SUPPORTING INFORMATION

Assessing the Activity Coefficients of Water in Cholinium-based Ionic Liquids: Experimental Data using an Hygrometer and Modeling by COSMO-RS

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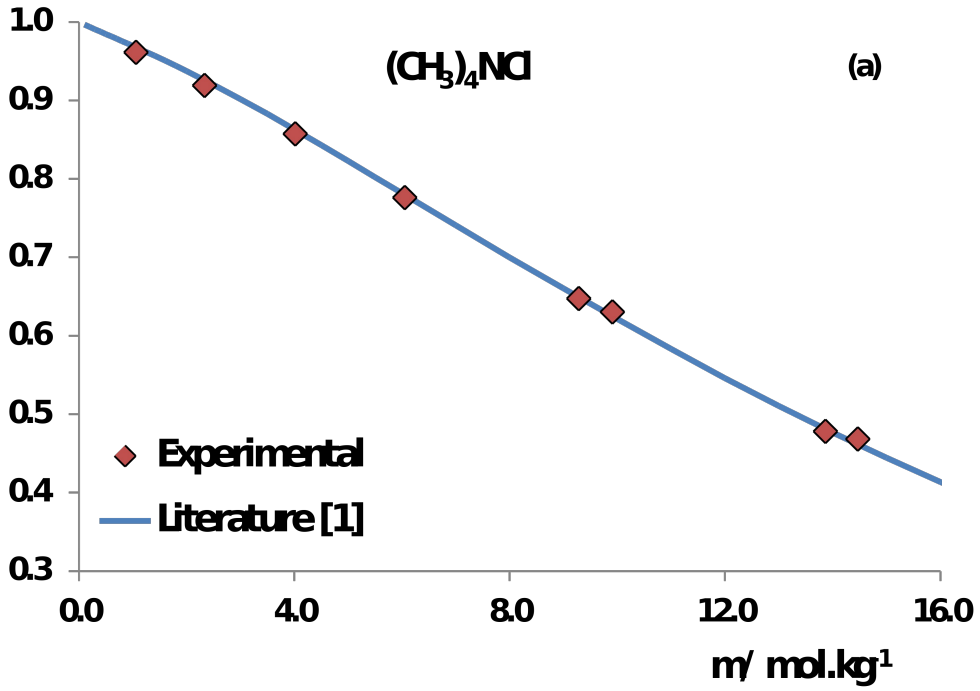
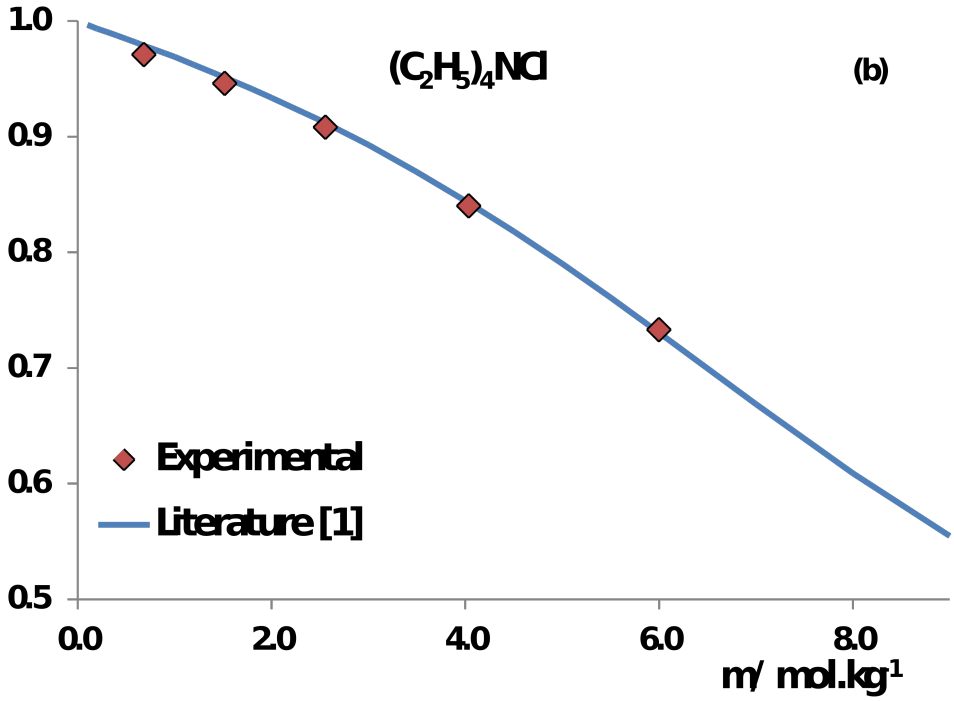

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
(CH3)4NCl
(a)
Experimental
Literature [1]
0.0
4.0
8.0
12.0
16.0
m/ mol.kg1


1.0
0.9
0.8
0.7
0.6
0.5
(C2H5)4NCl
(b)
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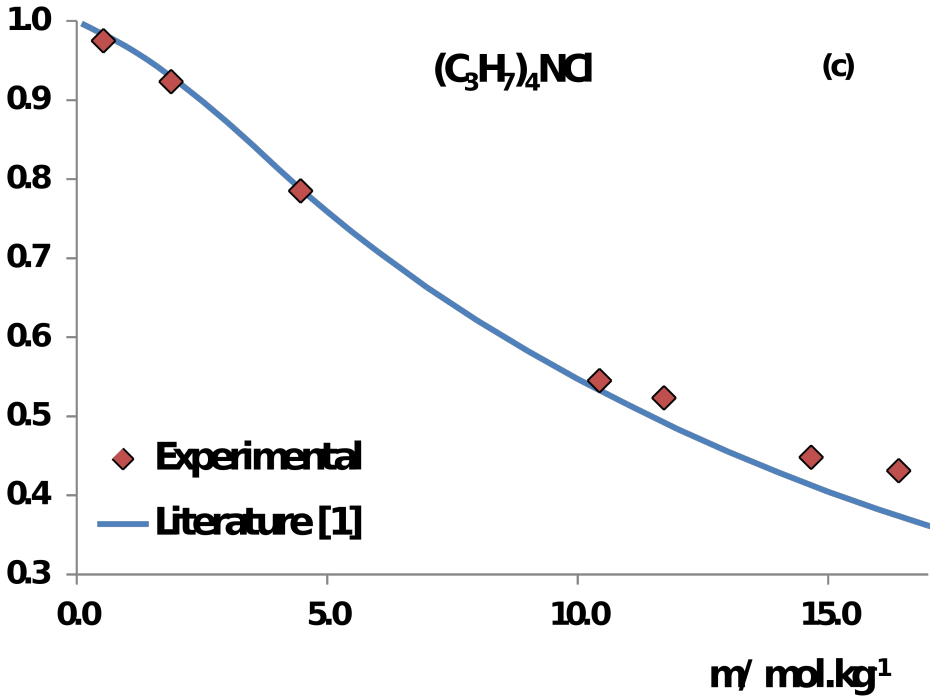
8.0
m/ mol.kg1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(c)
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0.8
0.7
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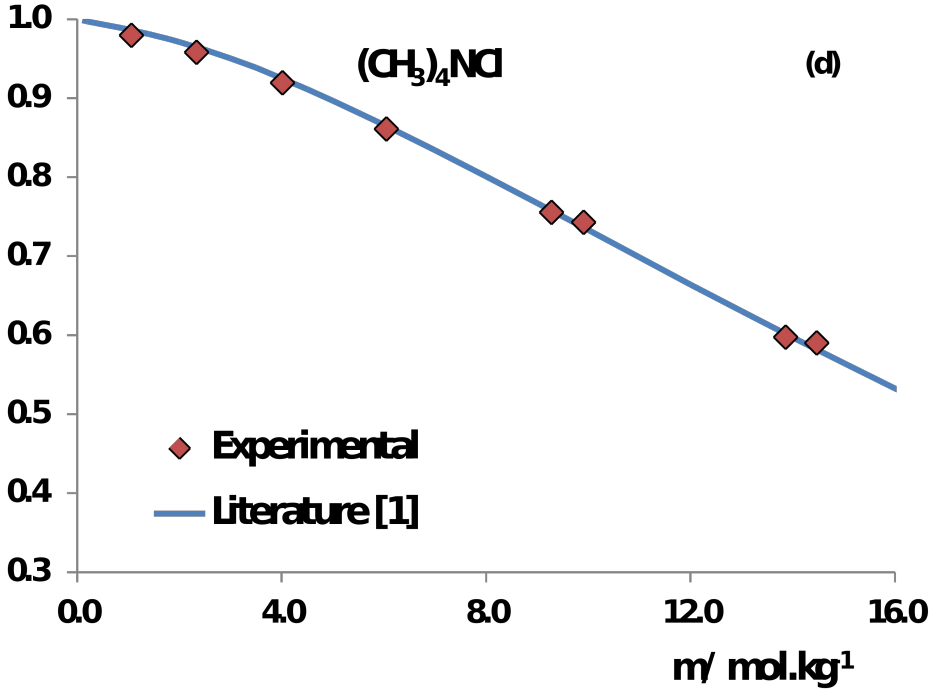
5.0
10.0
15.0
Experimental
Literature [1]
m/ mol.kg-1


(CH3)4NCl
(d)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.0
4.0
8.0
12.0
16.0
Experimental
Literature [1]
m/ mol.kg-1

