Supplementary Materials: PREDICTING MELTING POINTS OF BIOFRIENDLY CHOLINE-BASED IONIC LIQUIDS WITH MOLECULAR DYNAMICS

Karl Karu, Fred Elhi, Kaija Põhako-Esko and Vladislav Ivaništšev*

Additional figures

Below are all figures of diffusion coefficient temperature ($D - T$) dependences of the systems that were used to determine the melting point of the corresponding ionic liquids. Red, green, and dotted lines indicate respectively the fitted solid phase region, the fitted liquid phase region, and the experimental melting point.

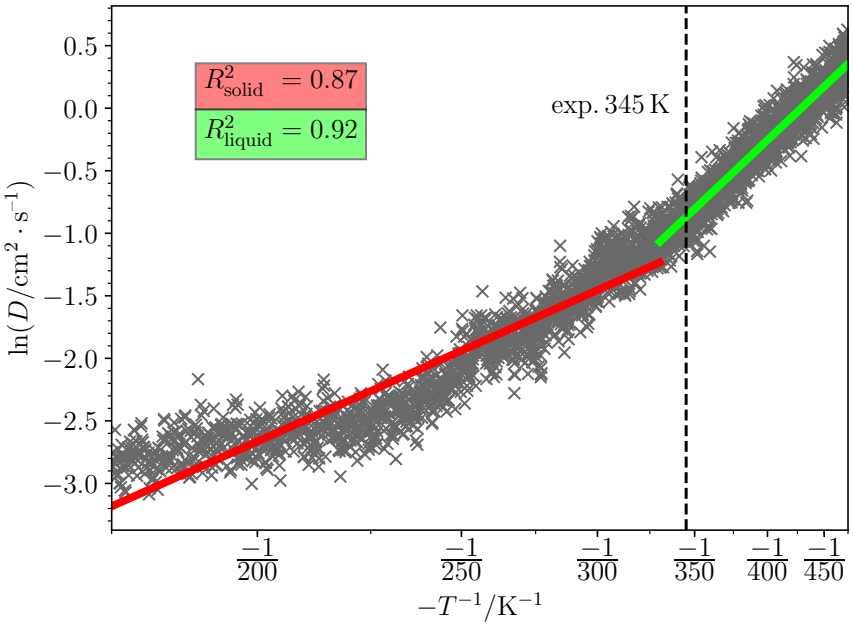

Figure S1. The diffusion coefficient (D) dependence on temperature (T) during annealing simulation of Choline Acetate. The solid phase was packed at 1.0 kg/dm^3 density with potential wells in CsCl lattice with 3:3:2 vector ratio.

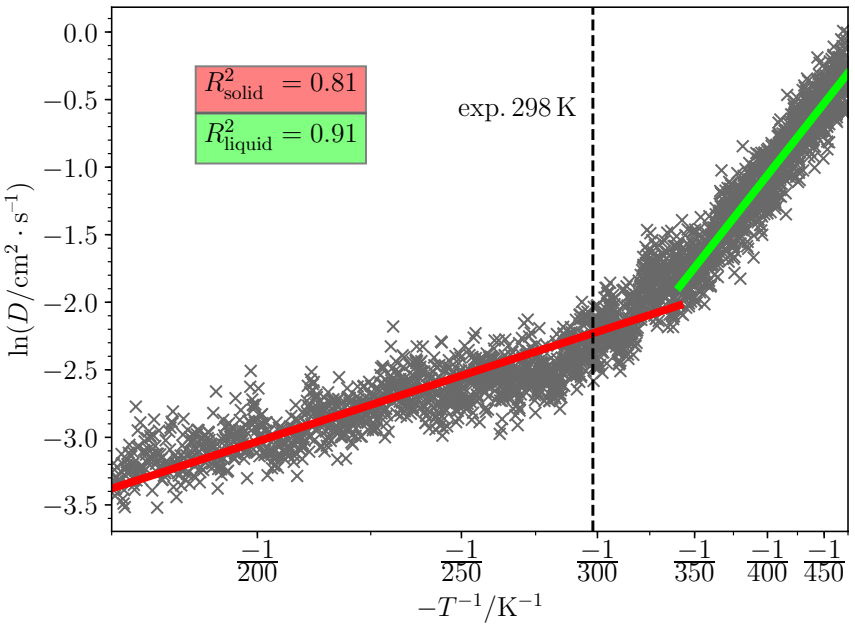

Figure S2. The diffusion coefficient (D) dependence on temperature (T) during annealing simulation of Choline Acesulfamate. The solid phase was packed at 1.6 kg/dm^3 density with potential wells in NaCl lattice with 4:3:2 vector ratio.

