Supporting information for: An Investigation of Ion-Pairing of Alkali Metal Halides in Aqueous Solutions Using the Electrical Conductivity and the Monte Carlo Computer Simulation Methods

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Model

The Mercedes-Benz + dipole water model[5] (MB+dipole) was used to describe the water in the electrolyte solution. In this model, the water molecule is represented as a two-dimensional Lennard-Jones disk with three equally separated hydrogen bonding arms, and interacts with another water molecule through the potential (see Figure S1):

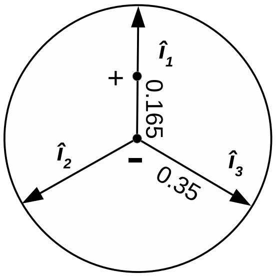

Figure S1: A MB + dipole water molecule has three hydrogen bonding arms, which are denoted as vectors: $\hat{\boldsymbol{\imath}}_k$ (k=1, 2, 3). There is a single negative charge placed in the centre of the molecule and a single positive charge on one of the hydrogen bonding arms $0.165 r_{HB}$ away from the centre.

$$U_{vv}(\boldsymbol{X_i}, \boldsymbol{X_j}) = U_{LJ}(r_{ij}) + U_{HB}(\boldsymbol{X_i}, \boldsymbol{X_j}) \tag{1}$$

$\boldsymbol{X_i}$ denotes the vector with coordinates and orientation of i'th particle, and r_{ij} is the distance between centres of molecules i and j. Lennard-Jones 12-6 potential is:

$$U_{LJ}(r_{ij}) = 4\epsilon_{LJ}\left[\left(\frac{\sigma_{LJ}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{LJ}}{r_{ij}}\right)^{6}\right], \tag{2}$$

where ϵ_{LJ} represents the depth of the potential well, and σ_{LJ} is Lennard-Jones diameter.

The hydrogen bond strength is a Gaussian function of the intermolecular distance and the angle between two hydrogen bonding arms:

$$U_{HB}(\boldsymbol{X_i}, \boldsymbol{X_j}) = \epsilon_{HB} G(r_{ij} - r_{HB}) \sum_{k,l=1}^{3} G(\hat{\boldsymbol{\imath}}_k \cdot \hat{\boldsymbol{u}}_{ij} - 1) G(\hat{\boldsymbol{\jmath}}_l \cdot \hat{\boldsymbol{u}}_{ij} + 1) \tag{3}$$

$G(x)$ is unnormalized Gaussian function:

$$G(x) = \exp(-x^2/2\sigma^2) \tag{4}$$

Unit vector $\hat{\boldsymbol{i}}_k$ represents k'th arm of i'th molecule (k=1, 2, 3). $\hat{\boldsymbol{u}}_{ij}$, which is also a unit vector is the direction vector of the line joining centres of i'th and j'th molecule. Parameters $\epsilon_{HB} = -1$ and $r_{HB} = 1$ determine the energy and the length of the optimal hydrogen bond. Value for model parameters are following: $\sigma_{LJ} = 0.7 \cdot r_{HB} = 0.7$, $\epsilon_{LJ} = 0.1\,|\epsilon_{HB}| = 0.1$, and $\sigma = 0.085$.

In addition, to describe the water-ion interaction, each water molecule has a dipole which is formed from a single negative charge in the center of a water molecule, and a single positive charge on one of hydrogen bonding arms ($0,185 r_{HB}$ away from the edge) [5].

An ion interacts with the water molecule through the potential:

$$U_{iv}(\boldsymbol{X_i}, \boldsymbol{X_j}) = U_{LJ}(r_{ij}) + \sum_{+,-} U_{SC}(\boldsymbol{X_i}, \boldsymbol{X_j}) \tag{5}$$

where U_{LJ} is a Lennard-Jones potential (equation 2), and:

$$U_{SC} = z_i z_j\,|\epsilon_{HB}|\,\alpha \frac{\exp(-\kappa r_{ij})}{r_{ij}}, \tag{6}$$

Here the sum is taken over both charges on the water molecule. r_{ij} denotes distance between ion and charge on the water molecule in units of r_{HB}, z is valence, and κ is screening constant, which value is 0.1. Parameter α for interaction between water molecule and ion equals 2.27.