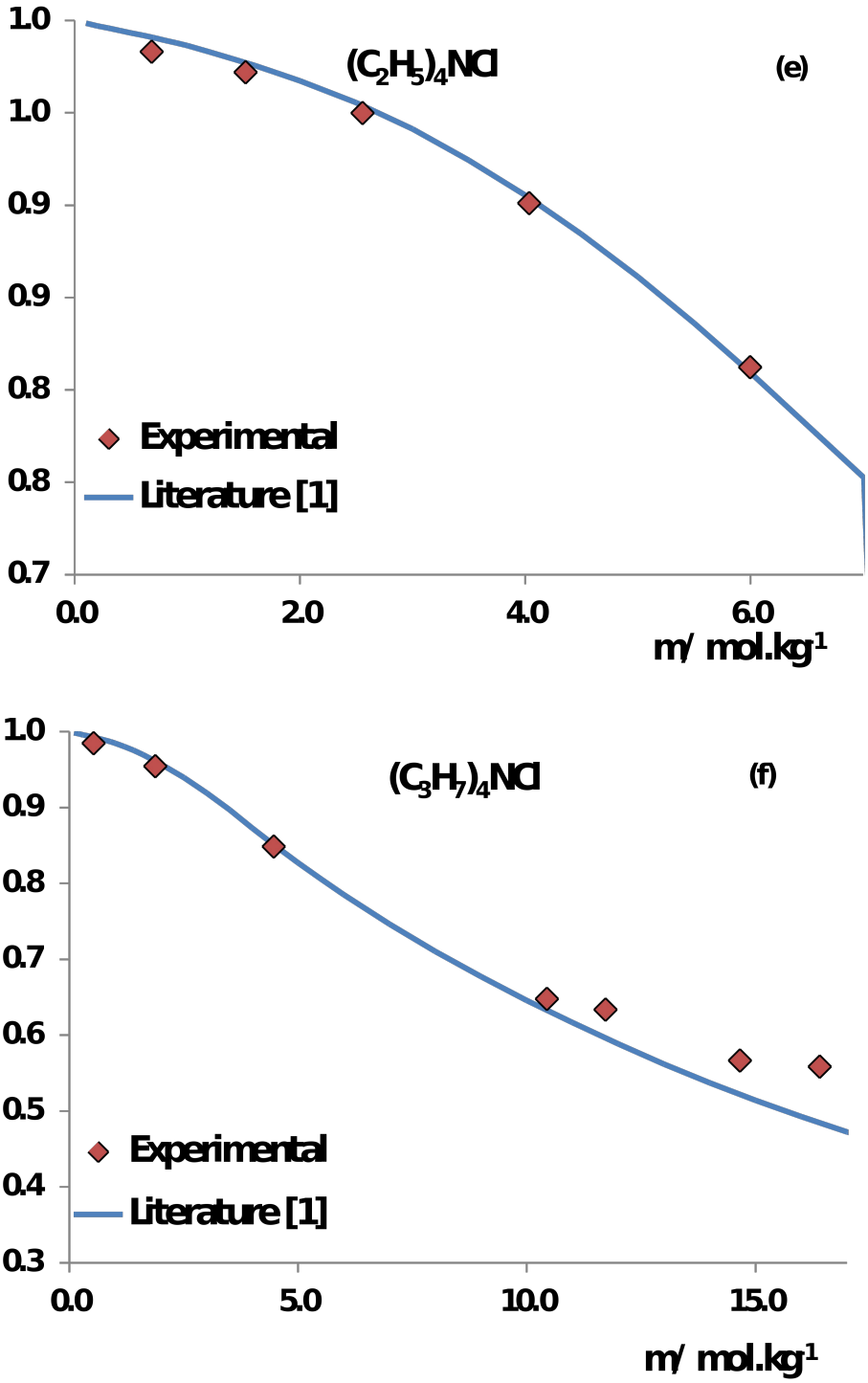
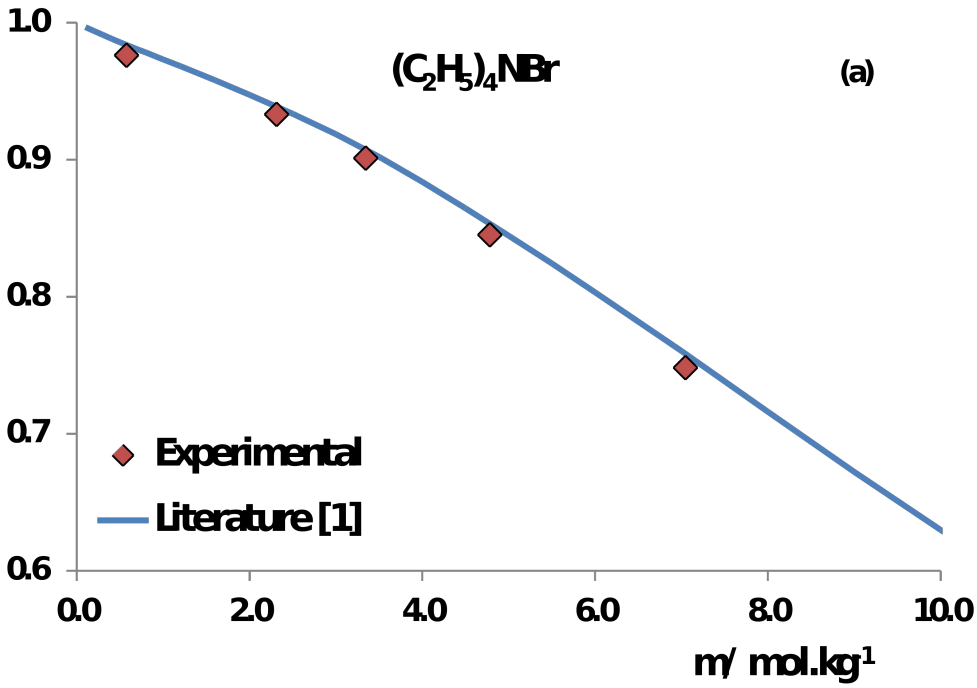
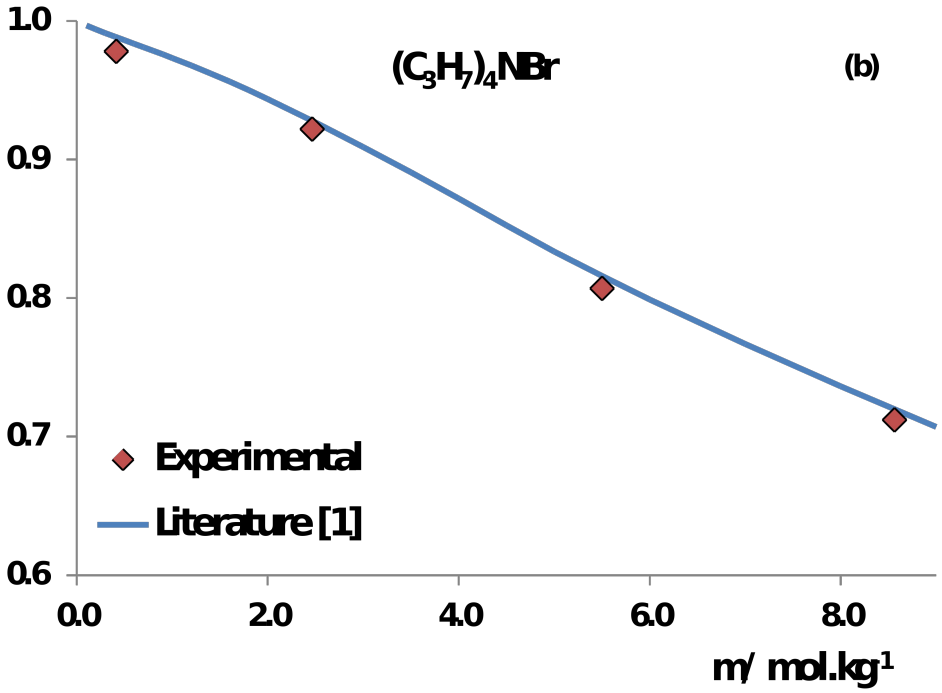


Fig. S1. Comparison of experimental water activity (a_w); (a), (b) & (c) and activity coefficient (γ); (d), (e) & (f) of some symmetrical tetraalkyl ammonium chlorides in aqueous solution at 298.2 K with reported values in literature [1]. The symbol and line represents experimental data and literature values, respectively.


1.0
0.9
0.8
0.7
0.6
(C2H5)4NBr
(a)
Experimental
Literature [1]
0.0
2.0
4.0
6.0
8.0
10.0
m/ mol.kg1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0.7
0.6
(C3H7)4NBr
(b)
Experimental
Literature [1]
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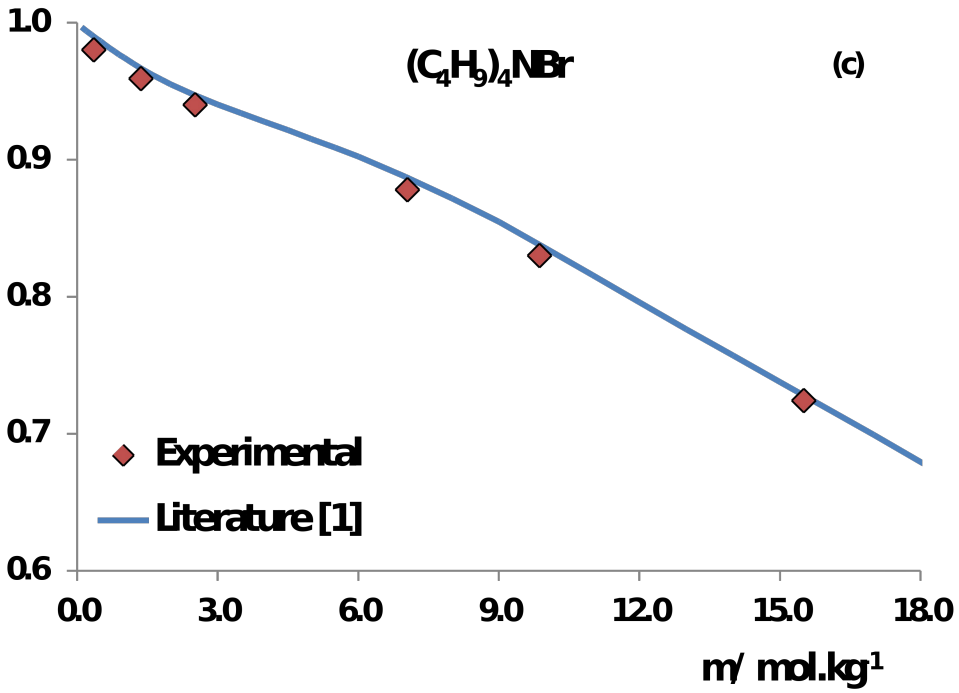
4.0
6.0
8.0
m/ mol.kg1


1.0
0.9
0.8
0.7
0.6
(C4H9)4NBr
(c)
Experimental
Literature [1]
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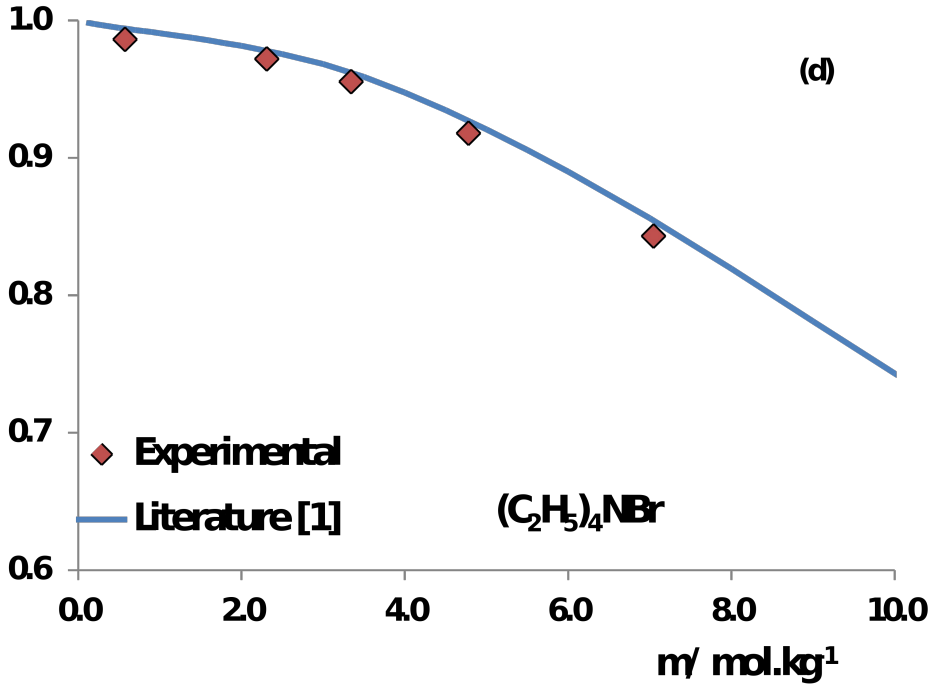
6.0
9.0
12.0
15.0
18.0
m/ mol.kg-1


