

Supporting Information:

Salt-Induced Liquid–Liquid Phase Separation: Combined Experimental and Theoretical Investigation of Water–Acetonitrile–Salt Mixtures

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1 Experimental Methods

2 Chemicals

3 Deionized and doubly distilled water (Water, Sigma–Aldrich, Deionized) and acetonitrile
4 (Acetonitrile, Sigma–Aldrich, HPLC, gradient grade, $\geq 99.9\%$) were used in the experiments.
5 The salts were dried in a vacuum oven (80°C , 133Pa) for 4 hours prior to use. We studied
6 the following salts: lithium chloride (LiCl , Vetec, reagent grade), sodium chloride (NaCl ,
7 Sigma–Aldrich, ReagentPlus, 99%), potassium chloride (KCl , Sigma–Aldrich, anhydrous,
8 ReagentPlus, 99%), cesium chloride (CsCl , Aladdin, 99% , AR), potassium fluoride (KF , Al-
9 addin, 99.5% , GR), sodium bromide (NaBr , Sigma–Aldrich, anhydrous, ReagentPlus, 99%),
10 potassium bromide (KBr , Sigma–Aldrich, anhydrous, ReagentPlus, 99%), lithium sulfate
11 (Li_2SO_4 , Aladdin, 98.5% , anhydrous, titration), sodium sulphate (Na_2SO_4 , Vetec, 99.0% ,
12 reagent grade), and magnesium sulfate (MgSO_4 , Sigma–Aldrich, 99.5% , anhydrous).

13 Measurements

14 The samples were kept in Thermo HAAKE SC150-A5B circulating water bath (Newington,
15 U. S. A.) with a digital temperature-control unit to maintain the required temperature (25°C)
16 within $\pm 0.1^\circ\text{C}$ and the room temperature was also kept at 25°C by air conditioner.

17 Cloud point

18 Salts were added to the solvents with fixed water–acetonitrile ratio ($9.5:0.5$, $9:1$, $8.5:1.5$,
19 $8:2$, $7.5:2.5$, $7:3$, $6.5:3.5$, $6:4$, $5:5$, $4:6$, $3:7$, $2:8$, and $1:9$; V/V) until cloud points appeared.^{S1–S5}
20 The mass of water, acetonitrile, and salt were determined by Sartorius (BT 125D, Beijing,
21 China) with an accuracy of $\pm 0.00001\text{g}$. We have measured the cloud point of ten salts (LiCl ,
22 NaCl , KCl , CsCl , KF , NaBr , KBr , Na_2SO_4 , Li_2SO_4 , and MgSO_4) in the water–acetonitrile
23 solvents with an accuracy of $\pm 0.01\text{ g}$.

24 Component analysis of coexistence phases

25 For a given salt, a fixed mass of salt was added to a water–acetonitrile solvent (volume

26 ratio of water to acetonitrile is 1:1), and the mixture was held for at least 8 hours in the
27 circulating water bath at 25°C. We do the same operations and by changing the mass of the
28 salt (ranging from cloud point to saturation of the system). When the WAS system reached
29 phase equilibrium, the acetonitrile-rich phase and water-rich phase were taken out by sy-
30 ringing and their volume and mass were measured respectively. The content of acetonitrile
31 and water were determined by gas chromatography (GC, Thermo, Trace, GC, Ultra) in the
32 coexisting phases (acetonitrile-rich and water-rich phases). For the acetonitrile-rich phase,
33 the content of salts was determined by inductive coupled plasma optical emission spectrom-
34 eter (ICP-OES, Thermo, iCAP 6300 ICP-OES). As for the water-rich phase, the content
35 of the following six salts (NaCl, KCl, CsCl, NaBr, KBr, and Na₂SO₄) were determined by
36 mass. More specifically, the solutions were first kept in the oven (80°C) at ambient pressure
37 and then were dried in a vacuum oven (80°C, 133Pa) until the solvents were completely
38 evaporated. The contents of the remaining salts (LiCl, Li₂SO₄ and MgSO₄) were also de-
39 termined by ICP-OES. The mass fraction errors of GC and ICP-OES are -3.39% to 3.63%
40 and -2.90% to 4.09%, respectively.

41 **Solubility of salts**

42 For a given salt, excessive salt was added to water-acetonitrile solvents (volume ratios
43 of water to acetonitrile were 7:3, 6:4, 5:5, 4:6, and 3:7), and the mixtures were dissolved by
44 ultrasound and held for at least 8 hours in the circulating water bath at 25°C. The liquid
45 was taken out by the syringe. The remaining salt (for NaCl, KCl, CsCl, NaBr, KBr, and
46 Na₂SO₄) precipitated at the bottom was filtered by filter paper and then dried completely.
47 The mass of the dissolved salt is calculated as, the total input of salt minus the amount of
48 the precipitated salt. For the solubility of LiCl, Li₂SO₄, and MgSO₄, we refer to the work of
49 Meng et al.^{S6,S7} The specific procedures are as follows: adding doubly distilled water to the
50 test tube after removing the liquid, dissolving the precipitated salt with crystalloid water,
51 and then transferring them to volumetric flask. Finally, the mass of salts in the volumetric
52 flask (the remaining salt without crystalloid water) was determined by ICP-OES. The mass

53 of the dissolved salt is calculated as follows, the total input of salt minus the amount of the
 54 rest salt without crystalloid water.