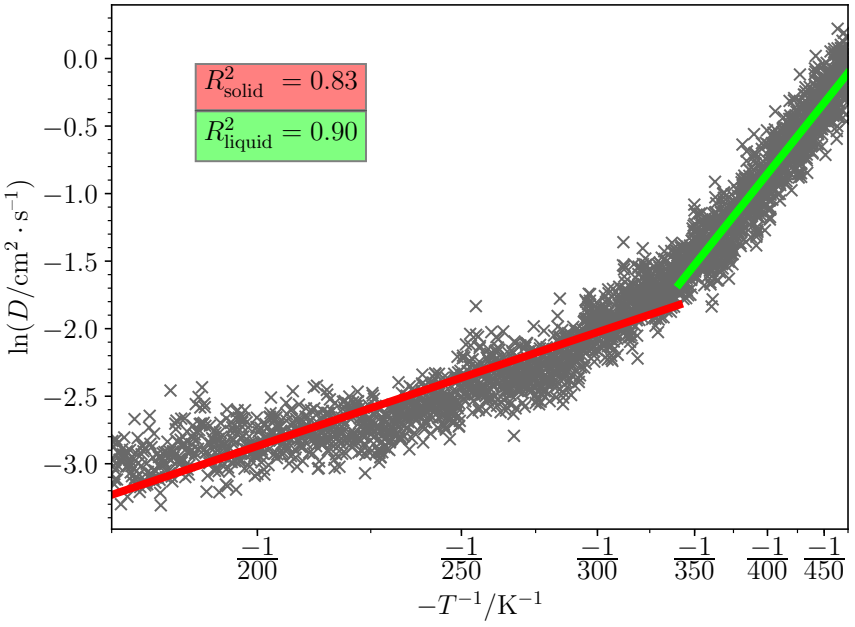

Figure S3. The diffusion coefficient (D) dependence on temperature (T) during annealing simulation of Choline Acetylsalicylate. The solid phase was packed at 1.2 kg/dm^3 density with potential wells in NaCl lattice with 3:3:2 vector ratio.

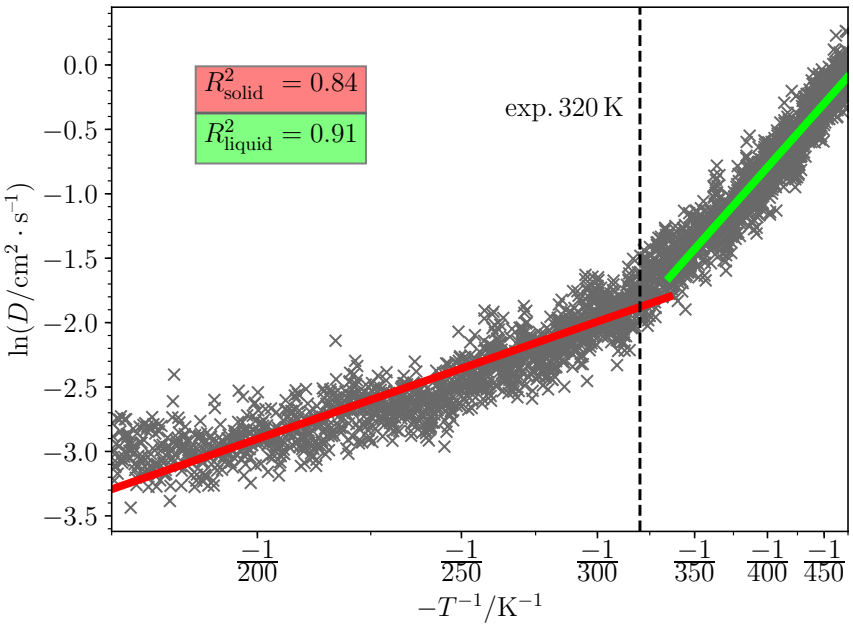

Figure S4. The diffusion coefficient (D) dependence on temperature (T) during annealing simulation of Choline Benzoate. The solid phase was packed at 1.2 kg/dm^3 density with potential wells in CsCl lattice with 3:3:3 vector ratio.