1.0
0.9
0.8
0.7
0.6
(d)
Experimental
Literature [1]
(C2H5)4NBr
0.0
2.0
4.0
6.0
8.0
10.0
m/ mol.kg-1

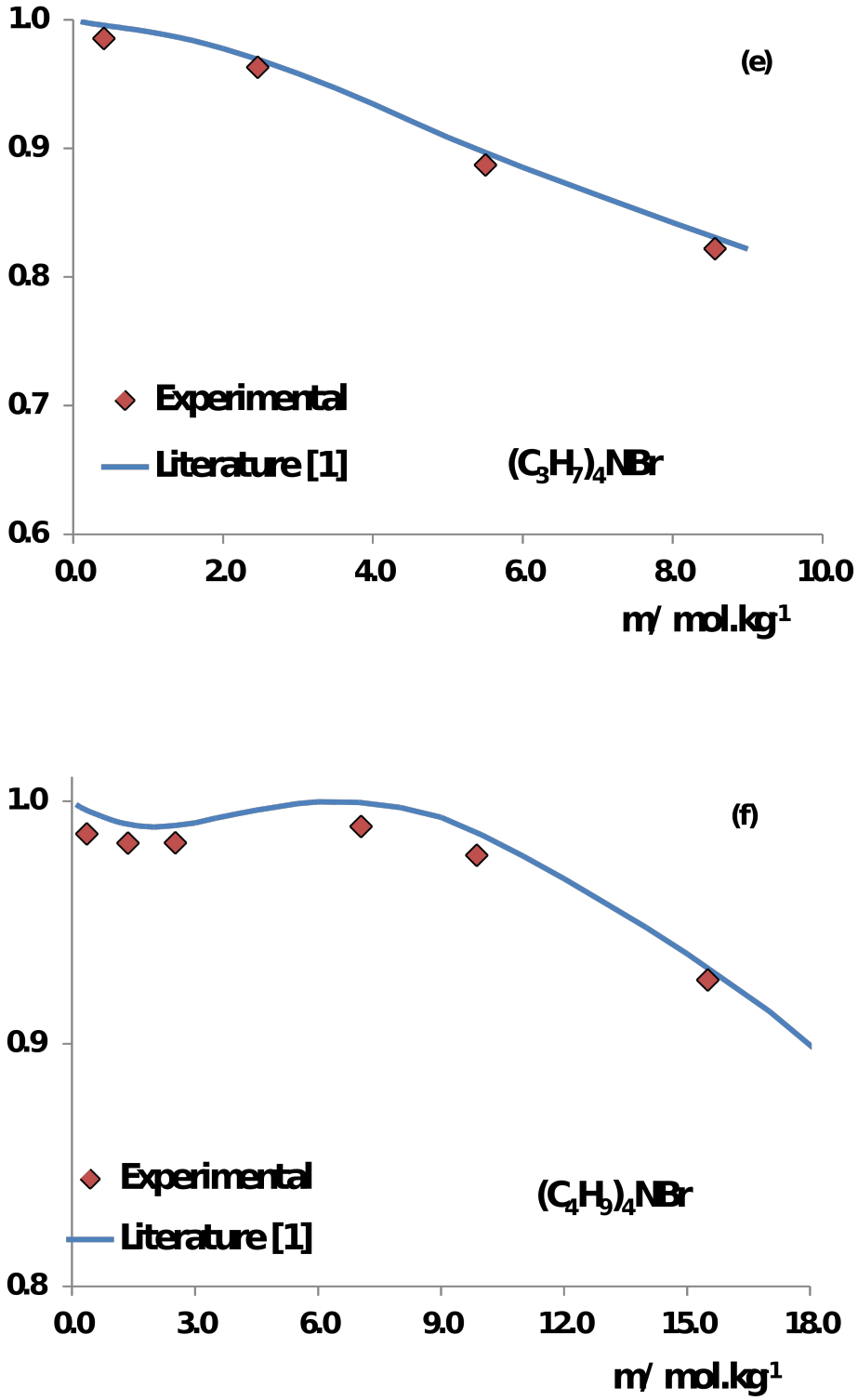


Fig. S2. Comparison of experimental water activity (a_w); (a), (b) & (c) and activity coefficient (γ); (d), (e) & (f) of some symmetrical tetraalkyl ammonium bromide in aqueous solution at 298.2 K with reported values in literature [1]. The symbol and line represents experimental data and literature values, respectively.

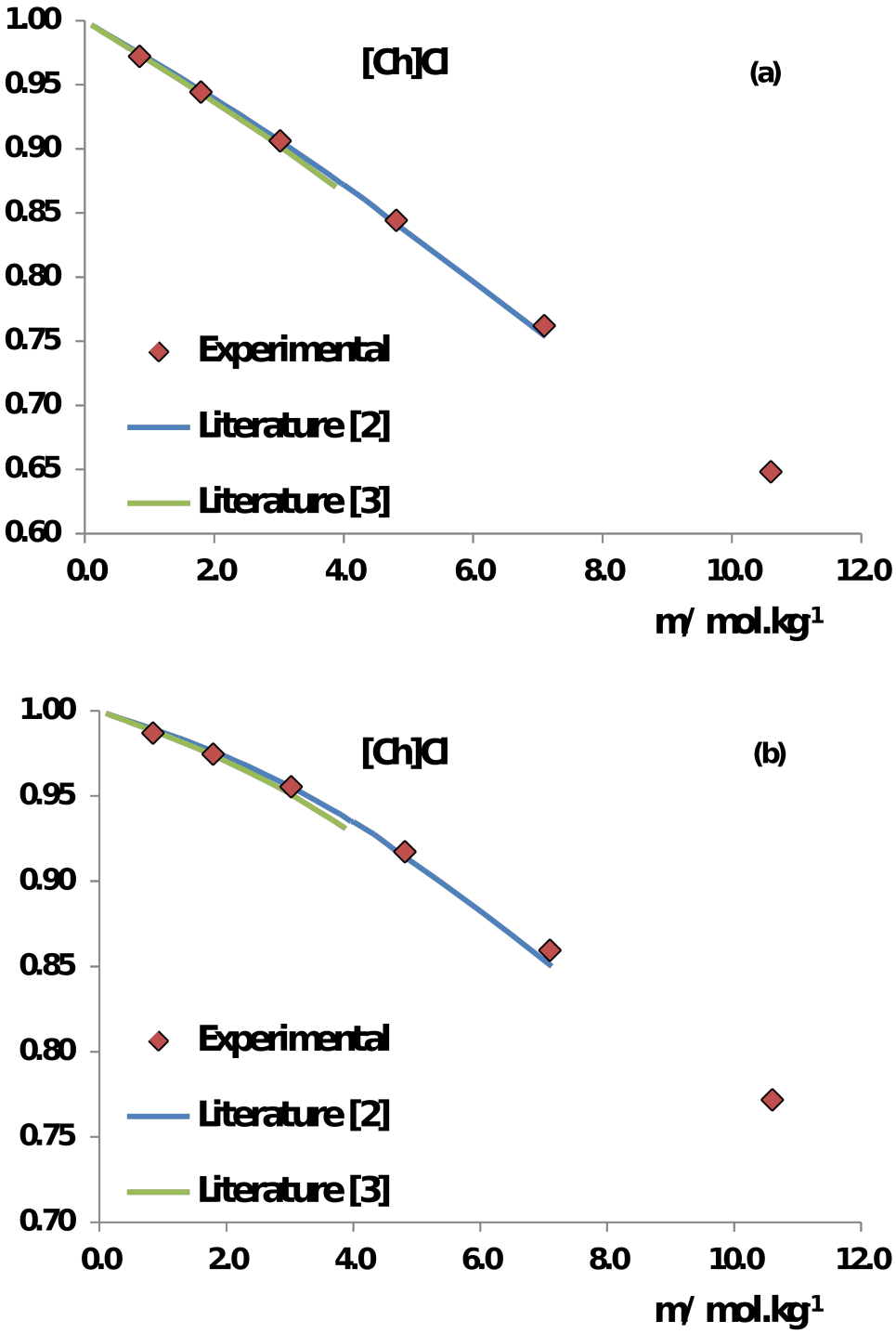


Fig. S3. Comparison between experimental water activity (a_w); (a) and activity coefficient (γ); (b) in choline chloride aqueous solution with literature values [2, 3] by isopiestic method at 298.2 K.

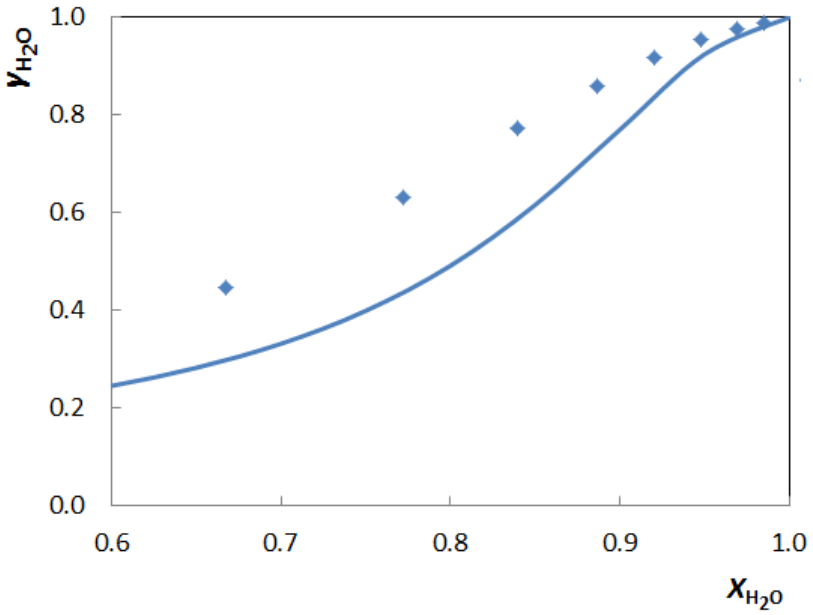


Fig. S4. Activity coefficient of water in [Ch]Cl at 298.2 K. The symbol and line represents experimental data and COSMO-RS, respectively.