Contact parameter σ_{iw} is for each ion determined as the arithmetic mean of σ_i and σ_{LJ}. Index i refers to an ion and index LJ to the water molecule. Lennard-Jones radii for ions studied are in Table S1. The depth of the potential well is the same as for the water-water interaction, that is ϵ_{LJ}.

Table S1: Lennard-Jones contact parameters[5] (σ_i), radii of first hydration shells (r_h), valences (z_i), number of water molecules in first hydration shell (n_{waters}), and number of hydrogen bonds between water molecules in the first hydration shell ($n_{\text{H-bonds}}$) of investigated ions. Distances are given in reduced units.

ion	σ_i	r_h	z_i	n_{waters}	$n_{\text{H-bonds}}$
Li^+	0.24	0.86	1	3.27 ± 0.01	0.93 ± 0.01
Na^+	0.37	0.92	1	3.48 ± 0.01	1.13 ± 0.01
K^+	0.52	1.01	1	3.85 ± 0.01	1.55 ± 0.01
Rb^+	0.58	1.08	1	4.23 ± 0.01	1.83 ± 0.01
Cs^+	0.66	1.15	1	4.63 ± 0.01	2.16 ± 0.01
Cl^-	0.71	1.12	-1	4.34 ± 0.01	0.84 ± 0.01
I^-	0.85	1.23	-1	4.80 ± 0.01	1.26 ± 0.02

In the contrast with previous studies using the MB + dipole model, where only a single ion was present in the system [5, 6, 7], a pair of positive and negative ion was considered here. Cation-anion interaction was taken to be of the same form as ion-dipole interaction (equation 5):

$$U_{ii}(r_{ij}) = U_{LJ}(r_{ij}) + U_{SC}(r_{ij}) \tag{7}$$

The contact parameter is the arithmetic mean of contact parameters for interacting ions and well depth is the same as in aforementioned cases. The parameter α in the equation for the screened

Table S2: Parameters α for studied salts.

Ion pair	α
LiCl	1.65
NaCl	1.74
KCl	1.90
RbCl	1.97
CsCl	2.14
NaI	1.73
KI	2.30
CsI	2.60

Coulomb potential (equation 6), which determines the strength of the electrostatic interaction between two ion, was set in such a way that the tendency for salt association would be in qualitative agreement with the results of more refined water models. [2, 1] The parameters α used in this study are collected in main Table S2.

All quantities were calculated and are thus reported in reduced units. Energy and temperature were normalized to the energy of the optimal hydrogen bond ($T^* = k_bT/|\epsilon_{HB}|$, $E^* = E/|\epsilon_{HB}|$), distances were normalized to the length of the optimal hydrogen bond ($r^* = r/r_{HB}$, $V^* = V/r_{HB}^2$), and reduced pressure, p^*, was defined as $p^*V^* = pV|\epsilon_{HB}|$.

Definitions of some relevant functions

Pair correlation functions were calculated for water-ion and cation-anion pairs. With the transformation of the ion-ion correlation function, $g(r)$, we calculated the potential of mean force, $w(r)$[3]:

$$w(r) = -k_bT \ln g(r) \tag{8}$$

Planar distribution function for water molecules, $g(x, y)$, around fixed ion pair was calculated as:

$$g(x, y) = \frac{\langle \rho(x, y) \rangle}{\langle \rho \rangle}, \tag{9}$$

where $\langle \rho(x, y) \rangle$ denotes the average water density in the surface element $\mathrm{d}x\,\mathrm{d}y$ with its centre in (x, y), and $\langle \rho \rangle$ is the average water density in the system.

With MB + dipole water model the orientation of water molecules with respect to the ion is also important. We define an angle between water molecule and ion with the angle between the vector of the water dipole moment and direction vector of the line joining centres of the water molecule and the ion (the direction is toward the ion, see Figure S2)[5]. The angular distribution function[5] for water molecules in the first hydration shell, $P(\phi)$ is just the number of water molecules with the angle ϕ, this is N. Formally it can be written as:

$$P(\phi) = N(\phi) \tag{10}$$

Example of angular distribution function can be seen in Figure S3.

