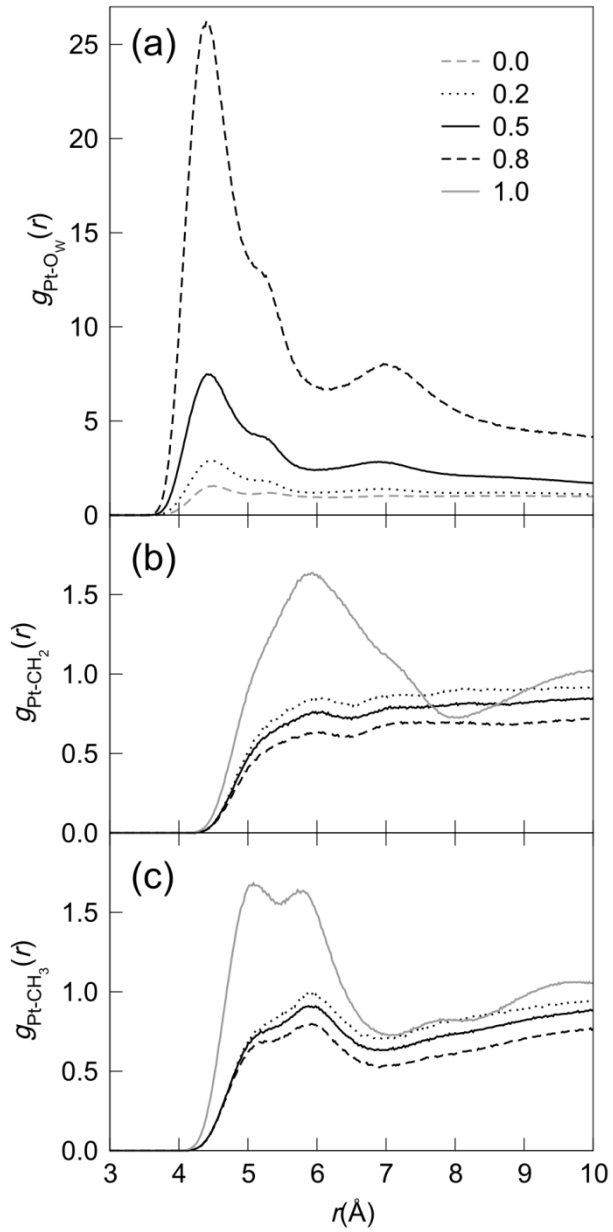

Figure S3. Radial distribution functions (RDFs), $g(r)$, from MD simulations of $(H_3O)[PtCl_6]$ (*using original full ionic charges*)[13,14] in water-DME mixtures for pairs: Pt-water oxygen (O_w) (a), DME methylene (CH_2) (b) and methyl (CH_3) (c) carbon atoms. Legend indicates the mixed solvent composition as mole fraction DME, X_{DME}.

Alternative Pt-O and Pt-C coordination numbers for $[PtCl_6]^{2-}$ in water-DME and water-methanol mixtures