55 Thermodynamics of the Water–Acetonitrile–Salt System

56 Alternative derivation of the hydration free energy

57 In this section, we provide an alternative derivation of the hydration free energy without
 58 using the combinatorial argument. We consider an incompressible mixture of water, ace-
 59 tonitrile and salt ions. For simplicity, we assume these entities have the same volume v .
 60 The ions can be either free or hydrated with hydration numbers p and m for the cations
 61 and anions, respectively. The water molecules can either hydrate the ions or be free. We
 62 further assume that the system volume V is not affected by the composition or hydration
 63 state and is given by an incompressibility constraint $V = (n_w + n_a + n_+ + n_-)v$. Thus, we
 64 only need to consider the ideal part of the Helmholtz free energy, since the excess part will
 65 be independent of composition and hence does not contribute to the free energy of mixing.
 66 For this consideration, we ignore the electrostatic interactions and the Born energy. Treating
 67 the free and hydrated ions as different species, the ideal part of the Helmholtz free energy is:

$$\begin{aligned}
 \frac{F^{\text{mix}}}{RT} &= \sum_i n_i \left(\frac{\mu_i^*}{RT} + \ln \frac{n_i v}{V} - 1 \right) \\
 &= n_{w,f} \left(\frac{\mu_w^*}{RT} + \ln \frac{n_{w,f} v}{V} - 1 \right) + n_a \left(\frac{\mu_a^*}{RT} + \ln \frac{n_a v}{V} - 1 \right) \\
 &\quad + n_{+,f} \left(\frac{\mu_{+,f}^*}{RT} + \ln \frac{n_{+,f} v}{V} - 1 \right) + n_{-,f} \left(\frac{\mu_{-,f}^*}{RT} + \ln \frac{n_{-,f} v}{V} - 1 \right) \\
 &\quad + n_{+,h} \left(\frac{\mu_{+,h}^*}{RT} + \ln \frac{n_{+,h} v}{V} - 1 \right) + n_{-,h} \left(\frac{\mu_{-,h}^*}{RT} + \ln \frac{n_{-,h} v}{V} - 1 \right)
 \end{aligned} \tag{S1}$$

68 n_i is the mole of species i , R is the universal gas constant, and T is the temperature. μ_w^* ,
 69 μ_a^* , $\mu_{+,f}^*$, $\mu_{-,f}^*$, $\mu_{+,h}^*$, and $\mu_{-,h}^*$ are the reference chemical potential of water, acetonitrile, free
 70 cations, free anions, hydrated cations, and hydrated anions, respectively. The subscript “h”

71 is for hydrated ions, and “f” is for free ions or free water molecules. The number of free
 72 water molecules and ions are $n_{w,f} = n_w - pn_{+,h} - mn_{-,h}$ and $n_{\pm,f} = (n_{\pm} - n_{\pm,h})$. The
 73 hydrating water molecules on each ion are indistinguishable, so they contribute $n_{+,h} \ln(p!)$
 74 and $n_{-,h} \ln(m!)$ respectively to $\mu_{+,h}^*$ and $\mu_{-,h}^*$.

75 Minimizing the free energy with respect to $n_{+,h}$ and $n_{-,h}$, subject to fixed total number
 76 of ions $n_{+,f} + n_{+,h} = n_{+,f}$ and $n_{-,f} + n_{-,h} = n_{-,f}$, we have

$$\ln \frac{n_{+,h}v}{V} - \ln \frac{(n_+ - n_{+,h})v}{V} - p \ln \frac{(n_w - pn_{+,h} - mn_{-,h})v}{V} = - \left(\frac{\mu_{+,h}^*}{RT} - p \frac{\mu_w^*}{RT} - \frac{\mu_{+,f}^*}{RT} \right) \quad (\text{S2})$$

77 and

$$\ln \frac{n_{-,h}v}{V} - \ln \frac{(n_- - n_{-,h})v}{V} - m \ln \frac{(n_w - pn_{+,h} - mn_{-,h})v}{V} = - \left(\frac{\mu_{-,h}^*}{RT} - m \frac{\mu_w^*}{RT} - \frac{\mu_{-,f}^*}{RT} \right) \quad (\text{S3})$$

78 where the right side of “=” in the parentheses is the hydration free energy.

$$f_+^{\text{hyd}} = \mu_{+,h}^* - p\mu_w^* - \mu_{+,f}^* \equiv E_+^{\text{hyd}} + RT \ln(p!) \quad (\text{S4})$$

79 and

$$f_-^{\text{hyd}} = \mu_{-,h}^* - m\mu_w^* - \mu_{-,f}^* \equiv E_-^{\text{hyd}} + RT \ln(m!) \quad (\text{S5})$$

80 We can write Eq S2 and S3 in the form of “chemical equilibrium constant”:

$$\frac{(n_{+,h}v/V)}{[(n_+ - n_{+,h})v/V][(n_w - pn_{+,h} - mn_{-,h})v/V]^p} = \exp\left(-\frac{f_+^{\text{hyd}}}{RT}\right) \quad (\text{S6})$$

81 and

$$\frac{(n_{-,h}v/V)}{[(n_- - n_{-,h})v/V][(n_w - pn_{+,h} - mn_{-,h})v/V]^m} = \exp\left(-\frac{f_-^{\text{hyd}}}{RT}\right) \quad (\text{S7})$$