The radius of the first hydratation shell, r_h, is, in the case of single ions, the distance of the first minimum in ion-water pair correlation function. The definition of the first hydration shell for ion

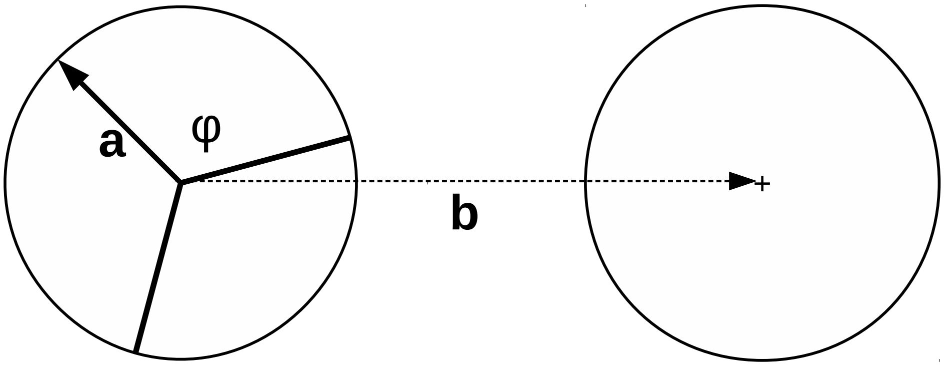

Figure S2: Definition of the angle between the water molecule and the ion. This is the angle φ between vectors **a** and **b**.

pairs is somewhat more complicated. When gathering statistics related to first hydration shell of the ion pair, both ions were fixed on abscissa axis. Let R be the shortest distance between edges of both ions and σ_i be the Lennard-Jones radius of an ion (index a refers to an anion and c to a cation), then abscissae of the ion centres are:

$$x_c = -\frac{1}{2}(\sigma_c + R) \tag{11}$$

$$x_a = \frac{1}{2}(\sigma_a + R) \tag{12}$$

The first hydration shell was defined as ellipse which centre has ordinate 0 and abscissa:

$$X_c = \frac{1}{2}\left(r_{ha} - r_{hc} + \frac{\sigma_a - \sigma_c}{2}\right) \tag{13}$$

Semi-major axis a, which lies in abscissa axis has length:

$$a = \frac{1}{2}\left(\frac{\sigma_a + \sigma_c}{2} + R + r_{ha} + r_{hc}\right) \tag{14}$$

Semi-minor axis b, has the same length as longer hydration radius (r_{ha} is the hydration radius for anion and r_{hc} for cation. A water molecule is said to be in the first hydration shell if coordinates of its centre (x, y) satisfy the following inequality:

$$\frac{(x - X_c)^2}{a^2} + \frac{y^2}{b^2} \leq 1 \tag{15}$$

Beside water molecules in the first hydration shell, number of hydrogen bonds formed by these waters (with water molecules in first hydration shell) was counted. A hydrogen bond was counted if absolute value of its energy exceeded one half of the absolute value of the energy of the optimal hydrogen bond.

First hydratation shell which is ellipse (equation 15) was divided into three regions: First is "cation's" region, where $x \leq x_c$; second is "anion's" region, where $x \geq x_a$; and third is region between ions ($x_c < x < x_a$). Water molecules in all three region must at the same time satisfy equation 15. On basis of this data we constructed the most probable configurations and orientations of waters in the first hydratation shell around ion pair.