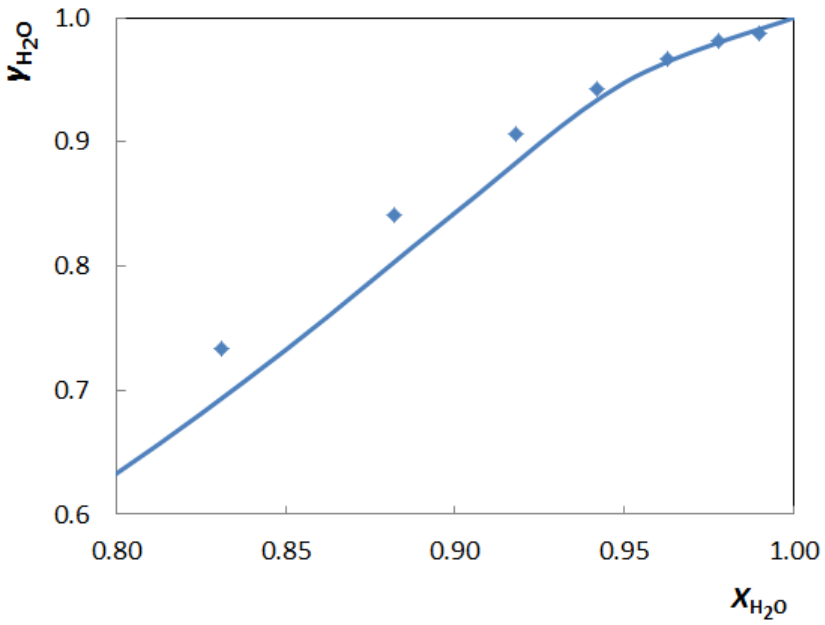


Fig. S5. Activity coefficient of water in [Ch]DHph at 298.2 K. The symbol and line represents experimental data and COSMO-RS, respectively.

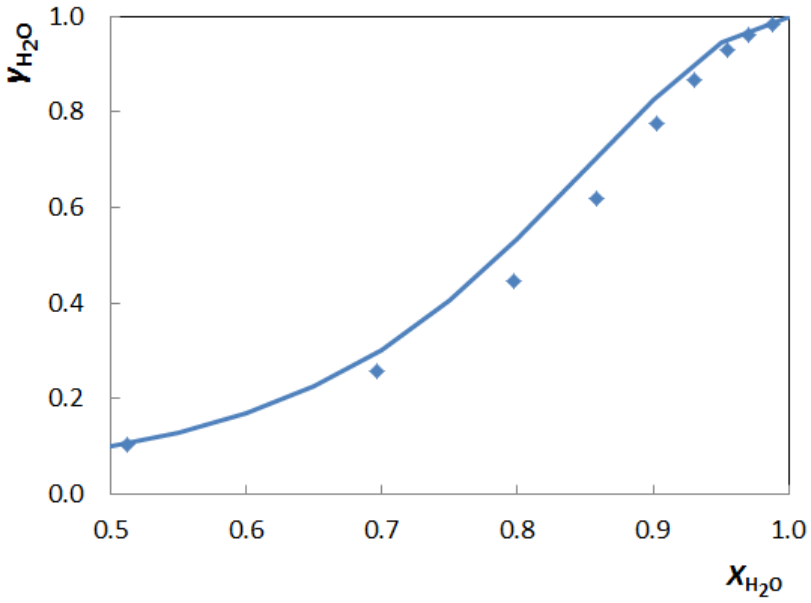


Fig. S6. Activity coefficient of water in [Ch]Ac at 298.2 K. The symbol and line represents experimental data and COSMO-RS, respectively.

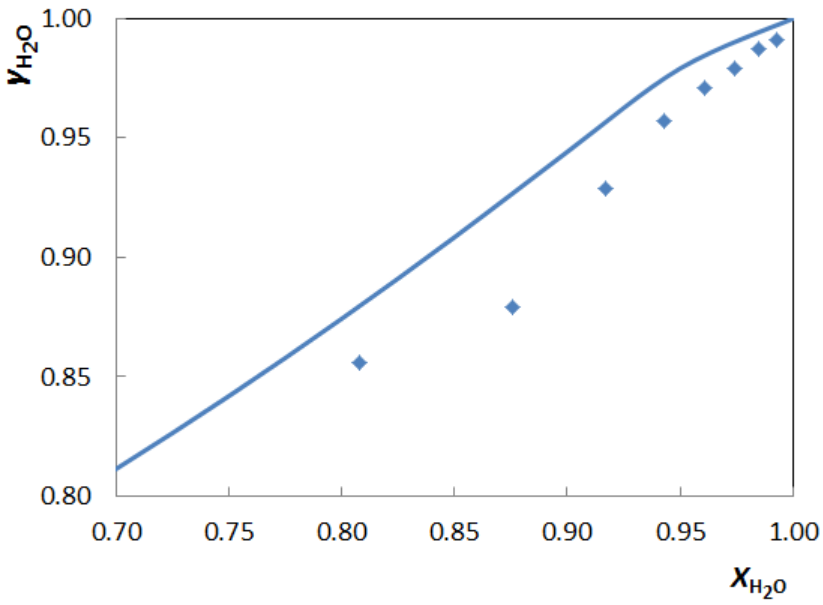


Fig. S7. Activity coefficient of water in [Ch]DHCit at 298.2 K. The symbol and line represents experimental data and COSMO-RS, respectively.

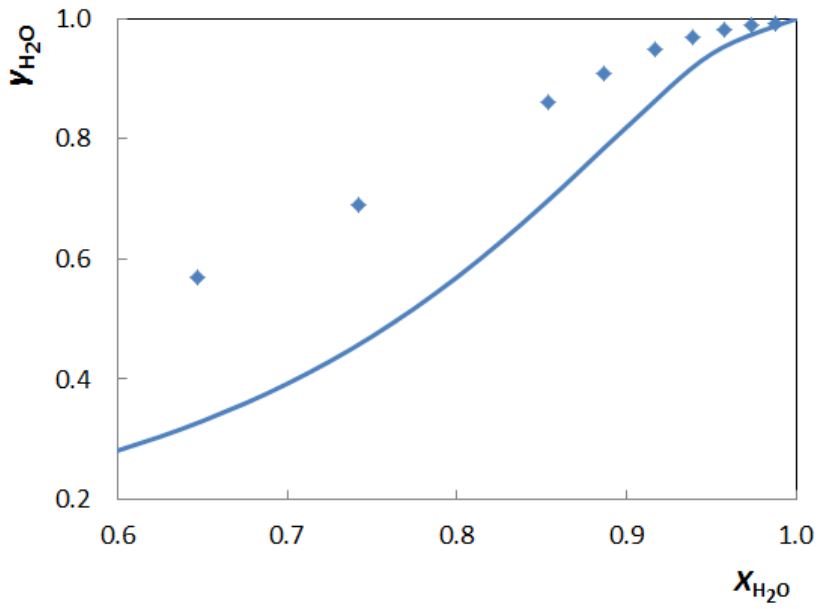


Fig. S8. Activity coefficient of water in [Ch]Bic at 298.2 K. The symbol and line represents experimental data and COSMO-RS, respectively.

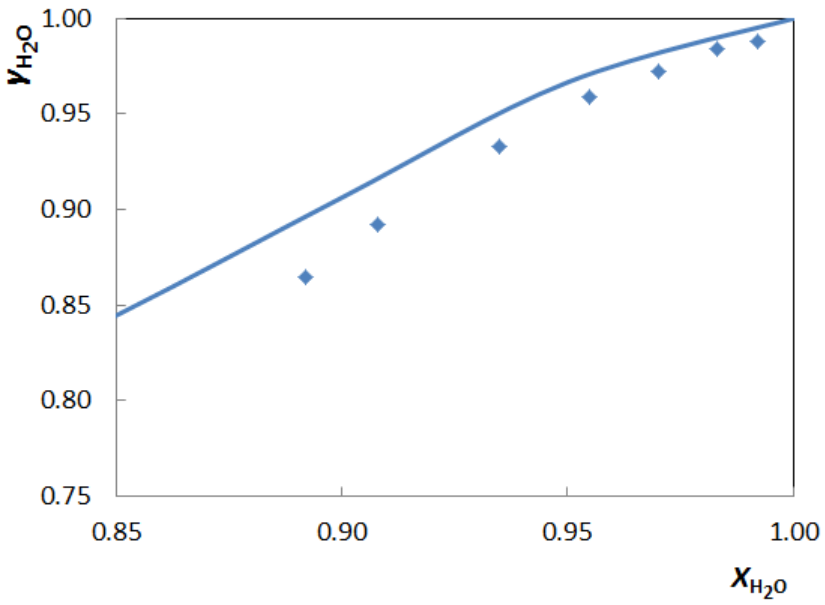


Fig. S9. Activity coefficient of water in [Ch]Bit at 298.2 K. The symbol and line represents experimental data and COSMO-RS, respectively.

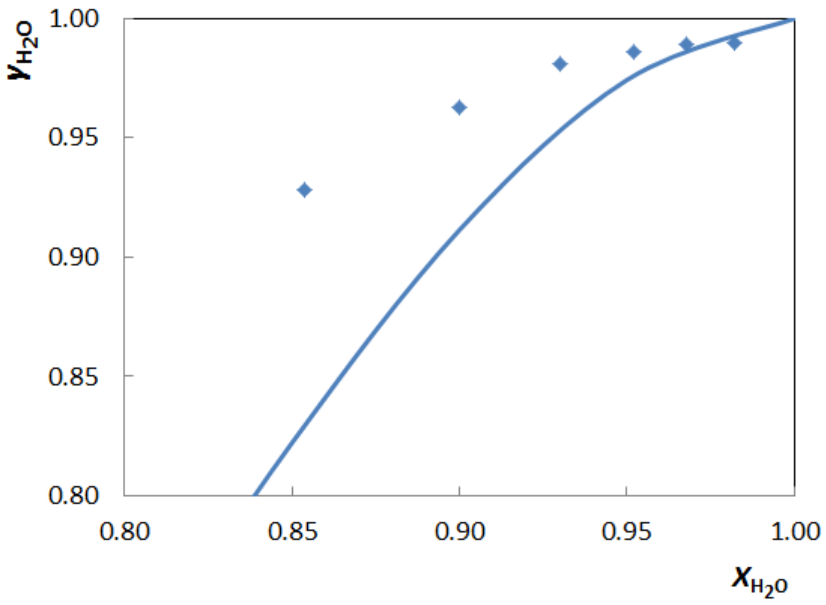


Fig. S10. Activity coefficient of water in [Ch]Sal at 298.2 K. The symbol and line represents experimental data and COSMO-RS, respectively.

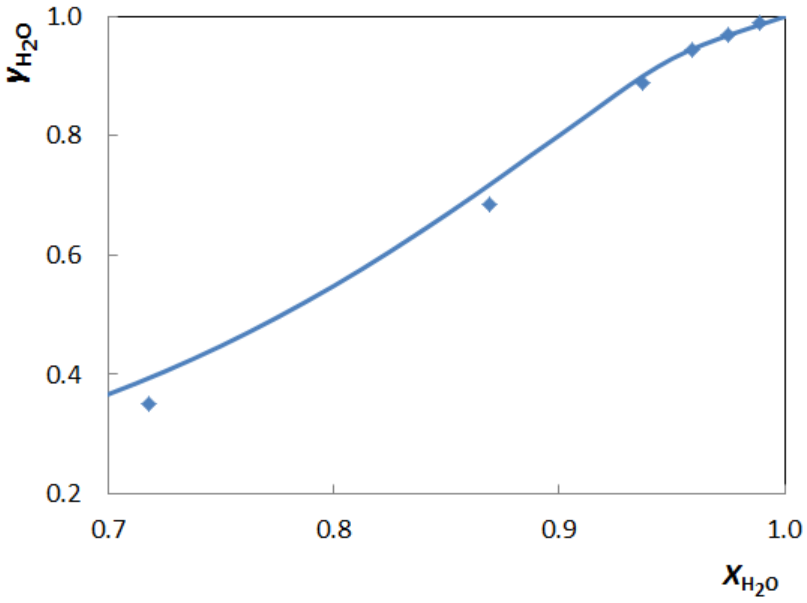


Fig. S11. Activity coefficient of water in [Ch]Gly at 298.2 K. The symbol and line represents experimental data and COSMO-RS, respectively.