82 Since these hydration free energies are very large and negative (the energies given in Table 1
 83 are at least order 100 RT ; the free energy will be of comparable magnitude), the equilibrium

84 constant is very large. So to a very good approximation, the fraction of free ions is negligible,
 85 and we can set $n_{\pm,f} = 0$ and $n_{\pm,h} = n_{\pm}$. The free energy is simplified to

$$\begin{aligned}
 \frac{F^{\text{mix}}}{RT} &= (n_w - pn_+ - mn_-) \frac{\mu_w^*}{RT} + n_a \frac{\mu_a^*}{RT} + n_+ \frac{\mu_{+,h}^*}{RT} + n_- \frac{\mu_{-,h}^*}{RT} \\
 &+ (n_w - pn_+ - mn_-) \ln \frac{(n_w - pn_+ - mn_-) v}{V} - (n_w - pn_+ - mn_-) + n_a \ln \frac{n_a v}{V} - n_a \\
 &+ n_+ \ln \frac{n_+ v}{V} - n_+ + n_- \ln \frac{n_- v}{V} - n_-
 \end{aligned} \tag{S8}$$

86 Because of electroneutrality, the mole numbers of cations and anions are not independent;
 87 they are related to the mole number of salts as $n_+ = \alpha n_s$ and $n_- = \beta n_s$. Taking the volume
 88 incompressibility constraint and electroneutrality into account, we get:

$$\begin{aligned}
 \frac{F^{\text{mix}}}{RT} &= [n_w - (p\alpha + m\beta) n_s] \left[\frac{\mu_w^*}{RT} + \ln \frac{n_w - (p\alpha + m\beta) n_s}{n_w + n_a + (\alpha + \beta) n_s} - 1 \right] \\
 &+ n_a \left[\frac{\mu_a^*}{RT} + \ln \frac{n_a}{n_w + n_a + (\alpha + \beta) n_s} - 1 \right] \\
 &+ n_s \left[\frac{\mu_{s,h}^*}{RT} + (\alpha + \beta) \ln \frac{n_s}{n_w + n_a + (\alpha + \beta) n_s} - (\alpha + \beta) \right]
 \end{aligned} \tag{S9}$$

89 where $\mu_{s,h}^* \equiv \alpha \mu_{+,h}^* + \beta \mu_{-,h}^* + RT (\alpha \ln \alpha + \beta \ln \beta)$

90 To isolate the hydration part of the free energy, we subtract the ideal part of mixing free
 91 ions with water and acetonitrile, which is

$$\begin{aligned}
 \frac{F^{\text{id}}}{RT} &= n_w \frac{\mu_w^*}{RT} + n_a \frac{\mu_a^*}{RT} + \alpha n_s \frac{\mu_{+,f}^*}{RT} + \beta n_s \frac{\mu_{-,f}^*}{RT} \\
 &+ n_a \ln \frac{n_a v}{V} - n_a + \alpha n_s \ln \frac{\alpha n_s v}{V} - \alpha n_s + \beta n_s \ln \frac{\beta n_s v}{V} - \beta n_s \\
 &+ n_w \ln \frac{n_w v}{V} - n_w
 \end{aligned} \tag{S10}$$

92 Taking the difference between Eq S8 and Eq S10 and substituting Eqs. S4-S5, we obtain

$$\begin{aligned}
\frac{F^{\text{hyd}}}{RT} &= n_s \left(\alpha \frac{E_+^{\text{hyd}}}{RT} + \beta \frac{E_-^{\text{hyd}}}{RT} + \alpha \ln p! + \beta \ln m! \right) \\
&+ [n_w - (p\alpha + m\beta) n_s] \ln \left[1 - (p\alpha + m\beta) \frac{n_s}{n_w} \right] \\
&- (p\alpha + m\beta) n_s \ln \frac{n_w v}{V} + (p\alpha + m\beta) n_s
\end{aligned} \tag{S11}$$

93 Substituting the volume from the incompressibility constraint, and noting that for an incom-
94 pressible system, the hydration Gibbs free energy is the same as the hydration Helmholtz
95 free energy, we recover Eq 10 in the main text.

96 **Excess free energy for water-acetonitrile mixture**

97 The water-acetonitrile excess free energy of mixing can be written as

$$G^{\text{w/a}} = n_w RT \ln \gamma_w^{\text{w/a}} + n_a RT \ln \gamma_a^{\text{w/a}} \tag{S12}$$

98 where $\gamma_w^{\text{w/a}}$ and $\gamma_a^{\text{w/a}}$ are the activity coefficients of water and acetonitrile. We define $g^{\text{w/a}} =$
99 $\omega \ln \gamma_w^{\text{w/a}} + (1 - \omega) \ln \gamma_a^{\text{w/a}}$, where ω is the water mole fraction in the liquid $\omega = \frac{n_w}{n_w + n_a}$.
100 For the expression of $g^{\text{w/a}}$, we compared the Villamañán's model^{S8} and Shealy's model^{S9}
101 in Figure S1 with French's experimental data (25°C),^{S10} the former fits better. Thus, we
102 choose Villamañán's model, which is given by

$$\begin{aligned}
\frac{g^{\text{w/a}}}{\omega(1 - \omega)} &= \mathcal{A}\omega + \mathcal{B}(1 - \omega) + [\mathcal{C}\omega + \mathcal{D}(1 - \omega)]\omega(1 - \omega) + [\mathcal{E}\omega + \mathcal{F}(1 - \omega)][\omega(1 - \omega)]^2 \\
&+ [\mathcal{G}\omega + \mathcal{H}(1 - \omega)][\omega(1 - \omega)]^3
\end{aligned} \tag{S13}$$