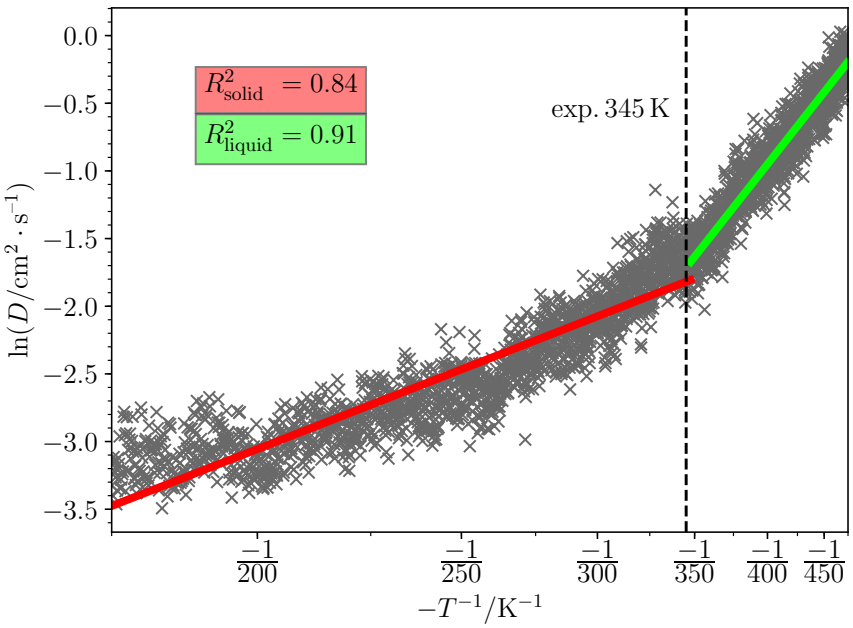

Figure S5. The diffusion coefficient (D) dependence on temperature (T) during annealing simulation of Choline Citrate. The solid phase was packed at 1.2 kg/dm^3 density with potential wells in CsCl lattice with 3:2:2 vector ratio.

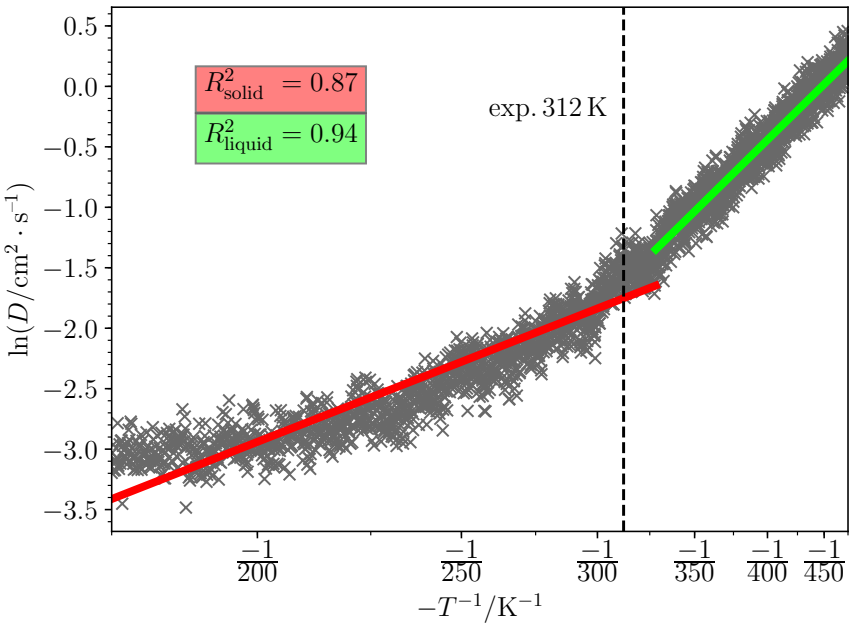

Figure S6. The diffusion coefficient (D) dependence on temperature (T) during annealing simulation of Choline Glutarate. The solid phase was packed at 1.4 kg/dm^3 density with potential wells in NaCl lattice with 3:3:3 vector ratio.