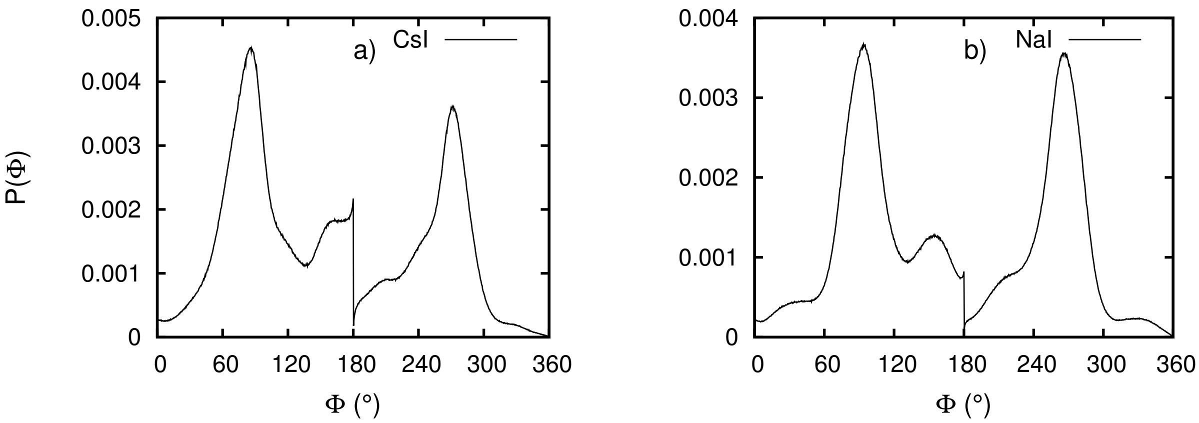

Figure S3: Example of angular distribution functions for water molecules between ions in CIP state for CsI (left) and NaI (right).

Potentials of mean force for studied salts

We present the potential of mean force (pmf) between different pairs of ions. Figure S4 a) and b) shows the potential of mean force as a function of the distance between two ions for alkali chlorides, and alkali iodides, respectively, while Figure S5 shows the same for sodium halides and caesium halides. The curves are qualitatively the same as the ones presented in the literature [2, 1]. They show a distinctive first and the second minimum, indicating the most probable separations of the two ions in the solutions. The first minimum corresponds to the two ions being in contact (contact ion pair, CIP), while the second minimum correspond to the so-called solvent separated pair (SIP), in which the two ions are separated by one water molecule.

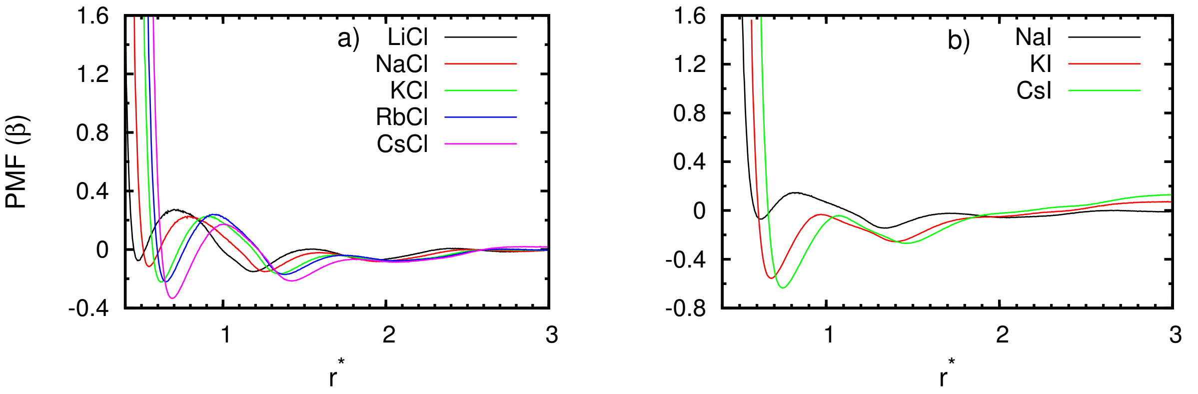

Figure S4: Potential of mean force as a function of r^* for chlorides (a) and iodides (b).

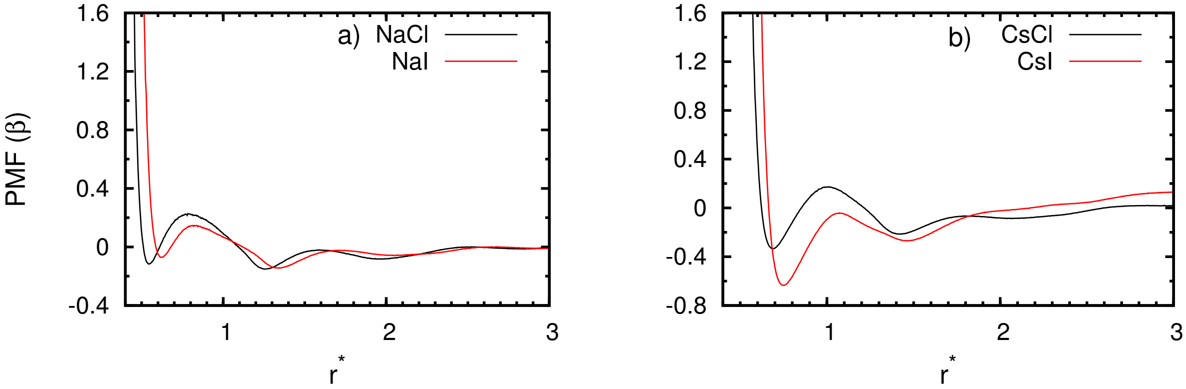

Figure S5: Potential of mean force as a function of r^* for sodium salts (a) and caesium salts (b).