103 The values of parameters \mathcal{A} to \mathcal{H} are listed in Table S1.

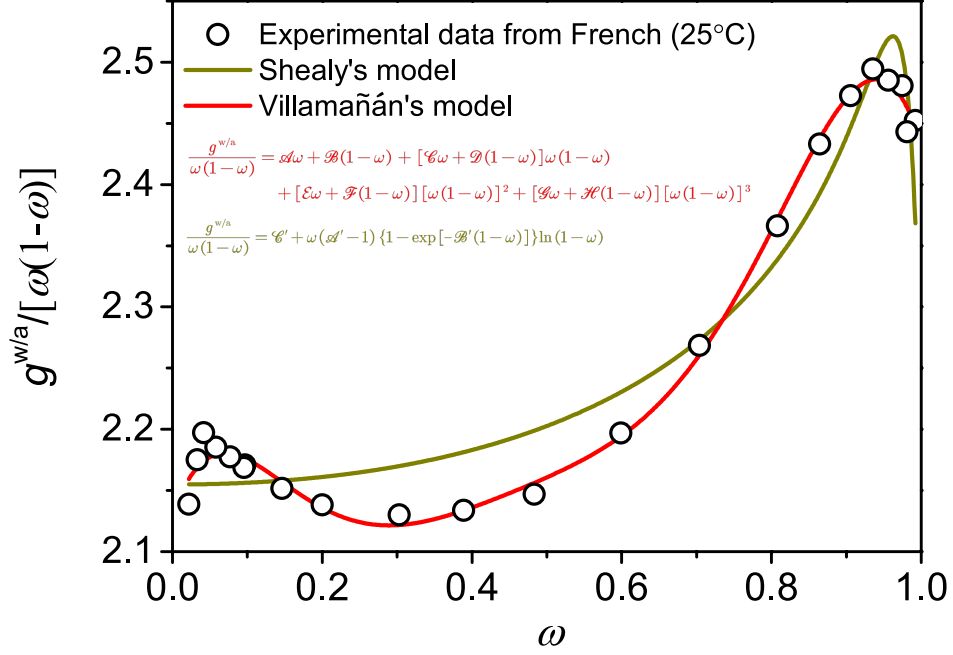


Figure S1: Experimental and fitting data for excess molar Gibbs free energy of water–acetonitrile mixture.

Table S1: Fitting Parameters in Eq (S13)

\mathcal{A}	\mathcal{B}	\mathcal{C}	\mathcal{D}	\mathcal{E}	\mathcal{F}	\mathcal{G}	\mathcal{H}
2.433	2.129	2.294	1.471	-19.157	-19.55	31.27	47.921

104 The final expression of $G^{w/a}$ is

$$G^{w/a} = (n_w + n_a) RT g^{w/a}(\omega) \quad (\text{S14})$$

105 **Electrostatic free energy from mean-spherical-approximation (MSA)**

106 For the equal ion sizes, invoking charge neutrality, the electrostatic part of the free energy
107 from the MSA theory^{S11} ($G_{\text{MSA}}^{\text{ele}}$) is written as

$$G_{\text{MSA}}^{\text{ele}} = -RT \frac{V}{\pi} \Theta^3 \left(\frac{2}{3} + \Theta a_0 \right) \quad (\text{S15})$$

108 The screening parameter Θ satisfies $\Theta(1 + \Theta\sigma) = \kappa/2$, where κ is the inverse Debye screen-
109 ing length given by Eq 12 in the main text for a single solvent. At present, a systematic
110 modification of MSA for binary solvent with different dielectric constant for each component
111 is not available. We thus make the ad hoc approximation by using a simple volume-fraction
112 average of the dielectric constant of the two liquids.

113 **Total free energy and chemical potential**

114 With expressions of G^{id} , G^{hyd} , G^{ele} , G^{Born} , and $G^{w/a}$. We have the total Gibbs free energy
115 of the WAS system $G_{\text{DH}}(n_w, n_a, n_s)$ and $G_{\text{MSA}}(n_w, n_a, n_s)$ based on Debye-Hückel (DH) and

116 based on MSA, respectively:

$$\begin{aligned}
\frac{G_{\text{DH}}(n_w, n_a, n_s)}{RT} &= n_w \left(\frac{\mu_w^*}{RT} + \ln x_w \right) + n_a \left(\frac{\mu_a^*}{RT} + \ln x_a \right) + n_s \left[\frac{\mu_s^*}{RT} + (\alpha + \beta) \ln x_s \right] \\
&+ n_w \ln \left[1 - (p\alpha + m\beta) \frac{n_s}{n_w} \right] \\
&- (p\alpha + m\beta) n_s \ln \frac{n_w - (p\alpha + m\beta) n_s}{n_w + n_a + (\alpha + \beta) n_s} + (p\alpha + m\beta) n_s \\
&- \frac{v_w}{4\pi a_0^3} (n_w + \tau n_a) \left[\ln(1 + \kappa a_0) - \kappa a_0 + \frac{1}{2} (\kappa a_0)^2 \right] \\
&+ \frac{N_{\text{av}} e^2 (\alpha z_+^2 + \beta z_-^2) n_s}{8\pi \epsilon_0 a_0 RT} \frac{n_w + \tau n_a}{n_w \epsilon_w + \tau n_a \epsilon_a} \\
&+ (n_w + n_a) g^{w/a}(\omega)
\end{aligned} \tag{S16}$$