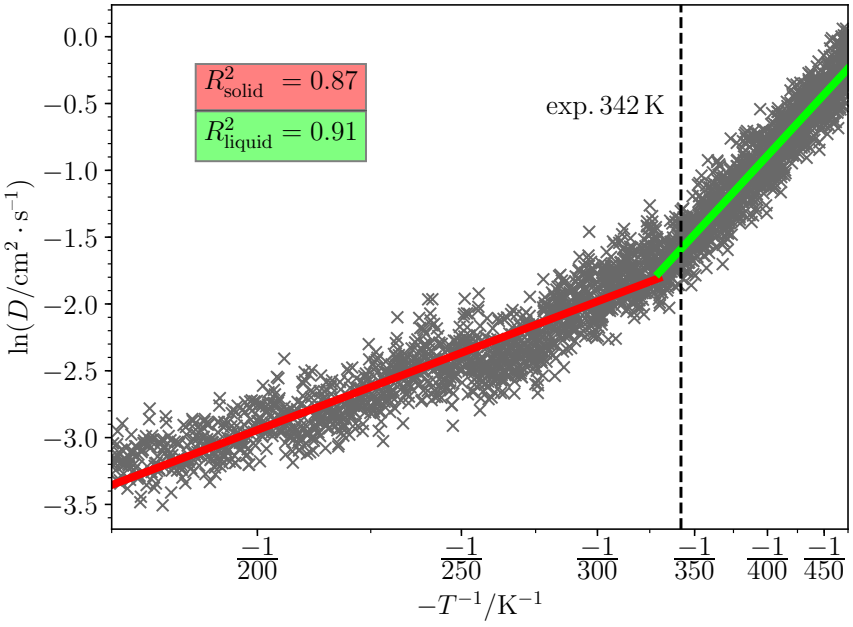

Figure S7. The diffusion coefficient (D) dependence on temperature (T) during annealing simulation of Choline Ibuprofenate. The solid phase was packed at 1.2 kg/dm^3 density with potential wells in CsCl lattice with 4:3:2 vector ratio.

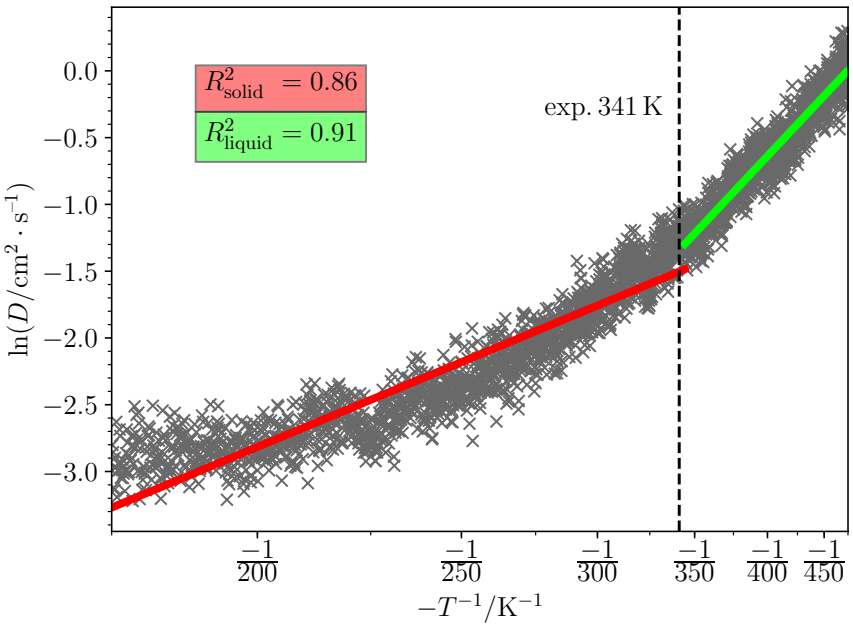

Figure S8. The diffusion coefficient (D) dependence on temperature (T) during annealing simulation of Choline Isobutanoate. The solid phase was packed at 1.0 kg/dm^3 density with potential wells in CsCl lattice with 3:3:2 vector ratio.

