1.1.1. Preliminary Tests

Mixing Time

The results obtained for the different stirring times are displayed in figure S1 in which the distribution coefficients of PDO, AA and BA are plotted versus the stirring time. It can be seen that the distribution coefficients only vary within their error bars for different mixing times. Hence, it is assumed that thermodynamic equilibrium is reached quickly, and thus, the stirring time is set to 2 h.

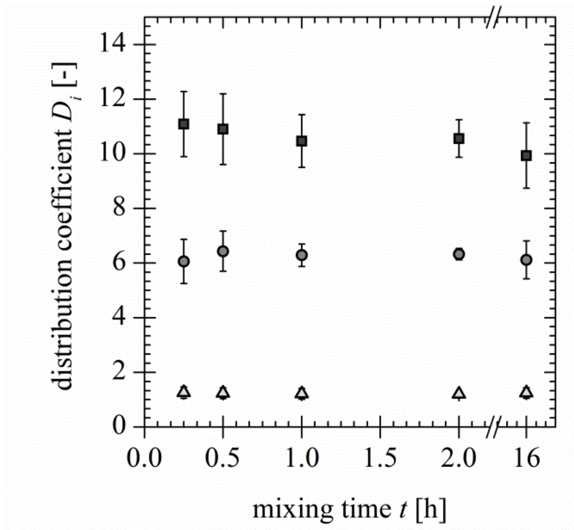

Fig. S1 Distribution coefficients of PDO (●), AA (▲) and BA (■) for different mixing times.

Settling Time

The time that is needed for the phases of an extraction system to be completely settled after mixing is important not only for the measurement of the liquid-liquid equilibrium but also for the application of the extraction system in a technical apparatus and its design. Systems that require long settling times to achieve complete phase separation are unsuitable for a continuous operation mode.

The settling time was determined using two different tie-lines, and thus different viscosities of the two phases, different density differences between the two phases and different interfacial tension. These parameters are the main factors affecting the time required to achieve complete phase separation. The results obtained for the distribution coefficient of the transferred components are shown in figure S2. The distribution coefficients vary slightly at the beginning, but after 1.0 h, no change can be observed until the experiment was completed after 20.0 h. The results obtained for the other distribution coefficients and the other tie-line are similar. Hence, the system settles quickly, and scale-up and a continuous operation mode are possible in regard to the settling. The settling time of the equilibrium experiments is set to 16 h, which is more than sufficient but is used due to the operational procedure.

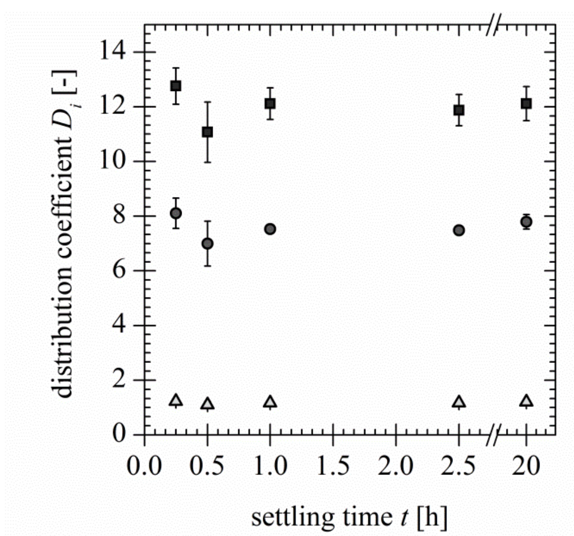

Fig. S2 Distribution coefficients of PDO (●), AA (▲) and BA (■) for different settling times.

1.1.2. Fermentation Broth

The motivation for the present investigation is the separation of PDO from fermentation broth. The previously described experiments are performed with synthetic media. To verify that this substitution is acceptable, experiments are performed using fermentation broth and synthetic media containing a mixture of pure chemicals in the same concentration range. Even though a precipitate was formed at the interface for the samples with fermentation broth, the tie-lines for the phase system show a good agreement with the tie-lines obtained with synthetic media (see figure S3). The formed precipitate was not analysed, but its consistency and the tendency of proteins to precipitate in ATPS lead to the assumption that it is formed by remaining proteins present in the fermentation broth.