117

$$\begin{aligned}
\frac{G_{\text{MSA}}(n_w, n_a, n_s)}{RT} &= n_w \left(\frac{\mu_w^*}{RT} + \ln x_w \right) + n_a \left(\frac{\mu_a^*}{RT} + \ln x_a \right) + n_s \left[\frac{\mu_s^*}{RT} + (\alpha + \beta) \ln x_s \right] \\
&+ n_w \ln \left[1 - (p\alpha + m\beta) \frac{n_s}{n_w} \right] \\
&- (p\alpha + m\beta) n_s \ln \frac{n_w - (p\alpha + m\beta) n_s}{n_w + n_a + (\alpha + \beta) n_s} + (p\alpha + m\beta) n_s \\
&- \frac{v_w (n_w + \tau n_a)}{16a_0^3 \pi} \left(\frac{1}{3} + \sqrt{2a_0 \kappa + 1} \right) (-1 + \sqrt{2a_0 \kappa + 1})^3 \\
&+ \frac{N_{\text{av}} e^2 (\alpha z_+^2 + \beta z_-^2) n_s}{8\pi \epsilon_0 a_0 RT} \frac{n_w + \tau n_a}{n_w \epsilon_w + \tau n_a \epsilon_a} \\
&+ (n_w + n_a) g^{w/a}(\omega)
\end{aligned} \tag{S17}$$

118 where we have redefined the reference chemical potential of the salt to absorb the hydration

119 energy:

$$\frac{\mu_s^*}{RT} = \frac{\mu_{s,f}^*}{RT} + \alpha \frac{E_+^{\text{hyd}}}{RT} + \beta \frac{E_-^{\text{hyd}}}{RT} + \alpha \ln p! + \beta \ln m! \tag{S18}$$

120 and τ stands for the volume ratio of acetonitrile to water $\tau = v_a/v_w$ in the electrostatic part

121 of the free energy. The chemical potential of the different species are then obtained from

122 $\mu_w = \frac{\partial G}{\partial n_w}$, $\mu_a = \frac{\partial G}{\partial n_a}$ and $\mu_s = \frac{\partial G}{\partial n_s}$. For convenience, we represent the composition using the

123 mole fraction of water in the binary liquid $\omega = n_w/(n_w + n_a)$, and the molar ratio of salt to
 124 water $r = n_s/n_w$.

125 For the chemical potentials of water, acetonitrile and salt we write them in the following
 126 form

$$\mu_i = \mu_i^{\text{id}} + \mu_i^{\text{hyd}} + \mu_i^{\text{ele}} + \mu_i^{\text{Born}} + \mu_i^{\text{w/a}} \quad (\text{S19})$$

127 where $i=w, a, \text{ or } s$. μ_i^{id} , μ_i^{hyd} , μ_i^{ele} , μ_i^{Born} , and $\mu_i^{\text{w/a}}$ refer to the chemical potential contribu-
 128 tion from ideal mixing, hydration effect, electrostatic interactions, Born energy, and excess
 129 free energy of the water–acetonitrile mixture. $\mu_i^{\text{ele(DH)}}$ and $\mu_i^{\text{ele(MSA)}}$ are the electrostatic
 130 interaction contributions calculated by DH and MSA.

131 For the chemical potential of water, we have

$$\frac{\mu_w^{\text{id}}}{RT} = \frac{\mu_w^*}{RT} + \ln \frac{\omega}{1 + (\alpha + \beta) \omega r} \quad (\text{S20})$$

$$\frac{\mu_w^{\text{hyd}}}{RT} = \ln [1 - (p\alpha + m\beta) r] + \frac{(p\alpha + m\beta) \omega r}{1 + (\alpha + \beta) \omega r} \quad (\text{S21})$$

$$\frac{\mu_w^{\text{ele(DH)}}}{RT} = -\frac{v_w}{4\pi a_0^3} \left[\ln(1 + \kappa a_0) - \kappa a_0 + \frac{1}{2} (\kappa a_0)^2 \right] + \frac{v_w}{8\pi a_0^3} \frac{(\kappa a_0)^3 [\omega + \tau(1 - \omega)] \epsilon_w}{1 + \kappa a_0 \omega \epsilon_w + \tau(1 - \omega) \epsilon_a} \quad (\text{S22})$$

$$\frac{\mu_w^{\text{ele(MSA)}}}{RT} = \left[\frac{v_w (-1 + \sqrt{2a_0\kappa + 1})}{24\pi a_0^3} - \frac{v_w \kappa \tau (1 - \omega) (\epsilon_a - \epsilon_w)}{8\pi a_0^2 \omega \epsilon_w + \tau (1 - \omega) \epsilon_a} \right] (-1 + \sqrt{2a_0\kappa + 1})^2 \quad (\text{S23})$$

$$\frac{\mu_w^{\text{Born}}}{RT} = \frac{N_{\text{av}} e^2 (\alpha z_+^2 + \beta z_-^2) \tau \omega r (1 - \omega) (\epsilon_a - \epsilon_w)}{8\pi \epsilon_0 a_0 RT [\omega \epsilon_w + \tau (1 - \omega) \epsilon_a]^2} \quad (\text{S24})$$

$$\frac{\mu_w^{\text{w/a}}}{RT} = g^{\text{w/a}} + (1 - \omega) \frac{dg^{\text{w/a}}}{d\omega} \quad (\text{S25})$$