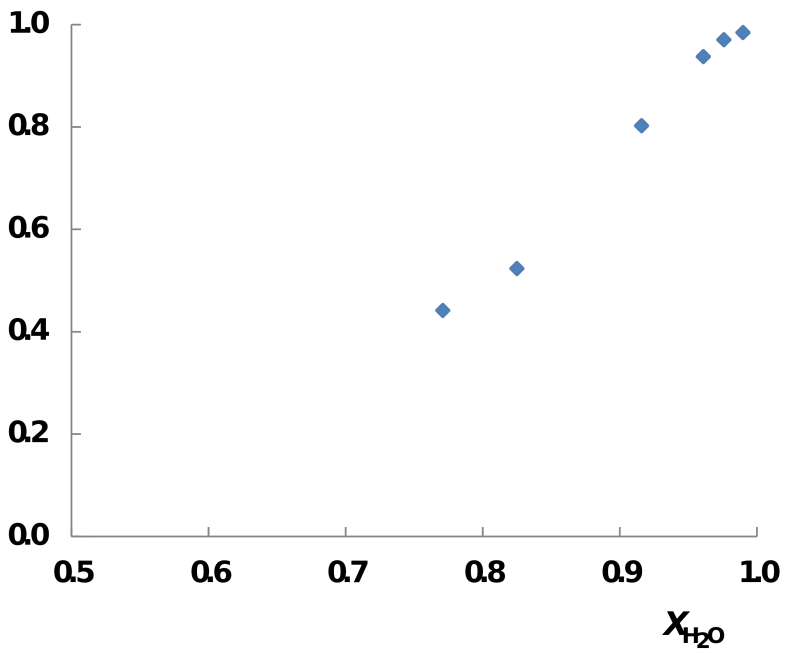


Fig. S12. Activity coefficient of water in [Ch]Lac at 298.2 K. The symbol and line represents experimental data and COSMO-RS, respectively.

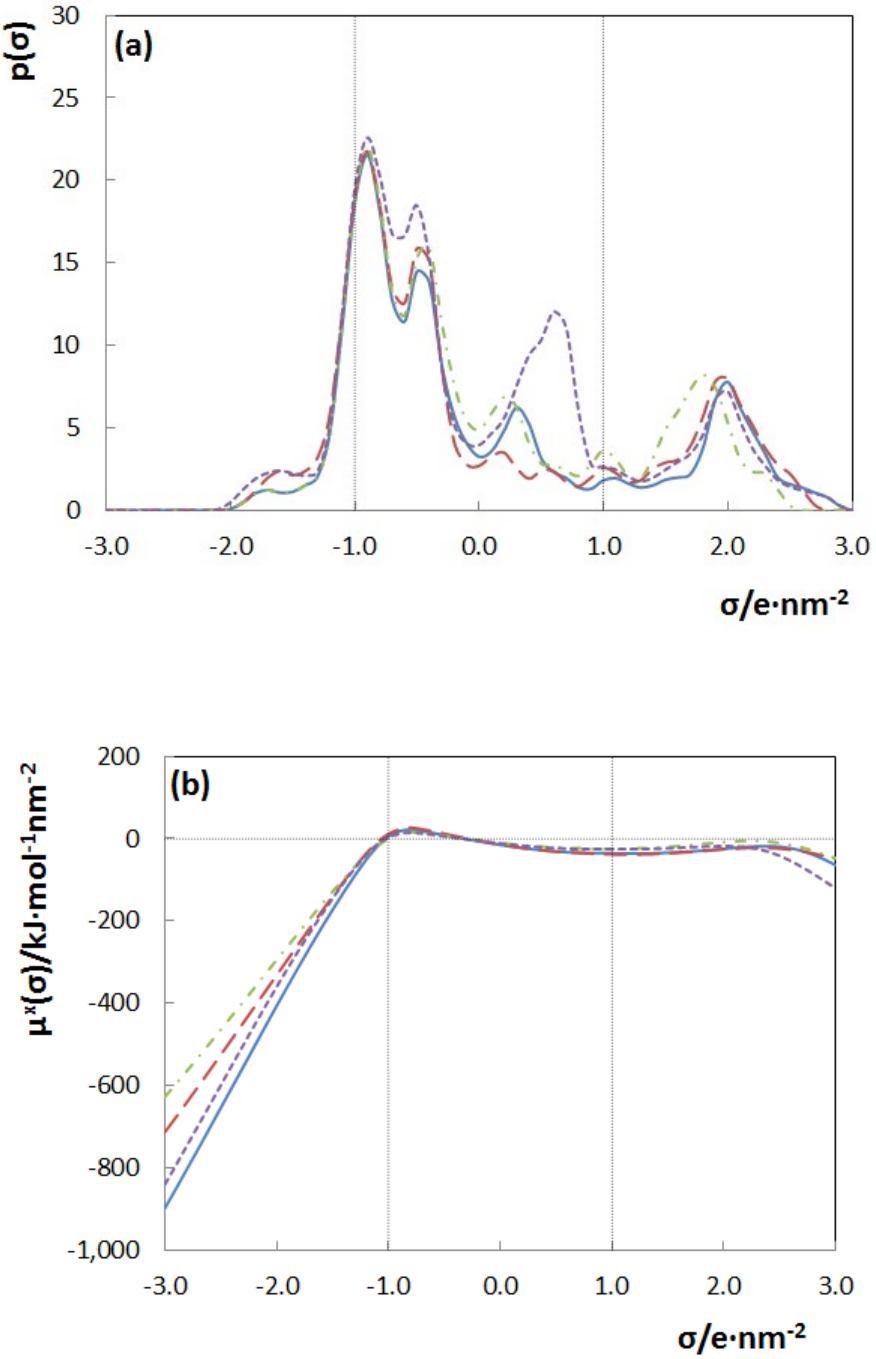


Fig. S13. Sigma profile (a) and potential (b) of [Ch]Ac (Full line), [Ch]Gly (long dashed line), [Ch]Lac (dashed-dotted line), and [Ch]Sal (dotted line).

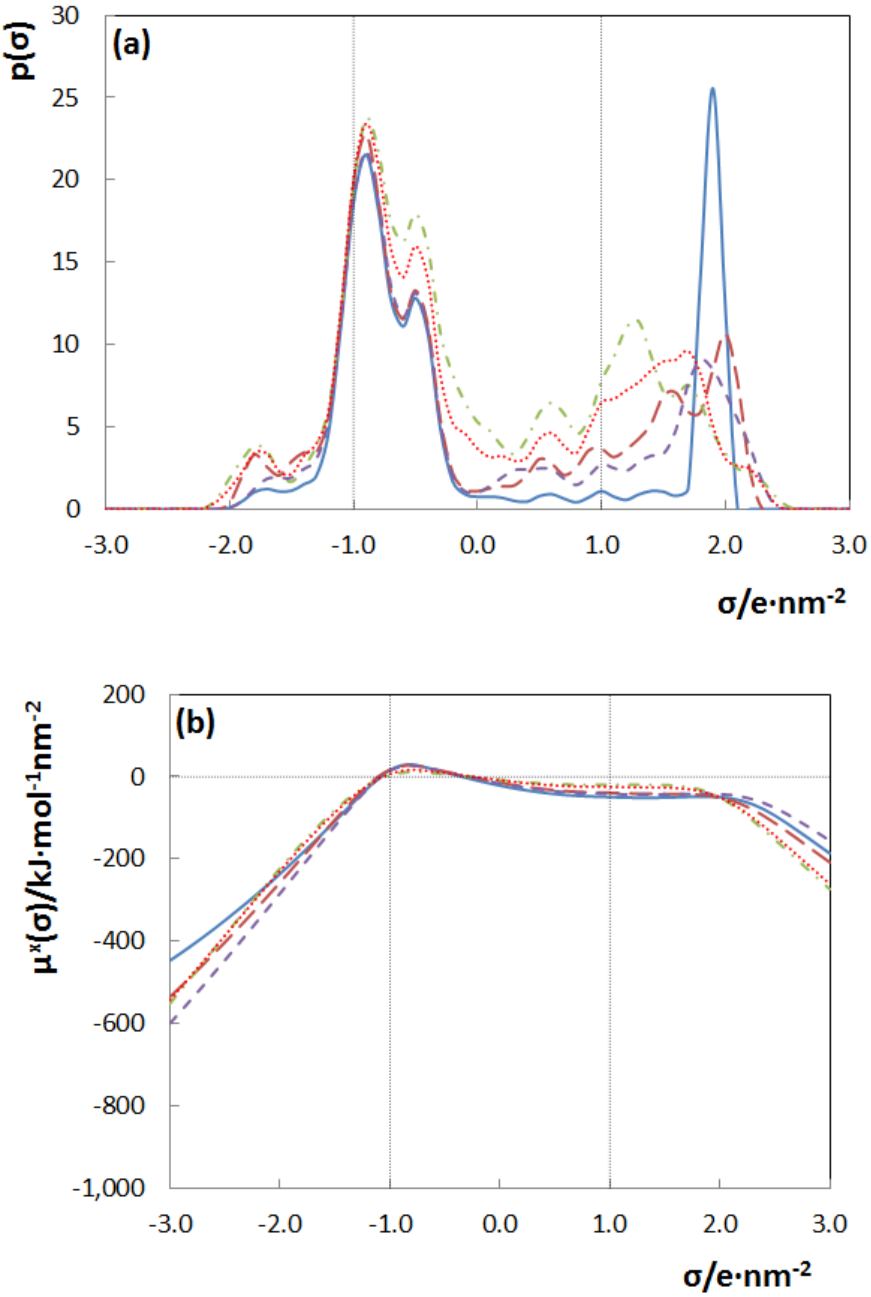


Fig. S14. Sigma profile (a) and potential (b) of [Ch]Cl (Full line), [Ch]DHph (long dashed line), [Ch]DHCit (dashed-dotted line), [Ch]Bic (short dashed line), and [Ch]Bit (dotted line).

