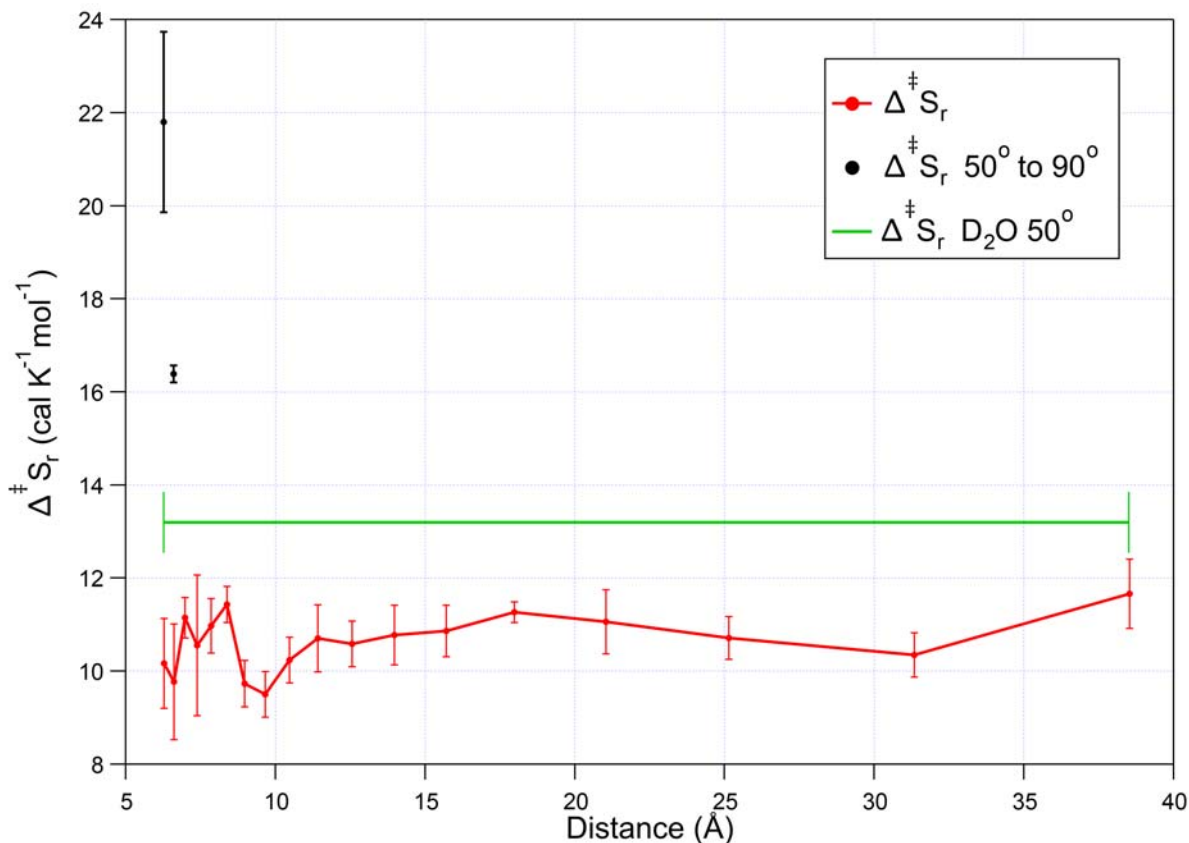


Supplement 1: Data sheets for E_a , $\Delta^\ddagger S_r$, and $\Delta^\ddagger G_r$ graphs and Eq. 13 $\Delta^\ddagger S_r$ graph

Data sheet for E_a

Label abbreviations: HT (Higher T range) and LT (Lower T range). Unc is the uncertainty/standard deviation σ . The adjusted r^2 is modified for the degrees of freedom and is smaller than the directly calculated r^2 . The 4pts value was used because it was not clear whether the line had a break.