137 For the chemical potential of acetonitrile, we have

$$\frac{\mu_a^{\text{id}}}{RT} = \frac{\mu_a^*}{RT} + \ln \frac{1 - \omega}{1 + (\alpha + \beta) \omega r} \quad (\text{S26})$$

$$\frac{\mu_a^{\text{hyd}}}{RT} = \frac{(p\alpha + m\beta) \omega r}{1 + (\alpha + \beta) \omega r} \quad (\text{S27})$$

$$\frac{\mu_a^{\text{le(DH)}}}{RT} = -\frac{\tau v_w}{4\pi a_0^3} \left[\ln(1 + \kappa a_0) - \kappa a_0 + \frac{1}{2} (\kappa a_0)^2 \right] + \frac{v_w}{8\pi a_0^3} \frac{(\kappa a_0)^3 [\omega + \tau(1 - \omega)] \tau \epsilon_a}{1 + \kappa a_0 \omega \epsilon_w + \tau(1 - \omega) \epsilon_a} \quad (\text{S28})$$

$$\frac{\mu_a^{\text{le(MSA)}}}{RT} = \left[\frac{\tau v_w (-1 + \sqrt{2a_0\kappa + 1})}{24\pi a_0^3} + \frac{v_w \kappa}{8\pi a_0^2} \frac{\tau \omega (\epsilon_a - \epsilon_w)}{\omega \epsilon_w + \tau(1 - \omega) \epsilon_a} \right] (-1 + \sqrt{2a_0\kappa + 1})^2 \quad (\text{S29})$$

$$\frac{\mu_a^{\text{Born}}}{RT} = \frac{N_{\text{av}} e^2 (\alpha z_+^2 + \beta z_-^2)}{8\pi \epsilon_0 a_0 RT} \frac{\tau \omega^2 r (\epsilon_w - \epsilon_a)}{[\omega \epsilon_w + \tau(1 - \omega) \epsilon_a]^2} \quad (\text{S30})$$

$$\frac{\mu_a^{\text{w/a}}}{RT} = g^{\text{w/a}} - \omega \frac{dg^{\text{w/a}}}{d\omega} \quad (\text{S31})$$

For the chemical potential of salt, we have

$$\frac{\mu_s^{\text{id}}}{RT} = \frac{\mu_s^*}{RT} + (\alpha + \beta) \ln \frac{\omega r}{1 + (\alpha + \beta) \omega r} \quad (\text{S32})$$

$$\frac{\mu_s^{\text{hyd}}}{RT} = -(\alpha + m\beta) \ln \frac{\omega - (\alpha + m\beta) \omega r}{1 + (\alpha + \beta) \omega r} + \frac{(\alpha + m\beta) (\alpha + \beta) \omega r}{1 + (\alpha + \beta) \omega r} \quad (\text{S33})$$

$$\frac{\mu_s^{\text{le(DH)}}}{RT} = -\frac{v_w}{8\pi a_0^3} \frac{(\kappa a_0)^3 \omega + \tau(1 - \omega)}{1 + \kappa a_0 \omega r} \quad (\text{S34})$$

$$\frac{\mu_s^{\text{le(MSA)}}}{RT} = -\frac{v_w \kappa}{8\pi a_0^2} \frac{\omega + \tau(1 - \omega)}{\omega r} (-1 + \sqrt{2a_0\kappa + 1})^2 \quad (\text{S35})$$

$$\frac{\mu_s^{\text{Born}}}{RT} = \frac{N_{\text{av}} e^2 (\alpha z_+^2 + \beta z_-^2)}{8\pi \epsilon_0 a_0 RT} \frac{\omega + \tau(1 - \omega)}{\omega \epsilon_w + \tau(1 - \omega) \epsilon_a} \quad (\text{S36})$$

The inverse Debye screening length κ written in terms of ω and r is

$$\kappa^2 = \frac{e^2}{\epsilon_0 k_B T} \frac{\alpha z_+^2 + \beta z_-^2}{v_w} \frac{\omega r}{\omega \epsilon_w + \tau(1 - \omega) \epsilon_a} \quad (\text{S37})$$

Critical point

The critical point is calculated from a semi-open system thermodynamic potential. We

consider one composition variable $c = \frac{n_s}{n_w + n_a}$ as in a canonical ensemble and obtain its

equilibrium value in terms of the other variable ω . We consider a semi-open system with the

152 following free energy normalized to $(n_w + n_a)$.

$$\varphi = g(\omega, c) - c\mu_s \quad (\text{S38})$$

153 where $g(\omega, c)$ is the Gibbs free energy normalized to $(n_w + n_a)$, it is just the right hand side
154 of Eq (??). μ_s is variable to c . Minimizing this free energy with respect to c , we have

$$g'_c - \mu_s = 0 \quad (\text{S39})$$

155 We perform the derivative on both sides of the equation

$$g''_{c\omega} + g''_{cc} \frac{dc}{d\omega} = 0 \quad (\text{S40})$$

156

$$\frac{dc}{d\omega} = -\frac{g''_{c\omega}}{g''_{cc}} \quad (\text{S41})$$

157 For the first derivate of the grand free energy with respect to ω , we have

$$\frac{d\varphi}{d\omega} = g'_\omega + g'_c \frac{dc}{d\omega} - \mu_s \frac{dc}{d\omega} \quad (\text{S42})$$