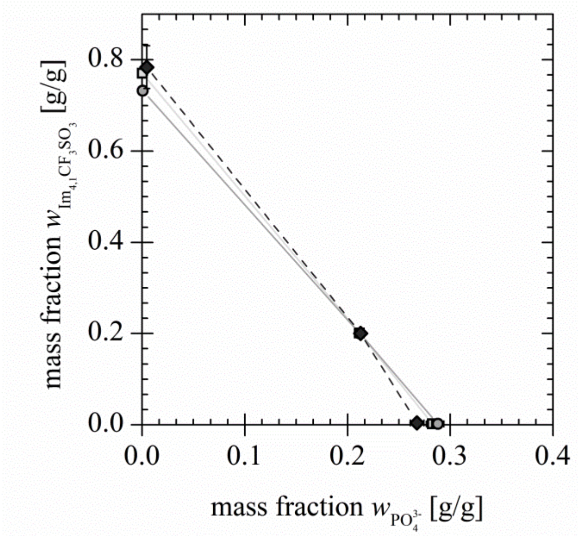

Fig. S3 Comparison of the tie-lines of the phase system for the synthetic medium ($w_{PDO,\,mix}$=0.01 (■) and $w_{PDO,\,mix}$=0.02 (●)) (—) and the fermentation broth ($w_{PDO,\,mix}$=0.014 (◆)) (---).

Effect of the PDO mass fraction

The influence of different PDO mass fractions on the tie-line of the phase system and on the PDO distribution coefficient was investigated because the PDO mass fraction changes during a multi-stage extraction process. The changes in the phase system are shown in figure S4.

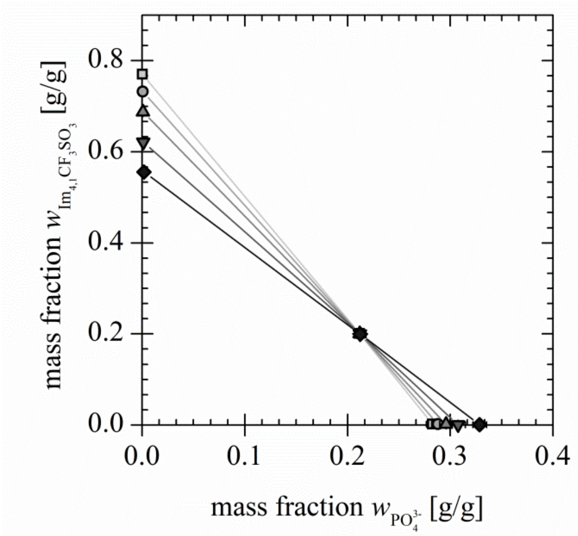

Fig. S4 Tie-lines of the phase system with different PDO mass fractions at the mixing point: $w_{PDO,\,mix}$=0.01 (■), $w_{PDO,\,mix}$=0.02 (●), $w_{PDO,\,mix}$=0.03 (▲), $w_{PDO,\,mix}$=0.05 (▼) and $w_{PDO,\,mix}$=0.07 (◆).

The slope of the tie-line decreases with an increase in the PDO mass fraction from $w_{PDO,\,mix}$=0.01 to $w_{PDO,\,mix}$=0.07, which means that on one hand, the phase ratio increases by approximately 52 %, while on the other hand, the mass fraction of $Im_{4,1}$ CF_3SO_3 in the top phase decreases (28 %), and the mass fraction of PO_4^{3-} in the bottom phase increases (16 %). These changes are due to the changes in the amounts of PDO, AA, BA and water present in each phase. This can be shown by comparing the components' mass fractions in relation to the total mass of both phases. The mass fractions are displayed in figure S5 and S6 versus the PDO mass fraction at the mixing point for the PO_4^{3-} and $Im_{4,1}$ CF_3SO_3-rich phase, respectively. The mass fractions of $Im_{4,1}$ CF_3SO_3 and PO_4^{3-} (and the corresponding cations, K^+/Na^+) are approximately constant, whereas the mass fraction of water increases in the top phase and decreases in the bottom phase when the PDO mass fraction increases. The PDO mass fraction itself increases in both phases, although the fraction in the top phase increases more. The results for AA and BA are not presented here because their trends are the same as for water, but their influence on the mass fractions of $Im_{4,1}$ CF_3SO_3 and PO_4^{3-} is negligible due to their small amounts. Due to the change in the water distribution between the two phases caused by an increase in the PDO mass fraction, the phase ratio also increases. One explanation for this transfer could be the change in the hydrophilicity of the top phase due to the increase in PDO.