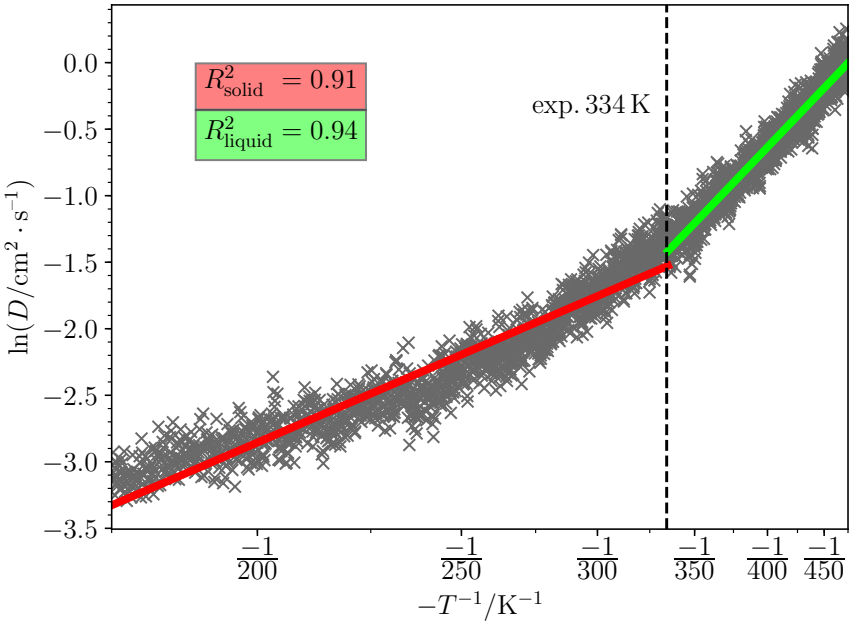

Figure S9. The diffusion coefficient (D) dependence on temperature (T) during annealing simulation of Choline Isovalerate. The solid phase was packed at 1.2 kg/dm^3 density with potential wells in CsCl lattice with 4:3:2 vector ratio.

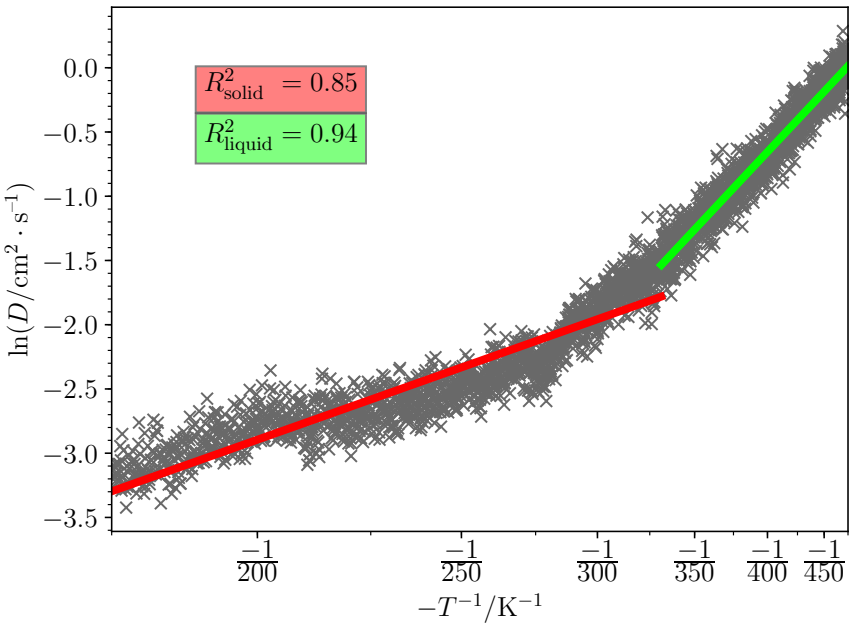

Figure S10. The diffusion coefficient (D) dependence on temperature (T) during annealing simulation of Choline Lactate. The solid phase was packed at 1.4 kg/dm^3 density with potential wells in CsCl lattice with 3:3:3 vector ratio. Dotted line in this case marks the experimental glass phase transition temperature.

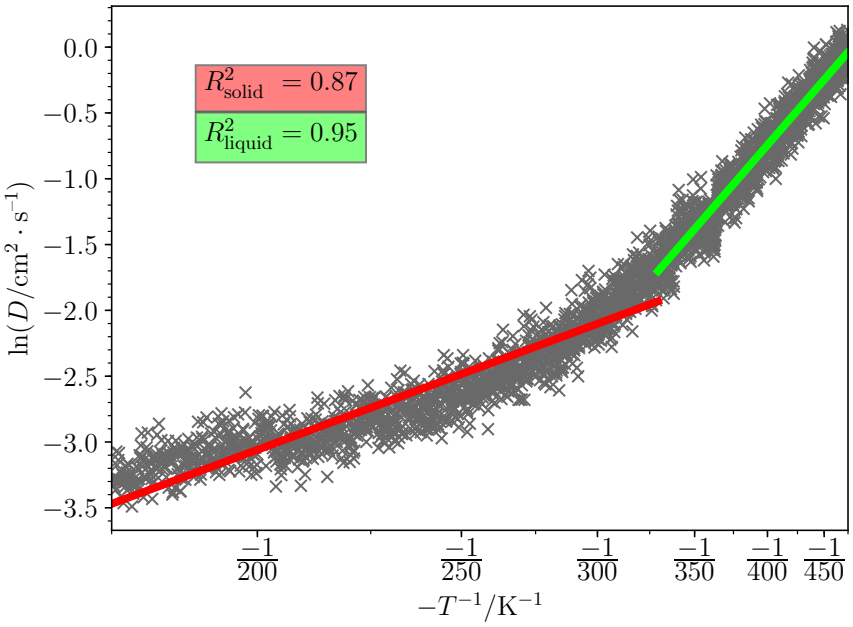

Figure S11. The diffusion coefficient (D) dependence on temperature (T) during annealing simulation of Choline Malonate. The solid phase was packed at 1.4 kg/dm^3 density with potential wells in NaCl lattice with 4:3:2 vector ratio.