158 Substituting Eq (S39) into Eq (S42)

$$\frac{d\varphi}{d\omega} = g'_\omega \quad (\text{S43})$$

159 The second derivative is

$$\frac{d^2\varphi}{d\omega^2} = g''_{\omega\omega} + g''_{\omega c} \frac{dc}{d\omega} \quad (\text{S44})$$

160 The third derivative is

$$\frac{d^3\varphi}{d\omega^3} = g'''_{\omega\omega\omega} + 3g'''_{\omega\omega c} \frac{dc}{d\omega} + 3g'''_{\omega cc} \left(\frac{dc}{d\omega}\right)^2 + g'''_{ccc} \left(\frac{dc}{d\omega}\right)^3 \quad (\text{S45})$$

161 The critical point is calculated by $\frac{d^2\varphi}{d\omega^2} = \frac{d^3\varphi}{d\omega^3} = 0$, and we use the relation $r = \frac{c}{\omega}$ to calculate
 162 r .

163 **Comparison of theoretical phase diagrams calculated by DH vs.**
 164 **MSA**

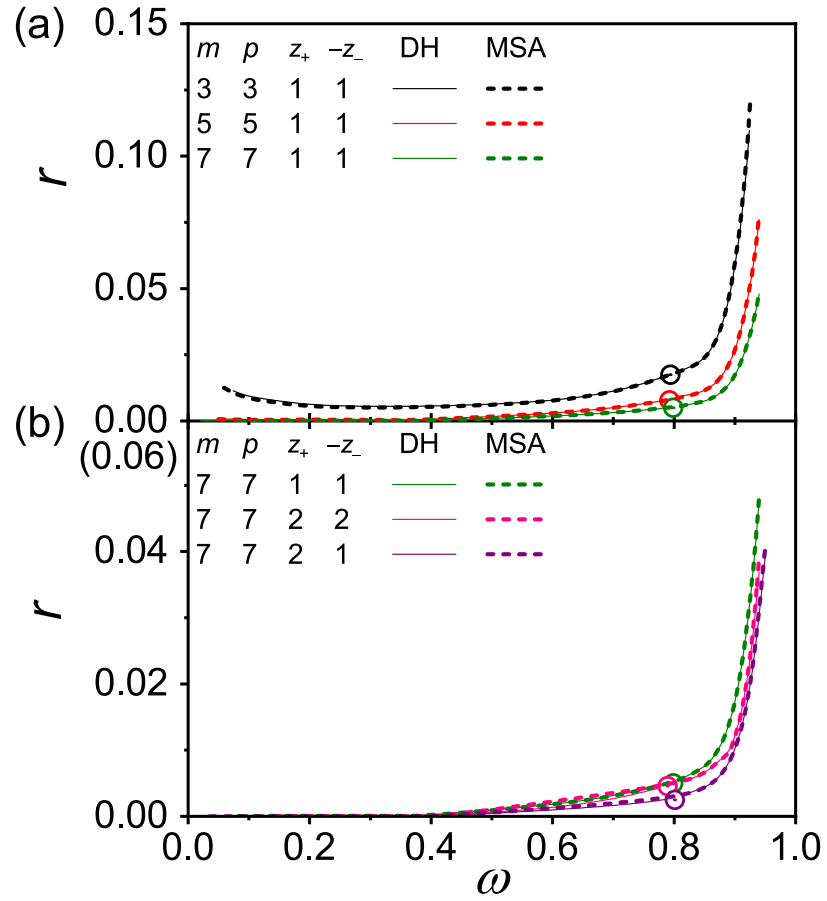


Figure S2: Comparison of theoretical phase diagrams of the WAS system calculated by the Debye-Hückel theory (DH) and the mean spherical approximation theory (MSA) for Debye radius $a_0 = 4.56$.