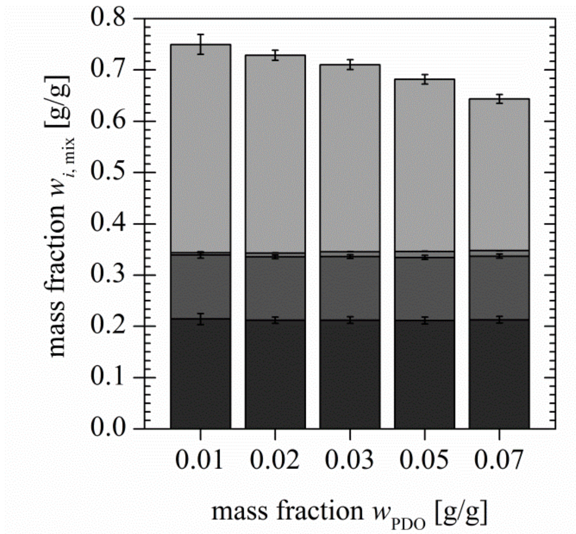

Fig. S5 Mass fractions in the PO_4^{3-} -rich phase in relation to the total mass: PO_4^{3-} (■), K^+/Na^+ (■), PDO (■) and H_2O (■).

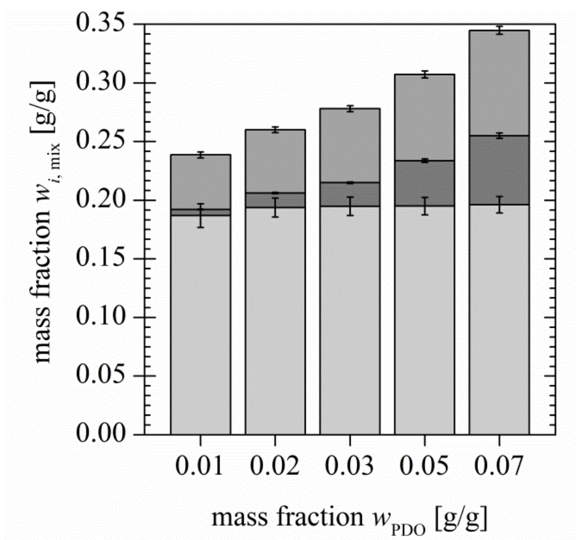

Fig. S6 Mass fractions in the top-phase in relation to the total mass: PDO (■), H_2O (■) and $Im_{4,1}$ CF_3SO_3 (■).

Effect of the addition of AA and BA

Figure S7 shows the difference between the system tie-lines for PDO mass fractions of $w_{PDO,\text{ mix}}$= 0.01 and 0.07 at the mixing point with and without the addition of AA and BA.

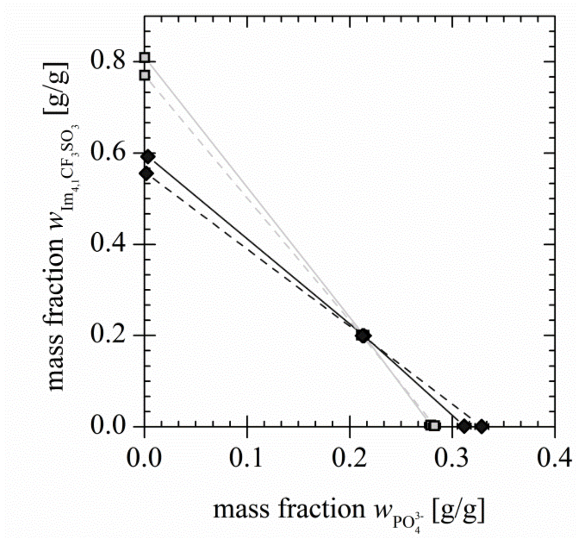

Fig. S7 Tie-lines of the phase system for different PDO mass fractions and with and without the addition of AA and BA: $w_{PDO, mix}$=0.01 (■) and $w_{PDO, mix}$=0.07 (◆); without AA and BA (─) and with AA and BA (---).