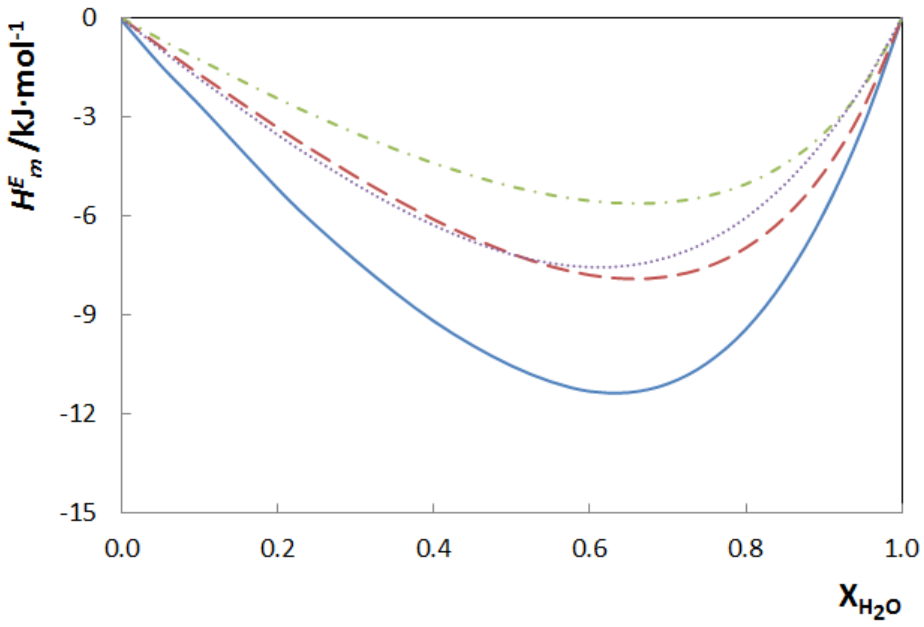


Fig. S15. Excess enthalpy of binary mixtures (H_2O + [Ch]Ac) (full line), (H_2O + [Ch]Gly) (long dashed line), (H_2O + [Ch]Lac) (dashed-dotted line), and (H_2O + [Ch]Lac) (dotted line) at 298.2 K predicted by COSMO-RS

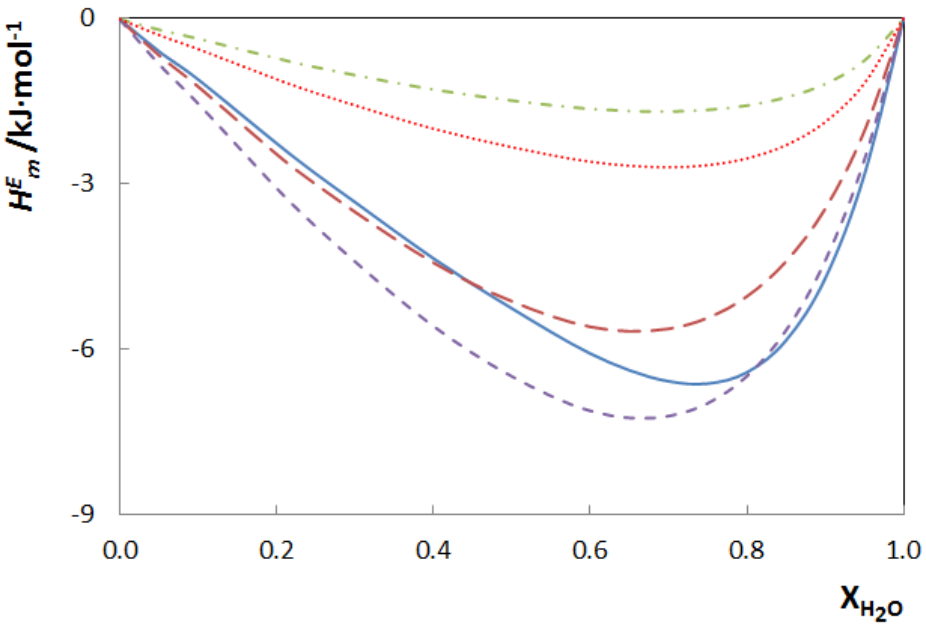


Fig. S16. Excess enthalpy of binary mixtures (H_2O + [Ch]Cl) (full line), (H_2O + [Ch]DHph) (long dashed line), (H_2O + [Ch]DHCit) (dashed-dotted line), (H_2O + [Ch]Bic) (short dashed line), and (H_2O + [Ch]Bit) (dotted line) at 298.2 K predicted by COSMO-RS

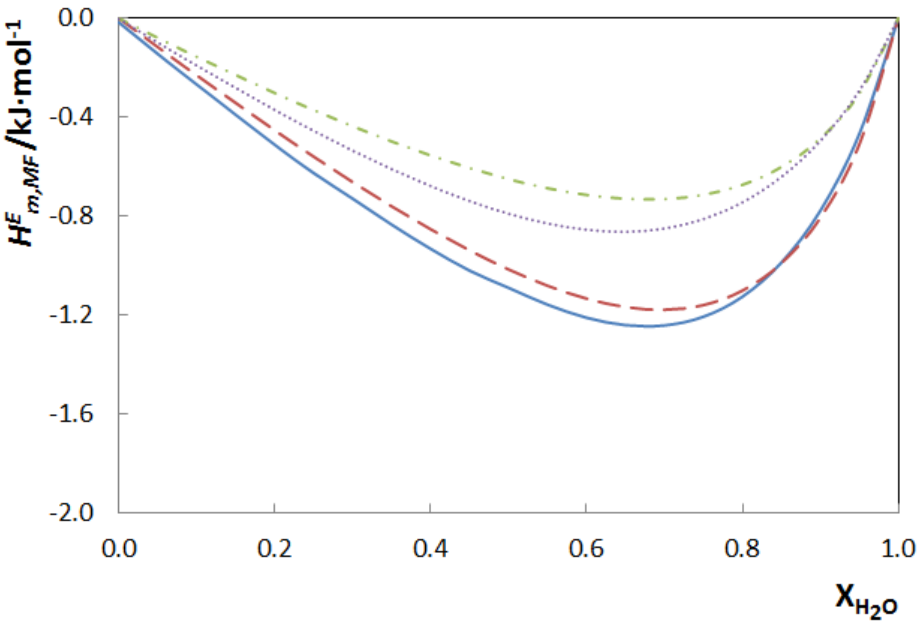


Fig. S17. Contribution of electrostatic-misfit interaction to the excess enthalpy of binary mixtures (H_2O + [Ch]Ac) (full line), (H_2O + [Ch]Gly) (long dashed line), (H_2O + [Ch]Lac) (dashed-dotted line), and (H_2O + [Ch]Lac) (dotted line) at 298.2 K predicted by COSMO-RS

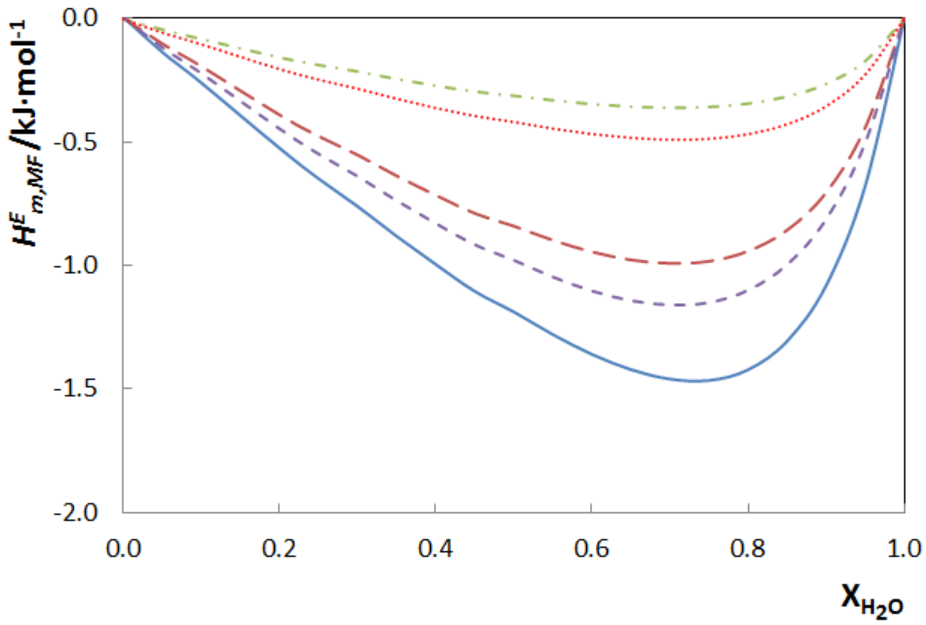


Fig. S18. Contribution of electrostatic-misfit interaction to the excess enthalpy of binary mixtures (H_2O + [Ch]Cl) (full line), (H_2O + [Ch]DHph) (long dashed line), (H_2O + [Ch]DHCit) (dashed-dotted line), (H_2O + [Ch]Bic) (short dashed line), and (H_2O + [Ch]Bit) (dotted line) at 298.2 K predicted by COSMO-RS

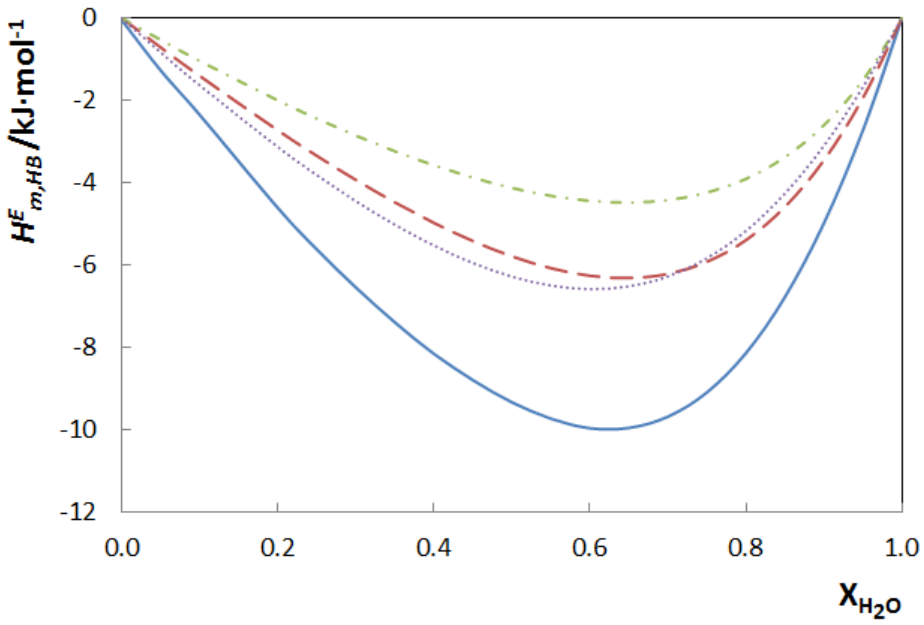


Fig. S19. Contribution of hydrogen bonds interaction to the excess enthalpy of binary mixtures (H_2O + [Ch]Ac) (full line), (H_2O + [Ch]Gly) (long dashed line), (H_2O + [Ch]Lac) (dashed-dotted line), and (H_2O + [Ch]Lac) (dotted line) at 298.2 K predicted by COSMO-RS.