Experimental data

Table S3: Densities, d_s, viscosites, η, and relative permittivities, ε, of water as a function of temperature, T.^{a}, b

T	d_s^b	$\eta \cdot 10^{3,c}$	ε^d
278.15	0.999967	1.5192	85.897
283.15	0.999702	1.3069	83.945
288.15	0.999102	1.1382	82.039
293.15	0.998206	1.0020	80.176
298.15	0.997048	0.8903	78.358
303.15	0.995651	0.7975	76.581
308.15	0.994036	0.7195	74.846
313.15	0.992219	0.6530	73.157

[a] Units: T in K; d_s in kg·dm^{-3}; η in Pa·s.;
[b] ref[4]
[c] ref[9]
[d] ref[10]

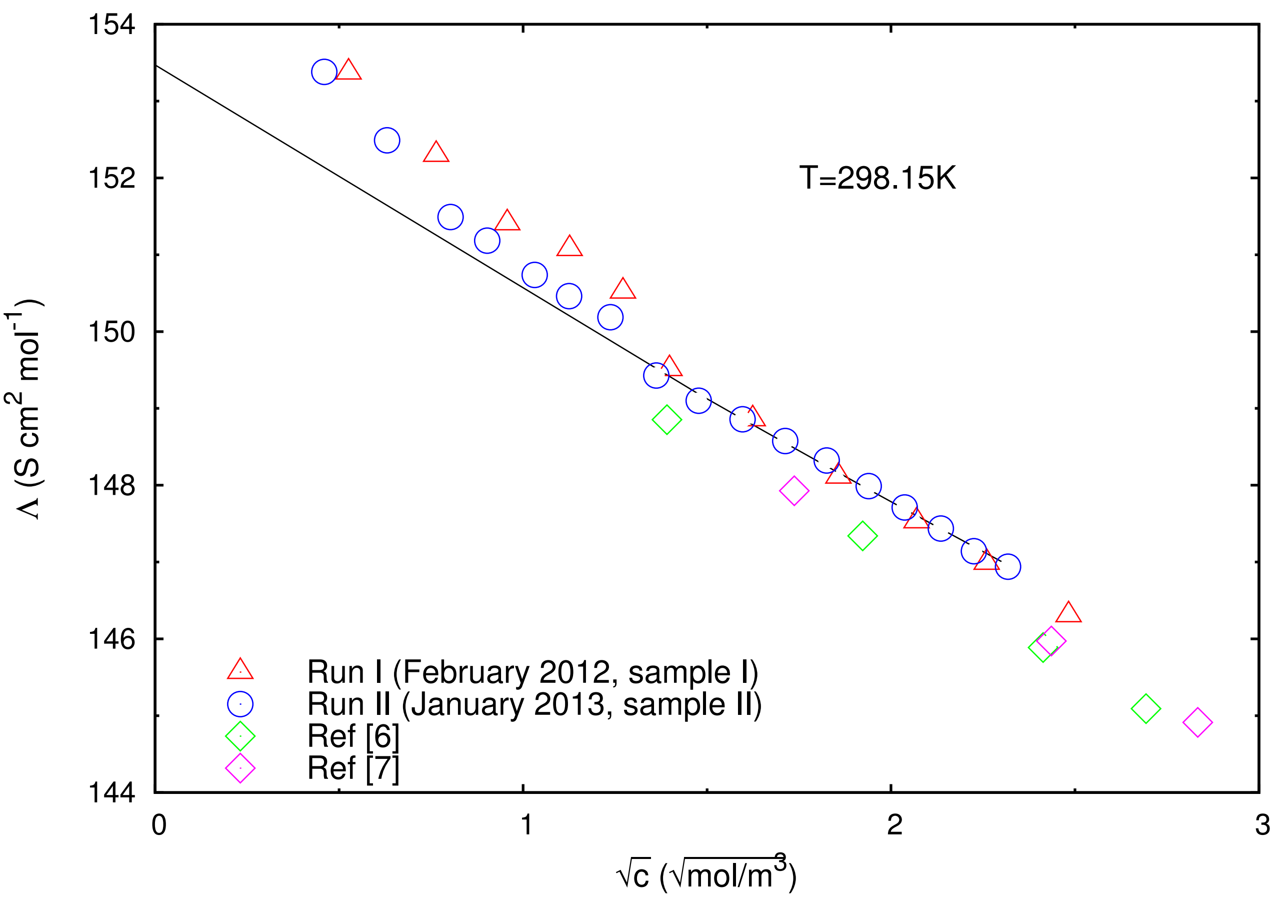

Figure S6: Molar conductivities, Λ, at 298.15 K of CsCl in water as obtained in two experiments and comparison with the available literature data.[8, 11] The line represents results of lcCM calculation on experimental data given in Table S2.

Table S4: Molar conductivities, Λ, as a function of molality, m, and rensity gradients, b, for lolutions of investigated alkali metal halides in water.

	T/K							
	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15
$10^3 \cdot m$/ mol·kg^{-1}	Λ/S·cm^2·mol^{-1}							
LiCl, b/kg^2·dm^{-3}·mol^{-1}=0.0252								
0.27056	69.621	79.954	90.470	101.957	113.723	126.037	138.733	151.679
0.57451	69.300	79.570	90.219	101.525	113.298	125.492	137.891	150.735
0.87074	69.083	79.320	89.739	100.911	112.712	124.814	137.312	150.157
1.21247	68.746	79.091	89.430	100.616	112.259	124.315	136.723	149.494
2.03874	68.390	78.520	89.124	100.222	111.732	123.434	135.756	148.571
3.11886	67.870	77.767	88.248	99.232	110.646	122.481	134.750	147.303
3.79452	67.488	77.462	87.925	98.884	110.398	122.208	134.346	146.818
5.11342	67.172	77.065	87.456	98.352	109.658	121.356	133.428	145.773