The slopes of the tie-lines for systems without AA and BA decrease in comparison to the slopes of the tie-lines for ones with AA and BA. This is again not related to a decrease or increase in the amounts of $Im_{4,1}$ CF_3SO_3 and PO_4^{3-}, but it is instead related to a change in the distribution of the other components. Figures S8 and S9 display the components' mass fractions in relation to the total mass of both phases of the PO_4^{3-} and $Im_{4,1}$ CF_3SO_3-rich phase, respectively. AA and BA are again not displayed due to their small amounts. The mass fractions of $Im_{4,1}$ CF_3SO_3 and PO_4^{3-} do not vary, but the fractions of water and PDO change when AA and BA are added. The mass fractions of both components increase in the top phase and decrease in the bottom phase when AA and BA are added, although this effect is more pronounced for water. Hence, the decrease in the $Im_{4,1}$ CF_3SO_3 mass fraction and the increase in the PO_4^{3-} mass fraction in their particular phases are caused by a transfer of water and PDO to the top phase due to the addition of AA and BA. This is also the reason for a change in the phase ratio between the top and bottom phase.

The changes in the slope of the tie-line and the phase ratio caused by the addition of AA and BA are smaller than the changes observed when the PDO mass fraction changes, although only 0.5 wt-% AA and BA were added.

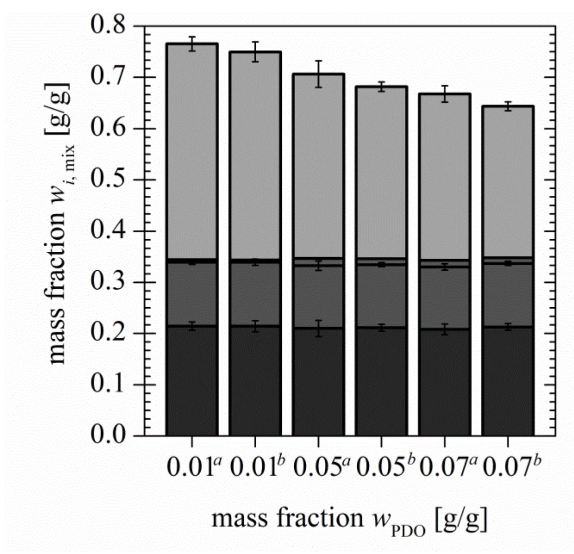

Fig. S8 Mass fractions in the PO_4^{3-}-rich phase in relation to the total mass: PO_4^{3-} (■), K^+/Na^+ (■), PDO (■) and H_2O (■); [a] without and [b] with AA and BA.

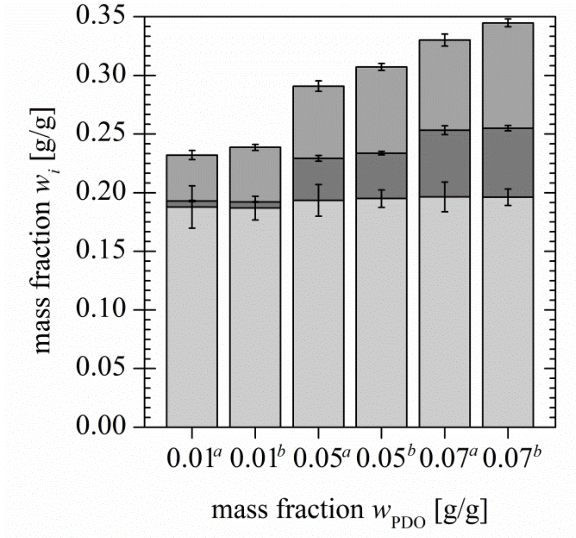

Fig. S9 Mass fractions in the $Im_{4,1}$ CF_3SO_3-rich phase in relation to the total mass: PDO (■), H_2O (■) and $Im_{4,1}$ CF_3SO_3 (■); [a] without and [b] with AA and BA.

1.1.3. Recovered IL

Measurements were performed to determine if a recovery of the IL is possible and if the recovered IL is as effective as fresh IL in the extraction. The resultant phase system tie-lines for fresh and recovered IL are displayed in figure S10. The tie-line for the recovered $Im_{4,1}$ CF_3SO_3 has a lower slope than the one for the fresh $Im_{4,1}$ CF_3SO_3. The magnitude of this decrease is similar to the decrease due to the addition of AA and BA.