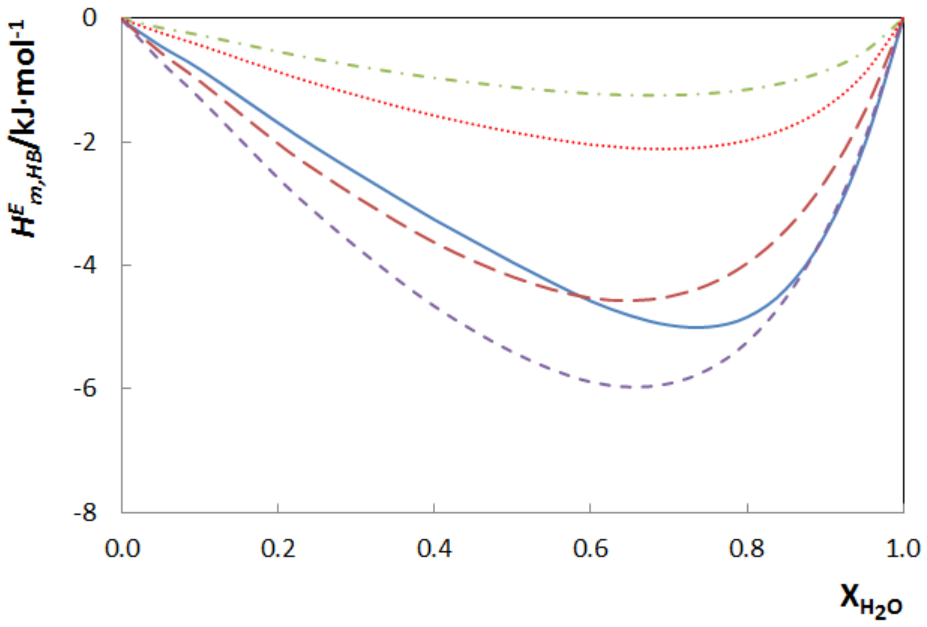


Fig. S20. Contribution of hydrogen bonds interaction to the excess enthalpy of binary mixtures (H_2O + [Ch]Cl) (full line), (H_2O + [Ch]DHph) (long dashed line), (H_2O + [Ch]DHCit) (dashed-dotted line), (H_2O + [Ch]Bic) (short dashed line), and (H_2O + [Ch]Bit) (dotted line) at 298.2 K predicted by COSMO-RS.

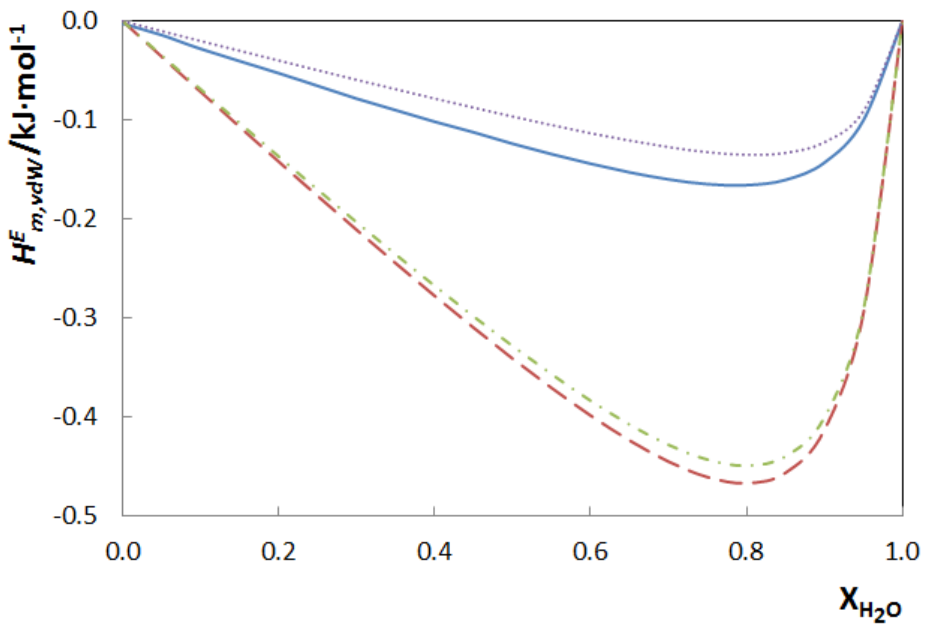


Fig. S21. Contribution of van der Waals forces to the excess enthalpy of binary mixtures (H_2O + [Ch]Ac) (full line), (H_2O + [Ch]Gly) (long dashed line), (H_2O + [Ch]Lac) (dashed-dotted line), and (H_2O + [Ch]Lac) (dotted line) at 298.2 K predicted by COSMO-RS.

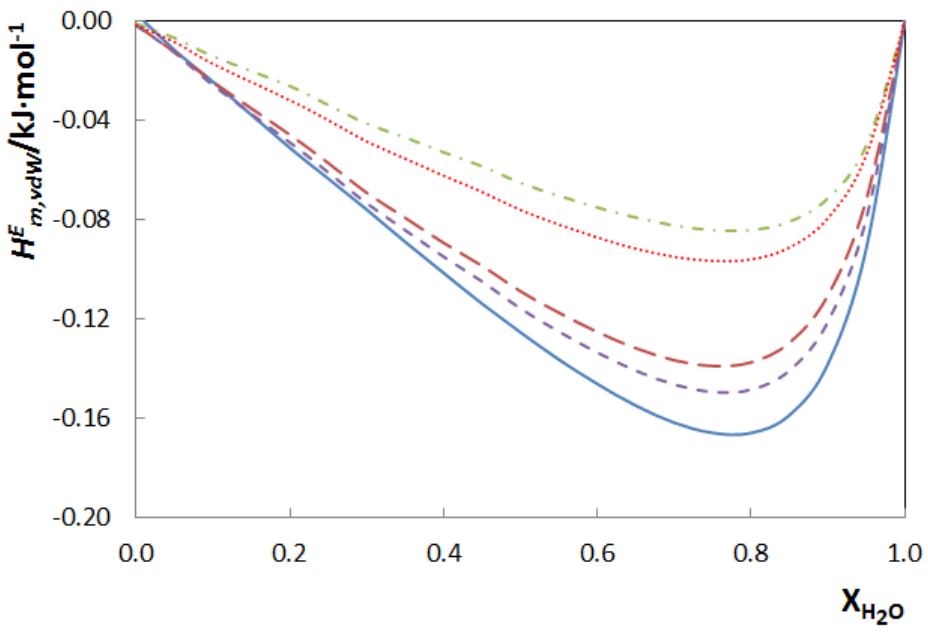


Fig. S22. Contribution of van der Waals forces to the excess enthalpy of binary mixtures (H_2O + [Ch]Cl) (full line), (H_2O + [Ch]DHph) (long dashed line), (H_2O + [Ch]DHCit) (dashed-dotted line), (H_2O + [Ch]Bic) (short dashed line), and (H_2O + [Ch]Bit) (dotted line) at 298.2 K predicted by COSMO-RS.

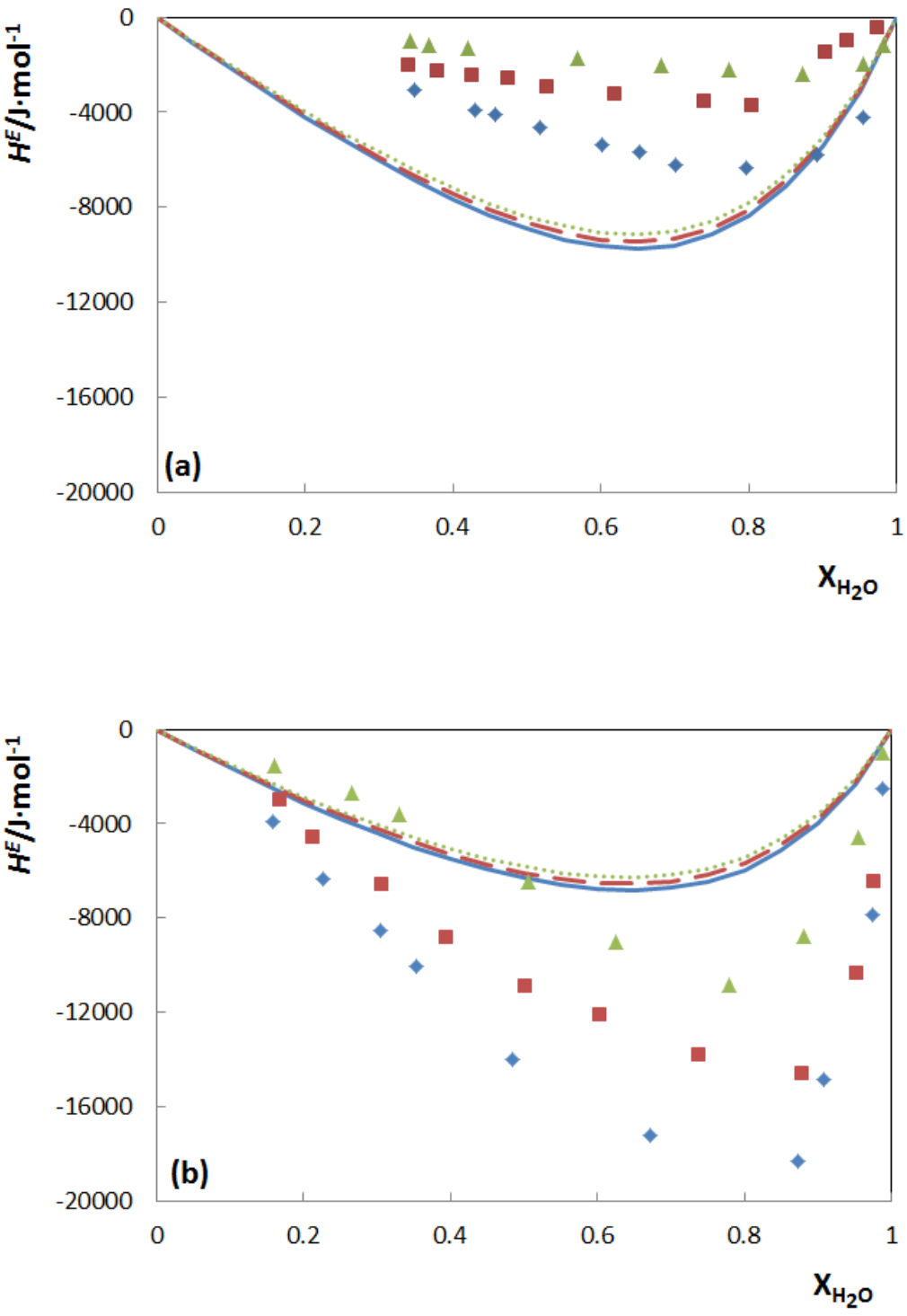


Fig. S23. Excess enthalpy of binary mixtures (a) [Ch]Gly + H_2O and (b) [Ch]Lac + H_2O at different temperatures [4]. Symbols (◊) 303 K, (□) 313 K, and (Δ) 323 K. The line represented the predicted values using COSMO-RS (Full line, dashed line, and dotted line, respectively).