5.82796	67.028	76.923	87.288	98.139	109.404	121.070	133.061	145.352
6.55713	66.709	76.540	86.923	97.731	108.947	120.557	132.553	144.667
KCl, b/kg^2·dm^{-3}·mol^{-1}=0.0468								
1.10918	92.466	105.327	118.675	132.569	146.876	161.582	176.649	192.005
1.52305	92.140	104.922	118.213	132.040	146.302	160.834	175.838	191.110
1.90376	91.868	104.610	117.863	131.549	145.741	160.335	175.231	190.543
2.32753	91.588	104.214	117.391	131.136	145.328	159.867	174.712	189.881
2.75233	91.246	103.928	117.111	130.797	144.992	159.485	174.210	189.415
3.14459	91.156	103.781	116.912	130.547	144.670	159.110	173.877	189.015
3.55644	90.913	103.529	116.654	130.267	144.364	158.795	173.516	188.607
4.06421	90.734	103.318	116.384	129.985	144.001	158.381	173.053	188.012
4.5035	90.552	103.110	116.146	129.703	143.683	158.028	172.676	187.626
4.95608	90.371	102.885	115.912	129.451	143.401	157.712	172.372	186.857
5.47657	90.160	102.653	115.653	129.177	143.117	157.405	171.590	186.461
RbCl, b/kg^2·dm^{-3}·mol^{-1}=0.0787								
0.70486	96.301	109.153	122.888	136.969	151.623	166.607	181.791	197.468
0.98629	95.923	108.998	122.623	136.710	151.269	166.159	181.327	196.853
1.26669	95.712	108.752	122.324	136.375	150.853	165.705	180.807	196.053
1.60511	95.478	108.496	122.031	136.059	150.287	165.106	180.126	195.650
2.49054	95.079	108.011	121.469	135.396	149.733	164.423	179.303	194.710
3.09672	94.709	107.584	120.974	134.843	149.124	163.752	178.668	193.903
3.71987	94.373	107.195	120.545	134.250	148.467	163.093	177.794	193.231
4.40905	94.068	106.846	120.132	133.891	148.064	162.588	177.356	192.493
5.15316	93.799	106.522	119.776	133.446	147.592	162.063	176.503	191.478