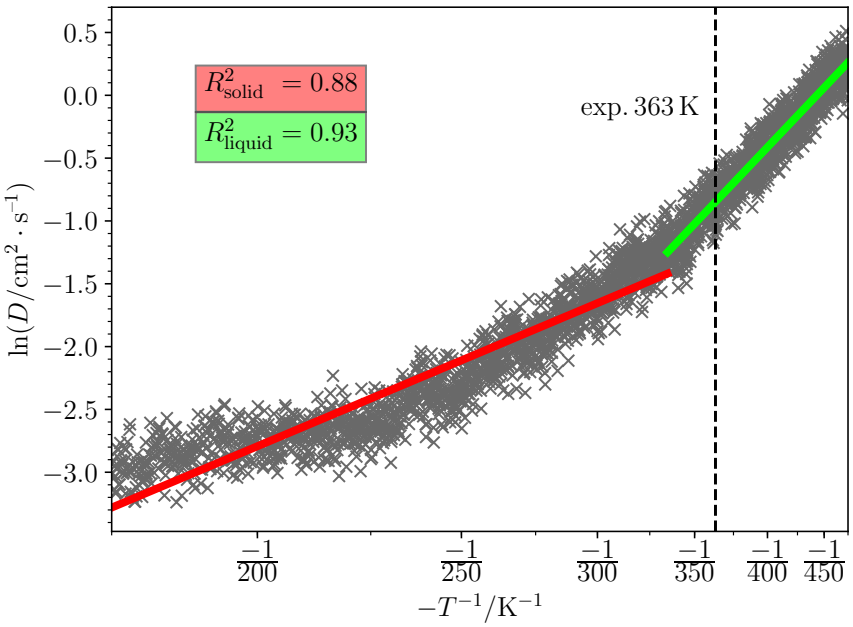

Figure S12. The diffusion coefficient (D) dependence on temperature (T) during annealing simulation of Choline 2-Methylbutanoate. The solid phase was packed at 1.2 kg/dm^3 density with potential wells in CsCl lattice with 3:2:2 vector ratio.

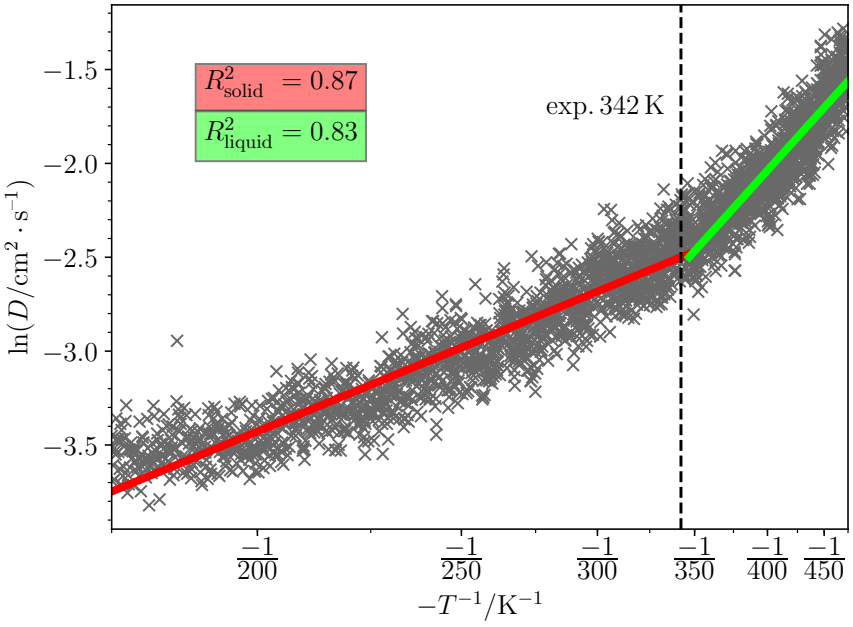

Figure S13. The diffusion coefficient (D) dependence on temperature (T) during annealing simulation of Choline Saccharinate. The solid phase was packed at 1.6 kg/dm^3 density with potential wells in NaCl lattice with 3:2:2 vector ratio.