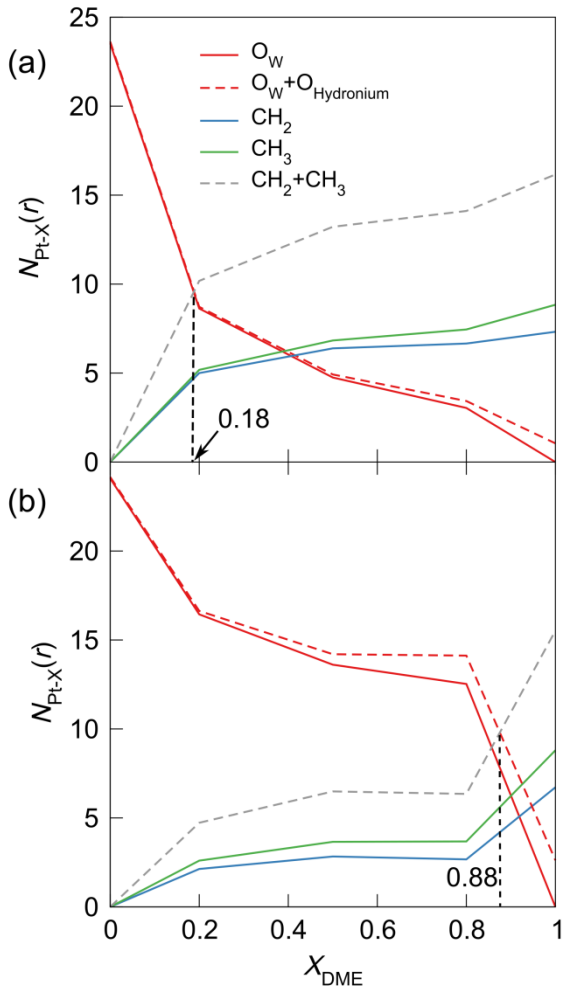

Figure S4. Pt-O_W (red), C_{DME}, methylene (CH_2, blue) and methyl (CH_3, green) coordination numbers, $N(r)$, for $[PtCl_6]^{2-}$ in water-DME mixtures (composition X_{DME}), obtained using a uniform RDF integration boundary r = 6.0 Å. Dashed red-lines indicate *total* Pt-O_w (water and H_3O^+) while dashed grey-lines the total Pt-C_{DME} coordination numbers respectively. The computed $N(r)$ values using MDEC-scaled ionic charges are shown in (a). Corresponding values from similar simulations with the original full ionic-charges are shown in panel (b). Vertical black dashed lines indicate the position of the total Pt-O_W and total Pt-C_{DME} coordination number intercepts, used for the estimation of the equi-solvation point (see main text).

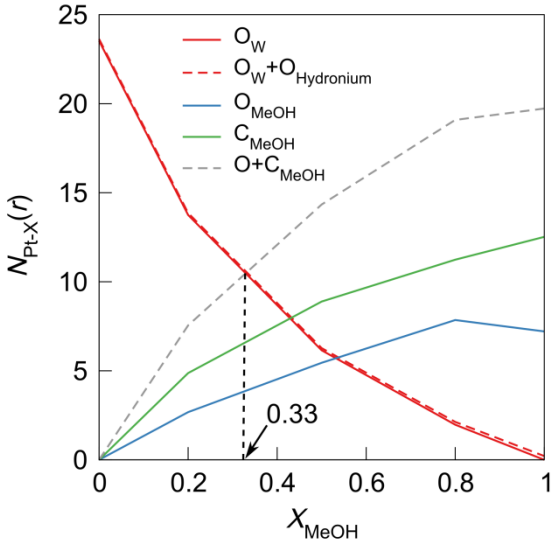

Figure S5. Pt-O_W (red), O_M (blue) and C_M (green) coordination numbers, $N(r)$, for $[PtCl_6]^{2-}$ in water-methanol mixtures (composition X_{MeOH}), obtained by integration of appropriate RDFs using a uniform integration boundary r = 6.0 Å. Dashed red and grey lines indicate respectively the *total* Pt-O_W (water and H_3O^+) and Pt-methanol (O_M + C_M) coordination numbers. The vertical black dashed line indicates the position of the total Pt-O_W and Pt-(O_M + C_M) coordination number intercept, used for the estimation of the equi-solvation point.

A preliminary evaluation of mixed solvent micro-heterogeneity

In **Figure S6** are represented the final configurations from two additional MD simulations of (a) water-methanol, and (b) water-DME mixtures. Both systems consisted of 500 water molecules and an appropriate number of co-solvent molecules, 1500 of methanol and 570 of DME, in cubic simulation cells with edge lengths 48 Å. These systems were simulated under NVT conditions, using otherwise simulation settings as described in Table S1 on p. S1 of the Supporting Information. Consequently, the volumetric contributions by water in these two systems are approximately equal.