length	Slope $\ln D/d(1/T)$	Unc_slope	E_a (cal/mol)	Unc E_a	q	label	Adj r^2
38.52	-1669.2	162	3317.0	321.9	0.1631	5pts	0.9449
31.34	-1484.7	55	2950.4	109.3	0.2005	5pts	0.9917
25.14	-1553.3	76	3086.7	151.0	0.2499	5pts	0.9858
21.04	-1611.8	135	3203.0	268.3	0.2987	5pts	0.9586
17.98	-1691.6	75	3361.5	149.0	0.3494	5pts	0.9882
15.71	-1636.5	59	3252.1	117.2	0.3999	5pts	0.9922
13.97	-1614.8	80	3208.9	159.0	0.4499	5pts	0.9855
12.56	-1615.0	79	3209.3	157.0	0.5001	5pts	0.9856
11.42	-1634.8	99	3248.7	196.7	0.5501	5pts	0.9725
10.47	-1588.0	54	3155.7	107.3	0.6001	5pts	0.9930
9.66	-1456.6	79	2894.6	157.0	0.6502	5pts	0.9825
8.97	-1484.6	53	2950.2	105.3	0.7001	5pts	0.9922
8.38	-1743.6	77	3464.9	153.0	0.7502	5pts	0.9885
7.85	-1664.8	149	3308.3	296.1	0.8002	5pts	0.9531
7.39	-1595.7	103	3171.0	204.7	0.8503	5pts	0.9753
6.98	-1724.5	122	3426.9	242.4	0.9004	5pts	0.9704
6.98	-1656.0	99	3290.8	196.7	0.9000	4pts	0.9789
6.61	-1704.6	173	3387.4	343.8	0.9504	5pts	0.9401
6.61	-1714.2	156	3406.5	310.0	0.9500	LT	0.9835
6.61	-2267.7	70	4506.4	139.1	0.9500	HT	0.9981
6.28	-2628.0	184	5222.4	365.6	1.0000	5pts	0.9711
6.28	-1758.2	113	3493.9	224.6	1.0000	LT	0.9917
6.28	-3193.0	388	6345.1	771.0	1.0000	HT	0.9709



Supplement Figure 1. The values of $\Delta^\ddagger S_r$ for pairwise diffusion *versus* distance from Equation 13. The vertical bars indicate the standard deviations of the slopes of the least squares lines found from the D_p values weighted by their individual experimental uncertainties. Due to the breaks at 50°C, the two shortest distances have two different $\Delta^\ddagger S_r$ values, one in the range 10°C to 50°C and the other 50°C to 90°C. The flat line shows the macroscopic $\Delta^\ddagger S_r$ for D₂O at 50 °C found from the data of Prielmeier et al.⁴⁸ in the same manner as for the salt solutions. The numerical values for the graphed points are listed on the next page.

Data sheet for $\Delta^{\ddagger}S_r$ for Figure Supp 1 calculated from Equation 13

Label abbreviations: HT (Higher T range) and LT (Lower T range). Unc is the uncertainty/standard deviation σ . The adjusted r^2 is modified for the degrees of freedom and is smaller than the directly calculated r^2 . The 4pts value was used because it was not clear whether the line had a break.

Length	Slope_dlnD/d/dlnT	Del_Sr (e.u.)	UncSr	q	Adj_r2	Label
38.52	5.201	11.66749251	0.741117227	0.163	0.9424	5 pts
31.34	4.631	10.35402759	0.474117603	0.2	0.9848	5 pts
25.14	4.852	10.71370819	0.457886168	0.25	0.9768	5 pts
21.04	5.032	11.06560273	0.690055997	0.3	0.9452	5 pts
17.98	5.308	11.26569216	0.22341095	0.35	0.9928	5 pts
15.71	5.124	10.86512554	0.557471726	0.4	0.9866	5 pts
13.97	5.152	10.77459832	0.642790607	0.45	0.9762	5 pts
12.56	5.06	10.58417744	0.49201268	0.5	0.9774	5 pts
11.41	5.125	10.70571779	0.72015387	0.55	0.9668	5 pts
10.47	4.983	10.23949649	0.492153354	0.6	0.986	5 pts
9.66	4.579	9.502632257	0.492416764	0.65	0.9756	5 pts
8.97	4.67	9.731542383	0.502336411	0.7	0.9876	5 pts
8.38	5.511	11.43419326	0.385976854	0.75	0.9876	5 pts
7.85	5.256	10.97366864	0.582116398	0.8	0.9427	5 pts
7.39	5.049	10.55469059	1.514964542	0.85	0.9759	5 pts
6.98	5.362	11.14587737	0.432666832	0.9	0.9636	4 pts
6.61	4.722	9.770514881	1.24322672	0.95	0.9551	LT
6.28	4.9584	10.16529893	0.967688131	1	0.9731	LT
6.61	8.248	16.93453905	0.193666919	0.95	1	HT
6.28	10.971	21.8015712	1.942297712	1	0.9996	HT