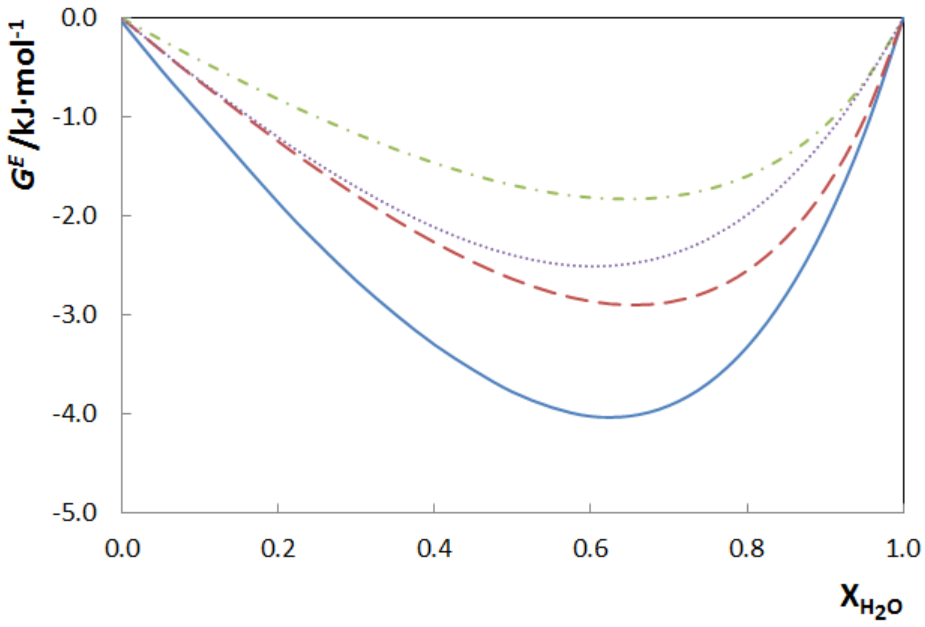


Fig. S24. Excess free Gibbs energy of binary mixtures (H_2O + [Ch]Ac) (full line), (H_2O + [Ch]Gly) (long dashed line), (H_2O + [Ch]Lac) (dashed-dotted line), and (H_2O + [Ch]Lac) (dotted line) at 298.2 K predicted by COSMO-RS.

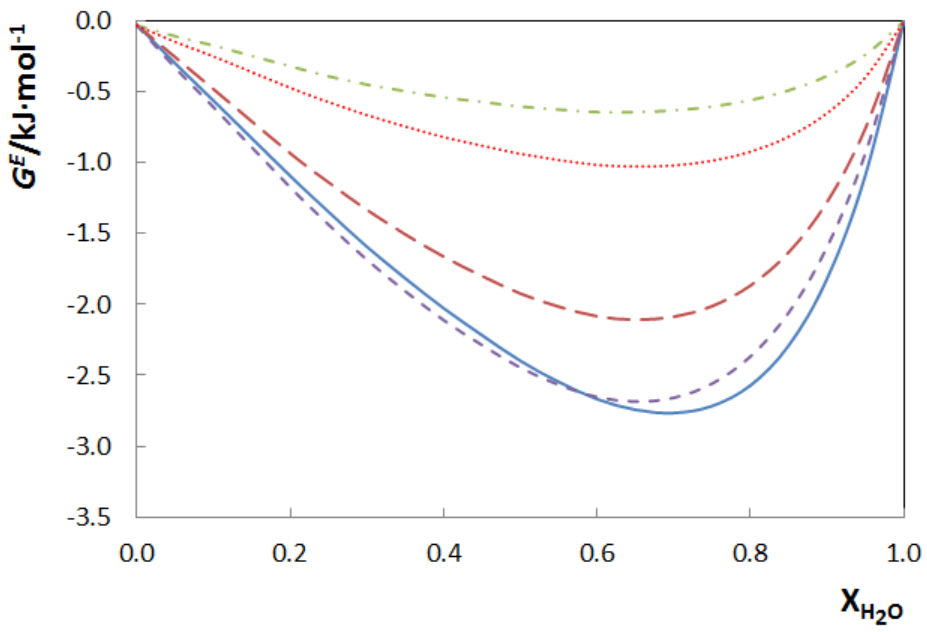


Fig. S25. Excess free Gibbs energy of binary mixtures (H_2O + [Ch]Cl) (full line), (H_2O + [Ch]DHph) (long dashed line), (H_2O + [Ch]DHCit) (dashed-dotted line), (H_2O + [Ch]Bic) (short dashed line), and (H_2O + [Ch]Bit) (dotted line) at 298.2 K predicted by COSMO-RS.

Table S1. Experiment and Predicted Activity Coefficient of Water in the Binary Mixtures of Water and Cholinium-based Ionic Liquid Along with their Average Absolute Deviation Calculated Using Equation S1

No.	x_{H2O}	γ_{EXP}	$\gamma_{COSMO-RS}$	Deviation/%
H_2O + [Ch]Cl				
1	0.985	0.987	0.992	0.5
2	0.969	0.975	0.967	0.8
3	0.948	0.955	0.918	4.0
4	0.920	0.917	0.839	9.3
5	0.887	0.859	0.743	15.5
6	0.840	0.772	0.623	23.9
7	0.772	0.632	0.491	28.8
8	0.668	0.448	0.363	23.5
AAD/%				13.3
H_2O + [Ch][Ac]				
1	0.988	0.984	0.995	1.1
2	0.970	0.961	0.975	1.4
3	0.955	0.930	0.950	2.1
4	0.931	0.867	0.900	3.7
5	0.903	0.776	0.835	7.0
6	0.858	0.618	0.721	14.2
7	0.797	0.446	0.568	21.4
8	0.697	0.257	0.365	29.7
AAD/%				10.1
H_2O + [Ch][Bic]				
No.	xw	γExp	γb	AAD-γb/%
1	0.988	0.992	0.996	0.4
2	0.974	0.988	0.981	0.7
3	0.958	0.982	0.955	2.8
4	0.939	0.970	0.916	5.9
5	0.917	0.949	0.865	9.7
6	0.887	0.908	0.793	14.5
7	0.854	0.862	0.716	20.4
8	0.742	0.690	0.507	36.2
9	0.647	0.570	0.389	46.5
AAD/%				15.2
H_2O + [Ch][Sal]				
1	0.982	0.990	0.996	0.6
2	0.968	0.989	0.991	0.2
3	0.952	0.986	0.985	0.1
4	0.930	0.981	0.977	0.5
5	0.900	0.963	0.965	0.2
6	0.854	0.928	0.944	1.6
AAD/%				0.5

H_2O + [Ch][DHph]				
1	0.990	0.988	0.997	0.9
2	0.978	0.981	0.987	0.6
3	0.963	0.967	0.966	0.1
4	0.942	0.943	0.928	1.6
5	0.918	0.906	0.878	3.2
6	0.882	0.841	0.802	4.9
7	0.831	0.733	0.702	4.5
AAD/%				2.2
H_2O + [Ch][Bit]				
1	0.992	0.988	0.999	1.1
2	0.983	0.984	0.994	1.0
3	0.970	0.972	0.984	1.2
4	0.955	0.959	0.968	1.0
5	0.935	0.933	0.945	1.3
6	0.908	0.892	0.912	2.2
7	0.892	0.865	0.893	3.1
AAD/%				1.5
H_2O + [Ch][DHCit]				
1	0.993	0.991	0.999	0.8
2	0.985	0.987	0.996	0.9
3	0.974	0.979	0.990	1.1
4	0.961	0.971	0.982	1.1
5	0.943	0.957	0.968	1.2
6	0.917	0.929	0.948	2.0
7	0.876	0.879	0.918	4.3
8	0.808	0.856	0.874	2.0
AAD/%				1.7
H_2O + [Ch][Gly]				
1	0.989	0.989	0.995	0.6
2	0.975	0.970	0.979	0.9
3	0.959	0.943	0.949	0.6
4	0.937	0.889	0.898	1.0
5	0.869	0.685	0.718	4.6
6	0.718	0.351	0.394	10.9
AAD/%				3.1
H_2O + [Ch][Lac]				
1	0.990	0.984	0.997	1.3
2	0.976	0.970	0.986	1.6
3	0.961	0.937	0.968	3.2
4	0.916	0.802	0.895	10.3
5	0.825	0.523	0.730	28.4
6	0.771	0.441	0.641	31.2
AAD/%				12.7

Table S2. The HOMO, LUMO, and HOMO-LUMO energy gap for the studied molecules and its complexes (energy is in Hartrees).

	HOMO	LUMO	HOMO-LUMO Energy Gap
H_2O	-0.2645	0.0201	0.2846
[Ch]Ac	-0.1841	-0.0058	0.1783
[Ch]Ac - H_2O	-0.1879	-0.0061	0.1818
[Ch]Ac - $2H_2O$	-0.1955	-0.0045	0.1910
[Ch]Ac - $3H_2O$	-0.1991	-0.0125	0.1866
[Ch]Bic	-0.1968	-0.0030	0.1938
[Ch]Bic - H_2O	-0.1964	-0.0081	0.1883
[Ch]Bic - $2H_2O$	-0.1971	-0.0140	0.1831
[Ch]Bic - $3H_2O$	-0.2019	-0.0171	0.1848
[Ch]Bit	-0.1685	-0.0362	0.1323
[Ch]Bit - H_2O	-0.1979	-0.0560	0.1419
[Ch]Bit - $2H_2O$	-0.1947	-0.0445	0.1502
[Ch]Bit - $3H_2O$	-0.1975	-0.0548	0.1427
[Ch]Cl	-0.2105	0.0007	0.2112
[Ch]Cl - H_2O	-0.2101	0.0024	0.2125
[Ch]Cl - $2H_2O$	-0.2143	0.0025	0.2168
[Ch]Cl - $3H_2O$	-0.2137	-0.0046	0.2091
[Ch]DHCit	-0.2064	-0.0500	0.1564
[Ch]DHCit - H_2O	-0.2097	-0.0492	0.1605
[Ch]DHCit - $2H_2O$	-0.2103	-0.0494	0.1609
[Ch]DHCit - $3H_2O$	-0.2098	-0.0515	0.1583
[Ch]DHph	-0.2186	-0.0095	0.2091
[Ch]DHph - H_2O	-0.2273	-0.0095	0.2178
[Ch]DHph - $2H_2O$	-0.2288	-0.0063	0.2225
[Ch]DHph - $3H_2O$	-0.2246	-0.0121	0.2125
[Ch]Sal	-0.2009	-0.0698	0.1311
[Ch]Sal - H_2O	-0.2026	-0.0710	0.1316
[Ch]Sal - $2H_2O$	-0.1978	-0.0658	0.1320
[Ch]Sal - $3H_2O$	-0.2018	-0.0719	0.1299
[Ch]Gly	-0.2009	-0.0013	0.1996
[Ch]Gly - H2O	-0.2040	-0.0027	0.2013
[Ch]Gly -2H2O	-0.2056	-0.0034	0.2022
[Ch]Gly -3H2O	-0.2048	-0.0030	0.2018
[Ch]Lac	-0.1983	-0.0077	0.1906
[Ch]Lac - H2O	-0.1899	-0.0094	0.1805
[Ch]Lac-2H2O	-0.1952	-0.0159	0.1793
[Ch]Lac -3H2O	-0.1952	-0.0158	0.1794

The average absolute deviation (AAD) was calculated using the following equation,

$$AAD/ = \frac{1}{N} \sum \frac{\left|\gamma_{\exp} - \gamma_{COSMO}\right|}{\gamma_{COSMO}} \times 100 \qquad \text{Equation S1}$$

where, N is the number of data, γ_{EXP} is the reported experimental data, γ_{COSMO} is the predicted value using COSMO-RS.

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