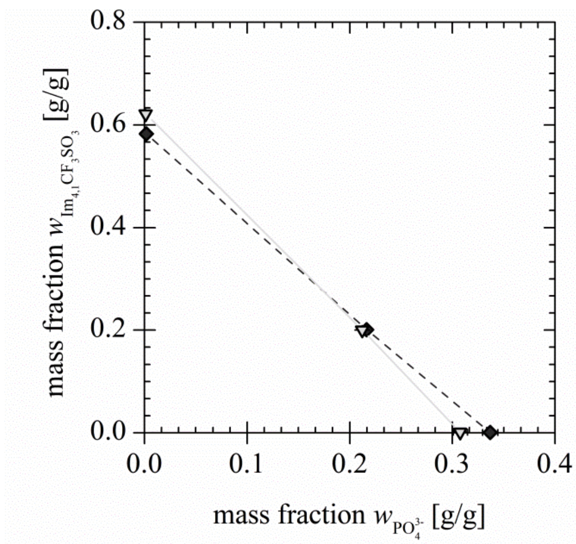

Fig. S10 Comparison of the tie-lines of the phase system for the fresh (▾, ─) and the recovered (◆, ---) IL.

Electronic Supplementary Material (ESI) for RSC Advances

phase	w_{PO4} [g/g]	$w_{IM4,1\ CF3SO3}$ [g/g]	w_{PDO} [g/g]	w_{AA} [g/g]	w_{BA} [g/g]
PO_4-rich	0.279 ± 0.0058	0.003 ± 0.0000	0.006 ± 0.0002		
mixing point	0.214 ± 0.0045	0.200 ± 0.0000	0.010 ± 0.0000		
$Im_{4,1}$ CF_3SO_3-rich	0.000 ± 0.0000	0.809 ± 0.0052	0.022 ± 0.0006		
PO_4-rich	0.284 ± 0.0063	0.003 ± 0.0000	0.012 ± 0.0002		
mixing point	0.214 ± 0.0043	0.200 ± 0.0001	0.020 ± 0.0000		
$Im_{4,1}$ CF_3SO_3-rich	0.001 ± 0.0000	0.775 ± 0.0076	0.047 ± 0.0002		
PO_4-rich	0.288 ± 0.0060	0.003 ± 0.0001	0.016 ± 0.0002		
mixing point	0.214 ± 0.0043	0.200 ± 0.0001	0.030 ± 0.0000		
$Im_{4,1}$ CF_3SO_3-rich	0.001 ± 0.0001	0.735 ± 0.0049	0.074 ± 0.0002		
PO_4-rich	0.296 ± 0.0070	0.002 ± 0.0001	0.020 ± 0.0001		
mixing point	0.213 ± 0.0043	0.200 ± 0.0000	0.050 ± 0.0000		
$Im_{4,1}$ CF_3SO_3-rich	0.002 ± 0.0002	0.663 ± 0.0037	0.123 ± 0.0003		
PO_4-rich	0.311 ± 0.0065	0.001 ± 0.0001	0.020 ± 0.0001		
mixing point	0.214 ± 0.0043	0.200 ± 0.0000	0.070 ± 0.0000		
$Im_{4,1}$ CF_3SO_3-rich	0.003 ± 0.0001	0.592 ± 0.0040	0.171 ± 0.0009		
PO_4-rich	0.335 ± 0.0084	0.001 ± 0.0001	0.017 ± 0.0002		
mixing point	0.214 ± 0.0043	0.200 ± 0.0000	0.100 ± 0.0000		
$Im_{4,1}$ CF_3SO_3-rich	0.004 ± 0.0001	0.524 ± 0.0029	0.218 ± 0.0012		
PO_4-rich	0.283 ± 0.0058	0.002 ± 0.0001	0.006 ± 0.0001	0.006 ± 0.0001	0.002 ± 0.0001
mixing point	0.212 ± 0.0041	0.201 ± 0.0006	0.010 ± 0.0000	0.005 ± 0.0000	0.005 ± 0.0000
$Im_{4,1}$ CF_3SO_3-rich	0.000 ± 0.0000	0.771 ± 0.0026	0.022 ± 0.0002	0.003 ± 0.0001	0.012 ± 0.0001
PO_4-rich	0.288 ± 0.0058	0.002 ± 0.0002	0.010 ± 0.0001	0.006 ± 0.0001	0.002 ± 0.0001
mixing point	0.212 ± 0.0041	0.200 ± 0.0001	0.020 ± 0.0000	0.005 ± 0.0000	0.005 ± 0.0000
$Im_{4,1}$ CF_3SO_3-rich	0.001 ± 0.0000	0.732 ± 0.0026	0.046 ± 0.0004	0.004 ± 0.0001	0.013 ± 0.0001
PO_4-rich	0.296 ± 0.0061	0.001 ± 0.0001	0.013 ± 0.0001	0.005 ± 0.0001	0.002 ± 0.0001
mixing point	0.212 ± 0.0041	0.200 ± 0.0003	0.030 ± 0.0000	0.005 ± 0.0000	0.005 ± 0.0000
$Im_{4,1}$ CF_3SO_3-rich	0.001 ± 0.0000	0.687 ± 0.0034	0.071 ± 0.0002	0.005 ± 0.0001	0.013 ± 0.0001