Data sheet for $\Delta^{\dagger}G_r$ Figure 7

q	Distance	DelGr_283	UncGr_283	DelGr_303	uncGr_303	DelGr_323	UncGr_323	DelGr_343	UncGr_343	DelGr_363	UncGr_363
0.163	38.5398773	-51.29249486	-106.0441449	-202.4490975	-98.16930368	-556.2661238	-94.22082031	-748.3383883	-104.2821731	-943.4144566	-129.6258816
0.2	31.41	-29.00780656	-57.97540312	-277.5658202	-57.5679339	-473.5923031	-59.31132444	-659.2145272	-63.01676344	-894.3863391	-79.63096541
0.25	25.128	28.29843621	-45.40936333	-241.1002346	-46.83109121	-433.8519048	-49.71634087	-621.1616914	-54.8859724	-862.2958206	-70.95798486
0.3	20.94	104.1406847	-42.24544499	-142.567059	-44.25032142	-426.2892457	-48.91958235	-559.7402871	-52.7887975	-756.3266289	-69.00921961
0.35	17.94857143	119.254374	-53.5210246	-98.21228432	-57.49766692	-279.0697813	-61.49892669	-546.7330035	-67.25762838	-817.3934832	-88.59896046
0.4	15.705	188.4796361	-51.49320982	-30.18226671	-55.41812443	-263.8514023	-60.94212747	-478.6174588	-68.42537747	-650.0520475	-87.95292417
0.45	13.96	247.3021906	-47.74190988	-13.98263679	-54.1790081	-201.6011378	-61.50264626	-422.3681644	-68.39759653	-592.02209	-89.07210482
0.5	12.564	241.5955245	-49.41640349	12.02012182	-55.24157299	-203.8550039	-60.12795988	-419.5684779	-69.24807967	-560.8796847	-91.18222976
0.55	11.42181818	282.7263097	-49.02981935	41.23617448	-55.44919126	-196.8067989	-61.83013898	-336.9154049	-72.35397214	-547.8787826	-99.06039281
0.6	10.47	290.9947135	-52.29336593	51.65788162	-59.92340948	-124.7611058	-64.46096814	-318.2141668	-77.82501896	-525.8458292	-103.2891827
0.65	9.664615385	217.3218087	-53.46398562	-22.14056872	-63.22958747	-153.463055	-72.76030127	-352.4457339	-85.76604924	-560.2588096	-118.7060874
0.7	8.974285714	212.3048993	-57.92045827	17.44910163	-68.56561905	-178.9176854	-75.22827263	-390.5448323	-96.8153285	-526.5564732	-127.6128878
0.75	8.376	239.713006	-61.92452328	-2.472451478	-75.93546493	-196.8278643	-86.14948896	-407.2604604	-105.9213321	-744.3849774	-180.0926238
0.8	7.8525	213.1479525	-67.16716405	-86.43919672	-84.59377422	-220.1499323	-98.31509554	-413.4045635	-127.9820058	-733.3785535	-209.4362096
0.85	7.390588235	168.765893	-76.10399092	-30.40050606	-91.34074649	-224.4995096	-112.0939723	-531.801499	-167.0694217	-624.5857507	-216.6623941
0.9	6.98	223.3577069	-81.60212416	-31.13599894	-103.6819365	-217.4396951	-125.0899176	-407.6074988	-162.2426725	-848.0908399	-383.9399637
0.95	6.612631579	204.5081392	-87.20651909	-23.93375301	-114.0812152	-166.0809333	-135.7589073	-512.6320242	-232.5114635	-884.1880446	-540.5490985
1	6.282	137.3519141	-105.761031	-92.01947484	-133.5607959	-253.672396	-167.6782882	-758.0482431	-532.2352243	-1211.06811	-0.242376544