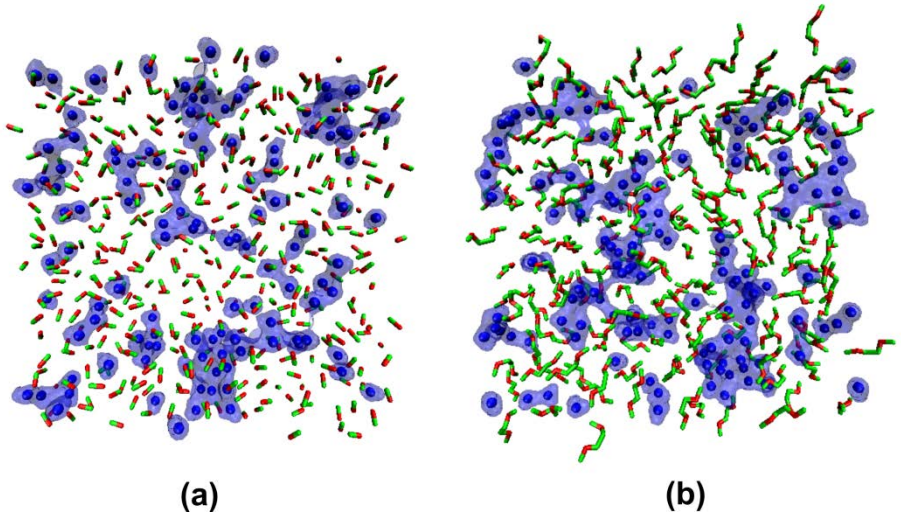

Figure S6. Representations of final configurations from MD simulations of water-methanol **(a)** and water-1,2-dimethoxyethane (DME) **(b)** mixtures, each containing 500 water molecules with 1500 methanol and 570 DME molecules respectively. All hydrogen atoms have been omitted, with water oxygen atoms shown as blue spheres, and co-solvent molecules with a "liquorice" representation, with carbon atoms coloured green and oxygen red. A transparent blue surface representation has been added for the water molecules to emphasize the water clustering found in these mixed solvent systems.

A preliminary evaluation of the inherent structural micro-heterogeneities of these two systems was performed using the MD trajectory analysis software TRAVIS' 'Domain Analysis' program.[12] This program performs radical Voronoi tessellation of each trajectory frame, assigning a unique polyhedron to each system particle, and computing the number of individual water "domains" or clusters (which may also include single, or "isolated", water molecules) based on the connectivity of these polyhedral (e.g. two water molecules are considered as belonging to the same domain/cluster when two of their constituent particles share a polyhedron face). Histograms showing the numbers of such domains, or "Domain count", occurring within the two simulated systems are plotted in **Figure S7**. The results show that on average a significantly greater number of separate water clusters (domains, as defined above) occur in the water-methanol mixture, suggesting that the water molecules are more uniformly distributed in this mixture as compared to the water-DME mixture. If one considers as criterion for the evaluation of structural micro-heterogeneity of binary solvent mixtures the extent of self-association of its components, the water-DME mixture may indeed be thought to exhibit greater micro-heterogeneity.

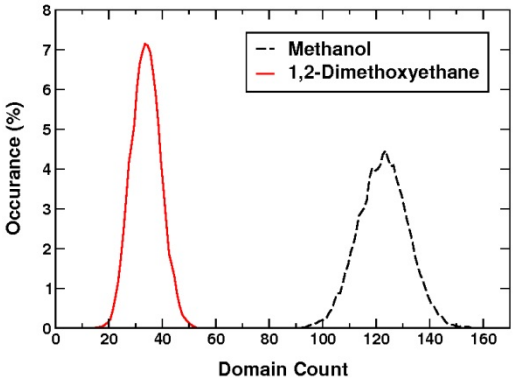

Figure S7. Histograms showing numbers of water domains, or clusters, occurring in the simulations trajectories described in the main Supporting Information text above, as determined using the software package TRAVIS' "Domain Analysis" feature.[12] The data pertaining to the water-methanol system is shown in dashed black line, while those of the water-DME system are shown in solid red line.

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