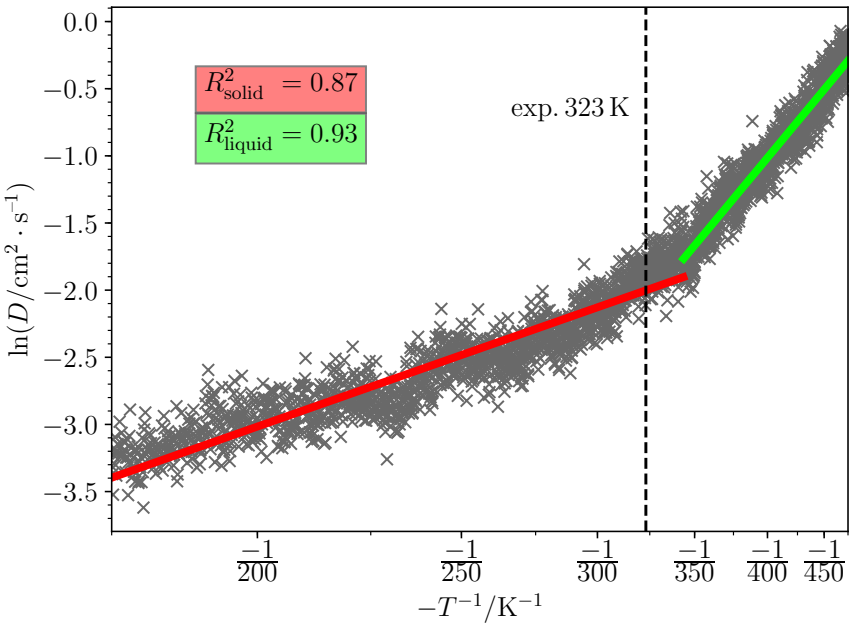

Figure S14. The diffusion coefficient (D) dependence on temperature (T) during annealing simulation of Choline Salicylate. The solid phase was packed at 1.2 kg/dm^3 density with potential wells in CsCl lattice with 4:3:2 vector ratio.

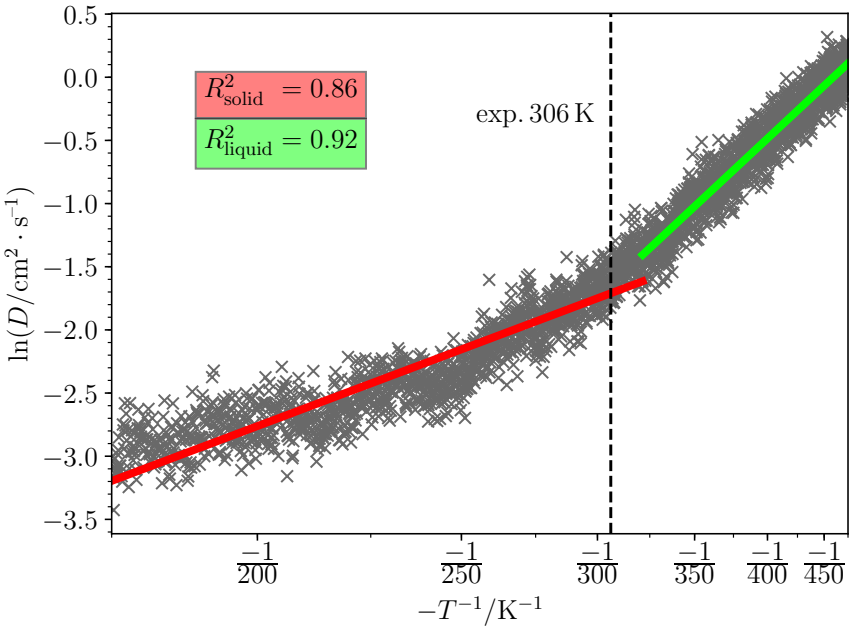

Figure S15. The diffusion coefficient (D) dependence on temperature (T) during annealing simulation of Choline TFSI. The solid phase was packed at 1.6 kg/dm^3 density with potential wells in CsCl lattice with 4:3:2 vector ratio.