Supplement 2: Untruncated estimates of single-ion diffusion coefficients for 0.8 M SrI₂ in D₂O at the experimental temperatures

Temperature	viscDovViscH	H2O_visc	H2O_rel visc	calc D_I_H2O	est D_I_D2O	Calc_D_Sr_H2O	est D_Sr_D2O
10	1.286	1.307	1.468044479	1.089885233	0.847500181	0.450940015	0.3506532
25	1.236	0.8903	1	1.6	1.294498382	0.662	0.535598706
30	1.224	0.7973	0.895540829	1.786629876	1.459664931	0.739218111	0.603936365
50	1.192	0.5467	0.614062676	2.60559722	2.185903708	1.07806585	0.904417659
70	1.174	0.4041	0.453891947	3.525068052	3.002613333	1.458496907	1.242331266
90	1.162	0.3149	0.353701	4.523594792	3.892938719	1.871637345	1.610703395

The calculated 25 °C data value for 0.8 M SrI₂ was adjusted to the experimental temperatures by dividing the two 25 °C diffusion coefficients listed above by the relative changes in H₂O viscosity listed in the 4th column. These values were then divided by the viscosity ratios listed in the 2nd column to get the two sets of estimated diffusion coefficients listed: iodide in column 6 and strontium in column 8.

Supplement 3: *If classical transition state theory were used for diffusion: the $k_B T/h$ contribution*

As reviewed by Peters et al., [Reaction rate theory and rare events, Elsevier, Amsterdam, 2017] classical TST does not apply to complex reaction surfaces such as for water self-diffusion. If classical TST were used, then the calculation of activation parameters from a T -dependent slope would include a contribution from $k_B T/h$. If the contribution were considered to be associated with $\Delta^\ddagger S$, then instead of

$$R \frac{d \ln D}{d \ln T} = \Delta^\ddagger S \quad (12)$$

we would use

$$R \frac{d \ln D}{d \ln T} = \Delta^\ddagger S + R \frac{d \ln(k_B T / h)}{d \ln T}$$

Since

$$\begin{aligned} \ln \frac{k_B T}{h} &= \ln \frac{k_B}{h} + \ln T \\ \frac{d \ln(k_B T / h)}{d(\ln T)} &= 0 + \frac{d \ln T}{d \ln T} = 1 \end{aligned}$$

so Equation 12 would be modified

$$R \frac{d \ln D}{d \ln T} = \Delta^\ddagger S + 1$$

the value of which is unitless as is the term $\Delta^\ddagger S/R$. Since the values of $\Delta^\ddagger S$ are around 10 e.u., the slope due to the $k_B T/h$ slope again is less than one fifth of the results. As a result, in cases where the $k_B T/h$ term is included in an activation calculation, its contribution is $T \text{ cal mol}^{-1}$ to $\Delta^\ddagger G$.

For d(1/T):

If the $k_B T/h$ term's contribution were to be associated with E_a , the derivative needed is $d(k_B T/h)/d(1/T)$.

$$\frac{d \ln(k_B T / h)}{d(1/T)} = \frac{d \ln k_B}{d(1/T)} + \frac{d \ln T}{d(1/T)} - \frac{d \ln h}{d(1/T)} = 0 + \frac{d \ln T}{d(1/T)} - 0 \approx T$$

To see why the final value is about T , use the approximation to find the slope between $(T+1)$ K and $(T-1)$ K. Apply approximation

$$\ln(n-1) - \ln(n+1) \approx -2 \left[\frac{1}{n} + \frac{1}{3n^3} + \dots \right]$$

Then for a 2° change in the numerator, $\Delta_2^\circ \ln T \approx -2/T$.