phase	w_{PO4} [g/g]	$w_{IM4,1\ CF3SO3}$ [g/g]	w_{PDO} [g/g]	w_{AA} [g/g]	w_{BA} [g/g]
PO_4-rich	0.308 ± 0.0068	0.001 ± 0.0001	0.017 ± 0.0002	0.005 ± 0.0001	0.001 ± 0.0001
mixing point	0.212 ± 0.0042	0.200 ± 0.0003	0.050 ± 0.0000	0.005 ± 0.0000	0.005 ± 0.0000
$Im_{4,1}$ CF_3SO_3-rich	0.001 ± 0.0000	0.621 ± 0.0040	0.123 ± 0.0008	0.006 ± 0.0001	0.013 ± 0.0001
PO_4-rich	0.329 ± 0.0067	0.001 ± 0.0001	0.016 ± 0.0002	0.004 ± 0.0001	0.001 ± 0.0001
mixing point	0.212 ± 0.0042	0.200 ± 0.0001	0.070 ± 0.0000	0.005 ± 0.0000	0.005 ± 0.0000
$Im_{4,1}$ CF_3SO_3-rich	0.002 ± 0.0000	0.556 ± 0.0025	0.167 ± 0.0023	0.008 ± 0.0001	0.013 ± 0.0001
PO_4-rich	0.184 ± 0.0044	0.019 ± 0.0001	0.009 ± 0.0001		
mixing point	0.120 ± 0.0026	0.280 ± 0.0000	0.010 ± 0.0000		
$Im_{4,1}$ CF_3SO_3-rich	0.001 ± 0.0000	0.740 ± 0.0043	0.013 ± 0.0001		
PO_4-rich	0.192 ± 0.0047	0.019 ± 0.0002	0.024 ± 0.0002		
mixing point	0.120 ± 0.0026	0.280 ± 0.0002	0.030 ± 0.0000		
$Im_{4,1}$ CF_3SO_3-rich	0.001 ± 0.0000	0.698 ± 0.0038	0.042 ± 0.0003		
PO_4-rich	0.201 ± 0.0047	0.017 ± 0.0002	0.036 ± 0.0002		
mixing point	0.120 ± 0.0026	0.280 ± 0.0000	0.050 ± 0.0000		
$Im_{4,1}$ CF_3SO_3-rich	0.002 ± 0.0000	0.648 ± 0.0032	0.073 ± 0.0007		
PO_4-rich	0.216 ± 0.0051	0.014 ± 0.0004	0.042 ± 0.0002		
mixing point	0.120 ± 0.0026	0.280 ± 0.0002	0.070 ± 0.0001		
$Im_{4,1}$ CF_3SO_3-rich	0.004 ± 0.0001	0.602 ± 0.0034	0.108 ± 0.0004		
PO_4-rich	0.183 ± 0.0044	0.019 ± 0.0002	0.008 ± 0.0001	0.007 ± 0.0002	0.004 ± 0.0001
mixing point	0.120 ± 0.0026	0.280 ± 0.0002	0.010 ± 0.0000	0.005 ± 0.0000	0.005 ± 0.0000
$Im_{4,1}$ CF_3SO_3-rich	0.001 ± 0.0000	0.746 ± 0.0022	0.014 ± 0.0002	0.002 ± 0.0001	0.007 ± 0.0001
PO_4-rich	0.194 ± 0.0046	0.017 ± 0.0001	0.024 ± 0.0001	0.007 ± 0.0001	0.004 ± 0.0001
mixing point	0.120 ± 0.0026	0.281 ± 0.0007	0.030 ± 0.0000	0.005 ± 0.0000	0.005 ± 0.0000
$Im_{4,1}$ CF_3SO_3-rich	0.002 ± 0.0001	0.688 ± 0.0031	0.045 ± 0.0006	0.003 ± 0.0001	0.007 ± 0.0001
PO_4-rich	0.210 ± 0.0049	0.013 ± 0.0001	0.033 ± 0.0006	0.006 ± 0.0001	0.003 ± 0.0001
mixing point	0.120 ± 0.0026	0.280 ± 0.0000	0.050 ± 0.0000	0.005 ± 0.0000	0.005 ± 0.0000
$Im_{4,1}$ CF_3SO_3-rich	0.003 ± 0.0001	0.629 ± 0.0035	0.079 ± 0.0011	0.004 ± 0.0001	0.008 ± 0.0001