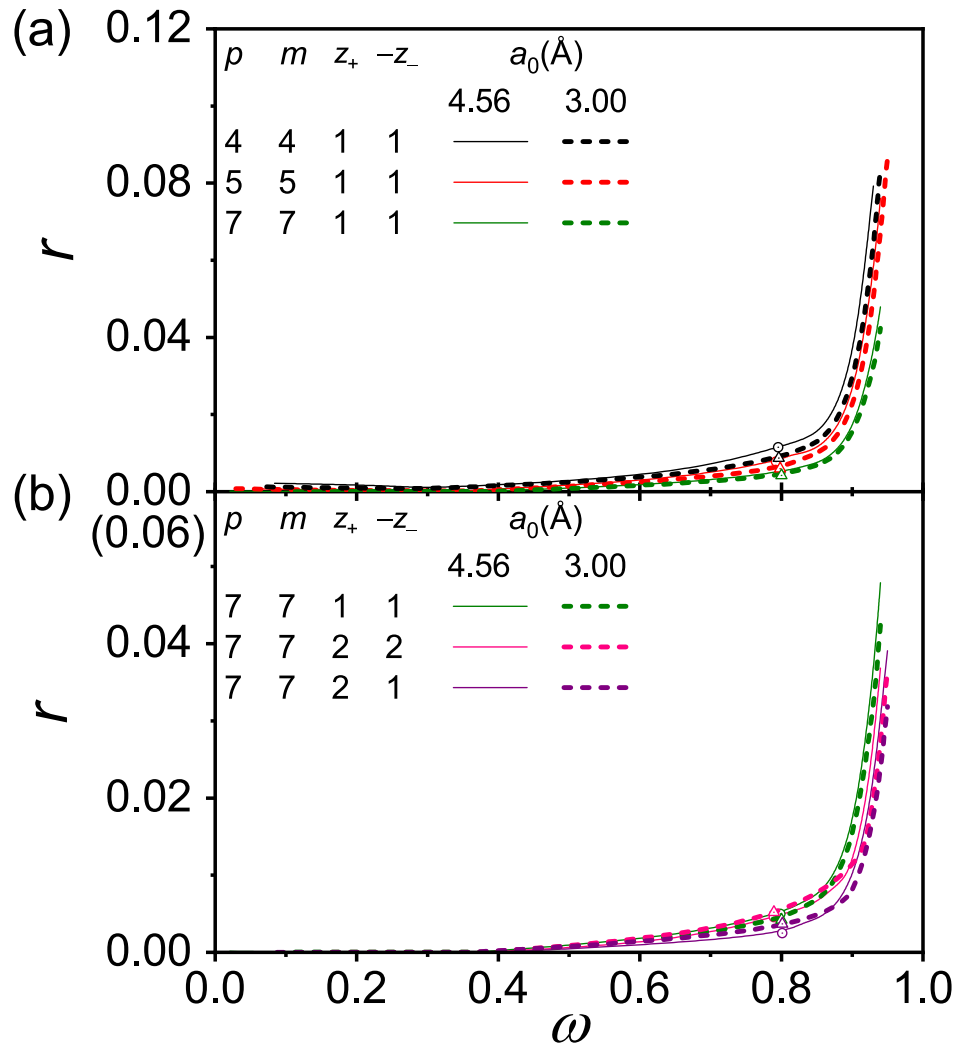


Figure S3: Comparison of theoretical phase diagrams of the WAS system calculated by using Debye radius of 4.56 Å and 3.00 Å. Circles are the critical points for 4.56 Å and triangles for 3.00 Å.

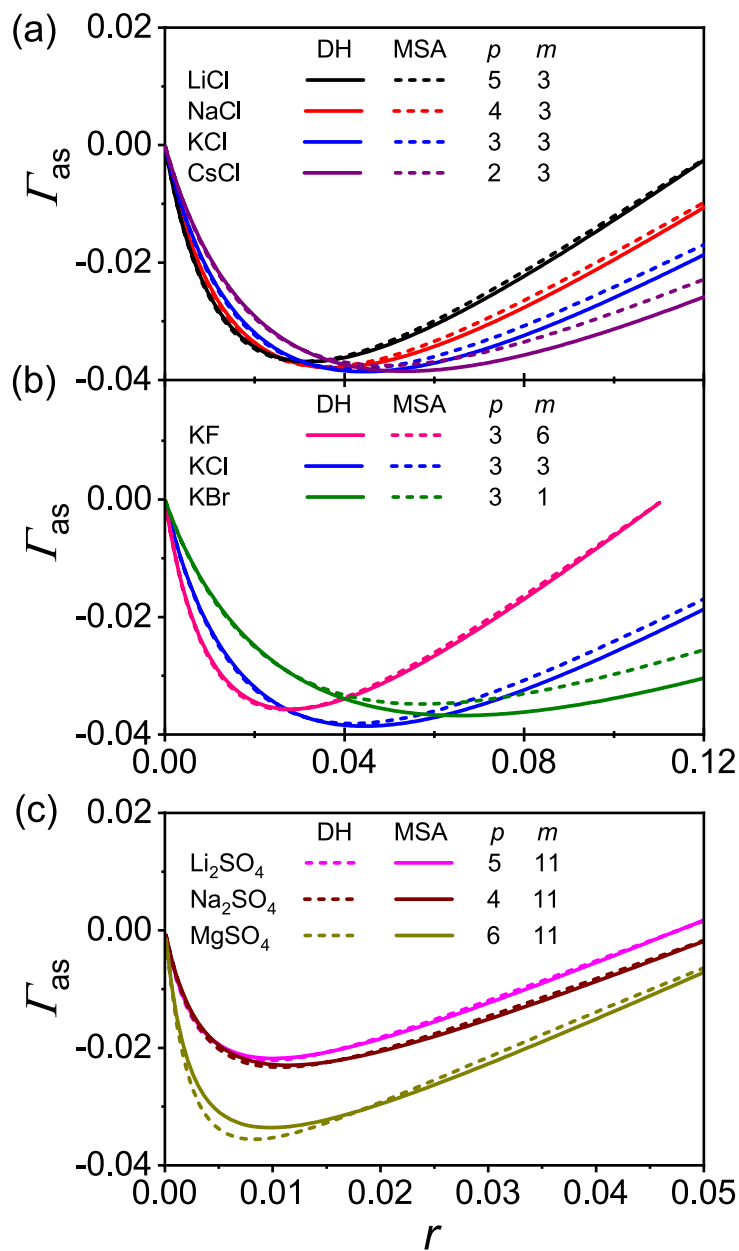


Figure S4: Binding coefficient between acetonitrile and salt Γ_{as} as a function of salt concentration r at $\omega = 0.99$.

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