For the denominator,
 $d(1/T) = (T \cdot 0 - 1 \cdot dT)/T^2$

which for a 2° change gives

$$d(1/T) = -dT/T^2.$$

So,

$$\frac{d \ln(k_B T / h)}{d(1/T)} \approx \frac{-2/T}{-dT/T^2} = T$$

with units of K. At 300 K the slope ≈ 300 K, and similarly for other Kelvin temperatures, and the slope has the same units as E_a/R . Since diffusion in the SrI_2 has E_a over $3000 \text{ cal mol}^{-1}$, E_a/R is at least five times as large.

Of course because both of the derivatives involve T and logarithms of the values, since only the product $k_B T$ appears ($k_B = 1.380658 \times 10^{-23} \text{ J K}^{-1} = 3.300 \times 10^{-24} \text{ cal K}^{-1}$) along with h ($h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s} = 1.583 \times 10^{-34} \text{ cal}\cdot\text{s}$) these fundamental values do not appear in the resulting derivatives.

Supplement 4: One line or two?

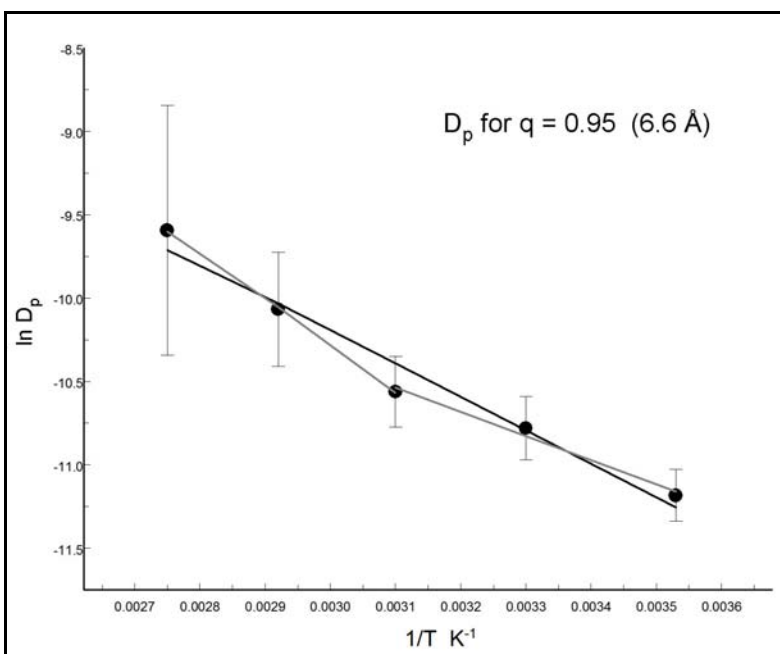
Comparing the quality of the two-segment fit to the one-line fit may be calculated as follows. The data in the table shows the square of the residuals (d^2) for each point. In order to compare the two sets and not double count the middle point, the larger of the two residual values is carried to the fifth column, which shows the d^2 values for the broken line set.

The F-statistic for the two fits is

$$F = 0.0505 / 0.0026 = 19.4$$

from the two sums shown in the bolded cells.

With 4 degrees of freedom for each fit, the F-test table shows a value for 1% is 15.98. As a result, there is >99% certainty the broken line is a better fit to the data.