phase	w_{PO4} [g/g]	$w_{IM4,1\ CF3SO3}$ [g/g]	w_{PDO} [g/g]	w_{AA} [g/g]	w_{BA} [g/g]
PO_4-rich	0.229 ± 0.0054	0.008 ± 0.0000	0.035 ± 0.0005	0.005 ± 0.0001	0.002 ± 0.0001
mixing point	0.120 ± 0.0026	0.282 ± 0.0001	0.069 ± 0.0000	0.005 ± 0.0000	0.005 ± 0.0000
$Im_{4,1}$ CF_3SO_3-rich	0.004 ± 0.0001	0.571 ± 0.0027	0.109 ± 0.0028	0.005 ± 0.0001	0.008 ± 0.0002
PO_4-rich	0.235 ± 0.0099	0.001 ± 0.0005	0.004 ± 0.0001		
mixing point	0.187 ± 0.0046	0.200 ± 0.0003	0.010 ± 0.0000		
$Im_{4,1}$ CF_3SO_3-rich	0.000 ± 0.0000	0.842 ± 0.0101	0.024 ± 0.0003		
PO_4-rich	0.252 ± 0.0078	0.001 ± 0.0005	0.009 ± 0.0001		
mixing point	0.187 ± 0.0046	0.200 ± 0.0001	0.030 ± 0.0000		
$Im_{4,1}$ CF_3SO_3-rich	0.000 ± 0.0000	0.773 ± 0.0094	0.080 ± 0.0007		
PO_4-rich	0.258 ± 0.0064	0.000 ± 0.0004	0.009 ± 0.0009		
mixing point	0.187 ± 0.0046	0.200 ± 0.0008	0.050 ± 0.0000		
$Im_{4,1}$ CF_3SO_3-rich	0.001 ± 0.0002	0.727 ± 0.0470	0.138 ± 0.0018		
PO_4-rich	0.265 ± 0.0064	0.000 ± 0.0005	0.010 ± 0.0001		
mixing point	0.187 ± 0.0046	0.200 ± 0.0004	0.070 ± 0.0000		
$Im_{4,1}$ CF_3SO_3-rich	0.000 ± 0.0002	0.636 ± 0.0074	0.195 ± 0.0009		
PO_4-rich	0.257 ± 0.0064	0.000 ± 0.0005	0.004 ± 0.0001	0.005 ± 0.0002	0.002 ± 0.0001
mixing point	0.196 ± 0.0048	0.200 ± 0.0006	0.010 ± 0.0000	0.005 ± 0.0000	0.005 ± 0.0000
$Im_{4,1}$ CF_3SO_3-rich	0.003 ± 0.0001	0.828 ± 0.0077	0.023 ± 0.0016	0.003 ± 0.0003	0.014 ± 0.0003
PO_4-rich	0.273 ± 0.0141	0.000 ± 0.0005	0.009 ± 0.0014	0.005 ± 0.0005	0.001 ± 0.0003
mixing point	0.196 ± 0.0048	0.200 ± 0.0004	0.030 ± 0.0000	0.005 ± 0.0000	0.005 ± 0.0000
$Im_{4,1}$ CF_3SO_3-rich	0.003 ± 0.0008	0.765 ± 0.0126	0.081 ± 0.0013	0.004 ± 0.0007	0.014 ± 0.0002
PO_4-rich	0.265 ± 0.0071	0.000 ± 0.0004	0.010 ± 0.0001	0.003 ± 0.0003	0.001 ± 0.0001
mixing point	0.197 ± 0.0048	0.200 ± 0.0005	0.050 ± 0.0000	0.005 ± 0.0000	0.005 ± 0.0000
$Im_{4,1}$ CF_3SO_3-rich	0.003 ± 0.0020	0.729 ± 0.0106	0.157 ± 0.0004	0.008 ± 0.0003	0.015 ± 0.0001
PO_4-rich	0.279 ± 0.0061	0.001 ± 0.0005	0.010 ± 0.0009	0.002 ± 0.0000	0.001 ± 0.0001
mixing point	0.191 ± 0.0047	0.203 ± 0.0029	0.068 ± 0.0003	0.005 ± 0.0000	0.005 ± 0.0000
$Im_{4,1}$ CF_3SO_3-rich	0.001 ± 0.0007	0.697 ± 0.0077	0.227 ± 0.0027	0.011 ± 0.0009	0.015 ± 0.0004