	T/K							
	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15
$10^3 \cdot m$/ mol·kg^{-1}	Λ/S·cm^2·mol^{-1}							
CsCl, b/kg^2·dm^{-3}·mol^{-1}=0.128								
1.86104						164.141	179.059	194.385
2.18934	95.105	107.654	121.008	134.815	149.100	163.715	178.624	193.944
2.55725	94.836	107.500	120.842	134.638	148.859	163.437	178.303	193.555
2.94186	94.597	107.285	120.602	134.371	148.576	163.133	178.018	193.197
3.34173	94.412	107.146	120.398	134.121	148.322	162.870	177.678	192.893
3.77338	94.173	106.907	120.165	133.868	147.988	162.472	177.238	192.380
4.16262	94.030	106.746	119.936	133.613	147.710	162.188	176.943	192.013
4.57387	93.873	106.543	119.726	133.369	147.437	161.869	176.615	191.658
4.96688	93.739	106.373	119.533	133.131	147.140	161.559	176.292	
5.38962	93.560	106.196	119.320	132.923	146.940	161.296		
NaI, b/kg^2·dm^{-3}·mol^{-1}=0.114								
0.27622	78.260	89.203	100.849	112.989	125.612	138.683	152.137	165.818
0.60118	77.807	88.927	100.541	112.673	124.868	137.812	151.171	164.774
0.95105	77.629	88.491	100.107	112.237	124.590	137.693	150.902	164.398
1.29685	77.187	88.191	99.701	111.833	124.224	137.096	150.277	163.828
1.68366	76.930	87.891	99.389	111.375	123.832	136.681	149.263	162.707
2.03231	76.846	87.783	99.263	111.200	123.372	135.852	149.010	162.542
2.59018	76.599	87.508	98.758	110.442	123.105	135.465	148.531	161.964
3.1263	76.085	87.094	98.390	110.172	122.846	135.145	148.166	161.610
3.83012	76.093	86.921	98.233	110.039	122.215	134.829	147.810	161.164
4.54204	75.922	86.643	97.933	109.753	121.813	134.426	147.358	160.679
5.19619	75.704	86.450	97.595	109.497	121.575	134.061	146.920	160.087
5.88908	75.294	86.029	97.318	108.954	121.111	133.656	146.543	159.157
6.56961	75.270	85.910	97.088	108.834	120.896	133.336	145.537	158.867
KI , b/kg^2·dm^{-3}·mol^{-1}=0.121								
0.25832					149.297			
0.49864					148.261			
0.75566					148.173			
1.03926					147.653			
1.30903					147.338			
1.60955					146.539			
1.89571					146.370			
2.30195					146.099			
2.74739					145.860			
3.24475					145.619			
3.70564					145.241			
4.17498					144.944			
4.67710					144.670			
5.30234					144.367			

	T/K							
	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15
$10^3 \cdot m$/ mol·kg^{-1}	Λ/S·cm^2·mol^{-1}							
CsI , b/kg^2·dm^{-3}·mol^{-1}=0.201								
0.2244	97.541	110.562	123.937	137.370	152.223	166.908	181.890	197.106
0.46177	97.150	110.102	123.506	137.416	151.696	165.898	180.905	196.126
0.71291	96.944	109.624	122.992	136.845	151.098	165.702	180.549	195.382
1.0383	96.469	109.346	122.698	136.503	150.718	165.280	180.149	195.174
1.38775	96.232	109.047	122.345	136.097	150.268	164.727	179.148	194.186
1.74053	96.011	108.774	122.038	135.450	149.602	163.970	178.701	193.603
2.08942	95.843	108.556	121.462	135.206	149.295	163.628	178.314	193.353
2.48367	95.388	108.066	121.237	134.844	149.060	163.416	177.949	192.934
2.92189	95.150	107.824	121.024	134.639	148.574	162.867	177.451	192.372
3.41216	94.971	107.619	120.708	134.280	148.150	162.501	177.146	191.871
4.06379	94.777	107.392	120.405	133.968	147.851	162.087	176.583	191.460
4.74312	94.597	107.120	120.093	133.559	147.411	161.604	176.064	190.342
5.58073	94.282	106.753	119.727	133.218	146.967	160.809	175.096	189.694

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