Extrapolated melting point prediction

Melting point predictions obtained from simulations with different temperature rates were used to extrapolated towards temperature rate 0 K $\cdot$ ns^{-1}. The extrapolated melting point prediction is, thus, the regression line intercept in Figure 5. The obtained results are in the table below. Only one

experimental value for each IL is chosen – the value used for root-mean-square-error calculation. Root-mean-square-error for regular predictions (10 $K \cdot ns^{-1}$) was 18–24K and root-mean-square-error for extrapolated predictions was 19–23K depending on the choice of experimental reference. With the exclusion of choline 2-methylbutanoate the error of extrapolated results is 12–18K compared to that of 17–22K.

Table S1. Experimental, predicted and extrapolated melting points (T_M).

Cation: choline Anion	Experimental T_M (K)	Predicted T_M (K)	Extrapolated T_M (K)
Acesulfamate	298 [1]	341	325
Acetate	353 [2], 324 [3], 345 [4], 354[a]	330	340
Benzoate	320 [3]	335	332
Citrate	345 [5], 376 [6], 378[a]	348	347
Glutarate	312 [7]	328	323
Ibuprofenate	342 [8]	330	340
Isobutanoate	308 [2], 341[a]	344	337
Isovalerate	334[a]	335	334
2-Methylbutanoate	363[a]	335	313
Saccharinate	342 [1]	347	346
Salicylate	323 [9]	343	339
TFSI	306 [10]	321	325

a – measured in this work

References

1. Nockemann, P.; Thijs, B.; Driesen, K.; Janssen, C.R.; Van Hecke, K.; Van Meervelt, L.; Kossmann, S.; Kirchner, B.; Binnemans, K. Choline Saccharinate and Choline Acesulfamate: Ionic Liquids with Low Toxicities. *J. Phys. Chem. B* **2007**, *111*, 5254–5263. doi:10.1021/jp068446a.
2. Petkovic, M.; Ferguson, J.L.; Gunaratne, H.N.; Ferreira, R.; Leitao, M.C.; Seddon, K.R.; Rebelo, L.P.N.; Pereira, C.S. Novel biocompatible cholinium-based ionic liquids - toxicity and biodegradability. *Green Chem.* **2010**, *12*, 643–649. doi:10.1039/B922247B.
3. Fukaya, Y.; Iizuka, Y.; Sekikawa, K.; Ohno, H. Bio ionic liquids: room temperature ionic liquids composed wholly of biomaterials. *Green Chem.* **2007**, *9*, 1155–1157. doi:10.1039/b706571j.
4. Muhammad, N.; Hossain, M.I.; Man, Z.; El-Harbawi, M.; Bustam, M.A.; Noaman, Y.A.; Mohamed Alitheen, N.B.; Ng, M.K.; Hefter, G.; Yin, C.Y. Synthesis and Physical Properties of Choline Carboxylate Ionic Liquids. *J. Chem. Eng. Data* **2012**, *57*, 2191–2196. doi:10.1021/je300086w.
5. Li, Z.; Liu, X.; Pei, Y.; Wang, J.; He, M. Design of environmentally friendly ionic liquid aqueous two-phase systems for the efficient and high activity extraction of proteins. *Green Chem.* **2012**, *14*, 2941–2950. doi:10.1039/c2gc35890e.
6. Mourao, T.; Tome, L.C.; Florindo, C.; Rebelo, L.P.N.; Marrucho, I.M. Understanding the Role of Cholinium Carboxylate Ionic Liquids in PEG-Based Aqueous Biphasic Systems. *ACS Sustain. Chem. Eng.* **2014**, *2*, 2426–2434. doi:10.1021/sc500444w.
7. Rengstl, D.; Fischer, V.; Kunz, W. Low-melting mixtures based on choline ionic liquids. *Phys. Chem. Chem. Phys.* **2014**, *16*, 22815–22822. doi:10.1039/C4CP02860K.
8. Diogo, H.P.; Moura Ramos, J.J. Study of the thermal behavior of choline ibuprofenate using differential scanning calorimetry and hot-stage microscopy. *J. Mol. Struct.* **2014**, *1078*, 174–180. doi:10.1016/j.molstruc.2014.02.031.
9. Wolf, J.; Aboody, R. Choline salicylate: a new and more rapidly absorbed durg for salicylate therapy. *Int. Record. Med.* **1960**, *173*, 234–241.
10. Villanueva, M.; Parajo, J.; Sanchez, P.B.; Garcia, J.; Salgado, J. Liquid range temperature of ionic liquids as potential working fluids for absorption heat pumps. *J. Chem. Thermodyn.* **2015**, *91*, 127–135. doi:10.1016/j.jct.2015.07.034.