phase	w_{PO4} [g/g]	$w_{IM4,1\ CF3SO3}$ [g/g]	w_{PDO} [g/g]	w_{AA} [g/g]	w_{BA} [g/g]
PO_4-rich	0.179 ± 0.0046	0.008 ± 0.0005	0.006 ± 0.0001		
mixing point	0.112 ± 0.0028	0.284 ± 0.0044	0.010 ± 0.0001		
$Im_{4,1}$ CF_3SO_3-rich	0.001 ± 0.0005	0.786 ± 0.0094	0.013 ± 0.0003		
PO_4-rich	0.186 ± 0.0047	0.008 ± 0.0010	0.018 ± 0.0010		
mixing point	0.112 ± 0.0028	0.280 ± 0.0002	0.030 ± 0.0000		
$Im_{4,1}$ CF_3SO_3-rich	0.000 ± 0.0001	0.754 ± 0.0164	0.042 ± 0.0005		
PO_4-rich	0.189 ± 0.0047	0.002 ± 0.0005	0.026 ± 0.0023		
mixing point	0.112 ± 0.0028	0.280 ± 0.0011	0.050 ± 0.0005		
$Im_{4,1}$ CF_3SO_3-rich	0.002 ± 0.0011	0.686 ± 0.0305	0.077 ± 0.0020		
PO_4-rich	0.208 ± 0.0054	0.005 ± 0.0005	0.030 ± 0.0009		
mixing point	0.112 ± 0.0028	0.281 ± 0.0004	0.070 ± 0.0000		
$Im_{4,1}$ CF_3SO_3-rich	0.002 ± 0.0001	0.650 ± 0.0087	0.109 ± 0.0018		
PO_4-rich	0.170 ± 0.0044	0.006 ± 0.0004	0.007 ± 0.0007	0.006 ± 0.0004	0.003 ± 0.0004
mixing point	0.115 ± 0.0029	0.282 ± 0.0011	0.010 ± 0.0000	0.005 ± 0.0000	0.005 ± 0.0000
$Im_{4,1}$ CF_3SO_3-rich	0.003 ± 0.0004	0.737 ± 0.0069	0.012 ± 0.0006	0.002 ± 0.0008	0.006 ± 0.0008
PO_4-rich	0.176 ± 0.0046	0.004 ± 0.0004	0.021 ± 0.0002	0.006 ± 0.0001	0.003 ± 0.0001
mixing point	0.114 ± 0.0029	0.281 ± 0.0022	0.030 ± 0.0001	0.005 ± 0.0000	0.005 ± 0.0000
$Im_{4,1}$ CF_3SO_3-rich	0.001 ± 0.0007	0.688 ± 0.0091	0.047 ± 0.0005	0.004 ± 0.0002	0.007 ± 0.0002
PO_4-rich	0.190 ± 0.0054	0.001 ± 0.0004	0.026 ± 0.0006	0.005 ± 0.0002	0.002 ± 0.0001
mixing point	0.113 ± 0.0028	0.282 ± 0.0010	0.049 ± 0.0001	0.005 ± 0.0000	0.005 ± 0.0000
$Im_{4,1}$ CF_3SO_3-rich	0.003 ± 0.0013	0.634 ± 0.0071	0.080 ± 0.0020	0.004 ± 0.0001	0.009 ± 0.0003
PO_4-rich	0.197 ± 0.0049	0.002 ± 0.0005	0.029 ± 0.0006	0.004 ± 0.0001	0.001 ± 0.0001
mixing point	0.112 ± 0.0028	0.280 ± 0.0005	0.070 ± 0.0001	0.005 ± 0.0000	0.005 ± 0.0000
$Im_{4,1}$ CF_3SO_3-rich	0.001 ± 0.0001	0.619 ± 0.0087	0.114 ± 0.0023	0.007 ± 0.0002	0.009 ± 0.0003