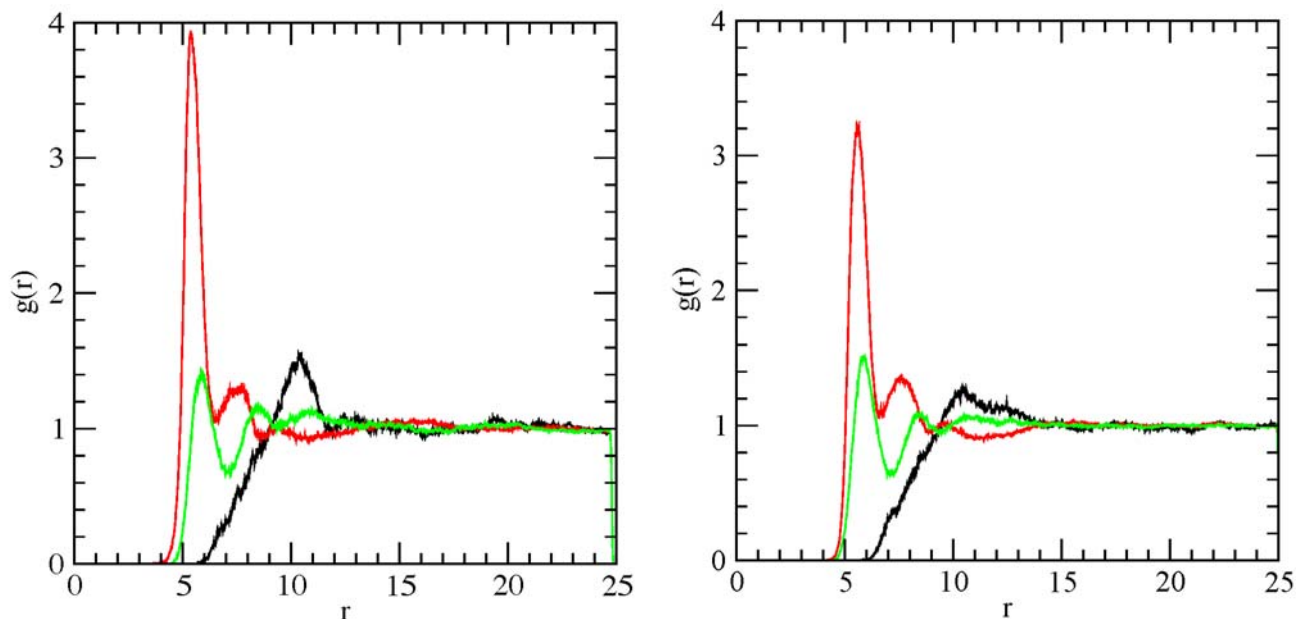
Graph: Plot of $\ln D_p$ versus $1/T$ for the value of $q = 0.95$, equivalent to a length scale of 6.6 Å. Two different fits are shown, one of a best straight line for all five points and also two straight line segments with a break at 50 °C. The uncertainties shown are from the counting statistics where the entire uncertainty for each has been attributed to the coherent part alone, which means these are overestimates.

Residuals and standard deviations of the mean for two fits to D_p data

$\ln D_p$	5-point line d^2	3-point Lower T d^2	3-point Higher T d^2	Broken-line d^2	T/K
-11.1835	0.005256	0.000496377		0.000496377	283
-10.78	0.0002	0.002276063		0.002276063	303
-10.561	0.029386	0.000646613	3.30825E-05	0.000646613	323
-10.0676	0.001256		0.000149225	0.000149225	343
-9.59394	0.014453		4.17836E-05	4.17836E-05	363
$\sum s_i^2$	0.0505511	0.003419053	0.000224091	0.00296	

Supplement 5:

Comparing simulations for 1 M SrI₂ solutions in water with two different force fields



The figures show the radial distribution functions versus distance in Å calculated for 1 M SrI₂ aqueous solutions (3760 waters, 80 Sr²⁺, and 160 I⁻). Color key: red curve Sr–I, green curve I–I, black curve Sr–Sr. The left graph has Sr²⁺ from the force field of Naleem et al.³⁸, and the right graph from the force field of Deublein et al.⁴⁰

In deriving the two different force fields, the groups optimized them by reproducing different experimental measurements for aqueous solutions of the strontium ions. Among the experimental physical properties being matched were:

In Naleem; The parameters were scaled to reproduce the Kirkwood-Buff force fields and then the results were compared to experimental values of activity derivatives, excess coordination numbers, partial molar volumes, translational self-diffusion coefficients, dielectric coefficients, enthalpy of mixing, and mean residence times for waters and anions around each cation.

In Deublein; the radial distribution function (RDF) of water around the cation, the hydration number of strontium, the potential of mean force between strontium and water, the hydration water residence time, the self-diffusion coefficient, the electric conductivity, and the enthalpy of hydration.

Because MD water is not triatomic H₂O, one would not expect the calculations to include any relationship with the scattering contrast that might exist for, e.g., non-adjacent Sr–O, I–O, Sr–D, or I–D pairs.