

Supplementary Material

Composition-dependence of relative static permittivity in ePPC-SAFT for mixed-solvent alkali halides

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|---|----|
| Figure S1. Comparisons of MIAC of (water + methanol + NaCl) calculated using the ePPC-SAFT with the 4 RSP models at 298.15 K and 0.1 MPa and experimental data. Literature of the experimental data is as listed and explained in Section 2.2 and Ref [17]. | 4 |
| Figure S2. Comparisons of MIAC of (water + methanol + NaCl) calculated using the ePPC-SAFT with RSP-2 (blue dashed lines) and RSP-4 (red dash-dotted lines) at 308.15 K and 318.15 K and 0.1 MPa and experimental data (symbols). Literature of the experimental data is as listed and explained in Section 2.2 and Ref [17]. | 5 |
| Figure S3. Comparisons of the MIAC of (water + methanol + KCl), (water + methanol + LiCl), (water + methanol + RbCl), (water + methanol + NaF), (water + ethanol + NaCl), (water + ethanol + KCl), (water + ethanol + CsCl), and (water + ethanol + NaF) calculated using the ePPC-SAFT with RSP-4 (red dash-dotted lines) at 298.15 K and 0.1 MPa and experimental data (symbols represent salt-free weight fraction of the alcohol, percentages noted in the sub-graphs). Literature of the experimental data is as listed and explained in Section 2.2 and Ref [17]. | 6 |
| Figure S4. Deviations of the MIAC calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + NaCl). | 8 |
| Figure S5. Deviations of the VLE pressure calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + NaCl). | 8 |
| Figure S6. Deviations of the density calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + NaCl). | 9 |
| Figure S7. Deviations of the MIAC calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + KCl). Deviations are not plotted against T as all data are at 298.15 K. | 9 |
| Figure S8. Deviations of the VLE calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + KCl). Deviations are not plotted against T as all data are at 298.15 K. | 10 |
| Figure S9. Deviations of the density calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + KCl). Deviations are not plotted against T as all data are at 298.15 K. | 10 |
| Figure S10. Deviations of the MIAC calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + LiCl). Deviations are not plotted against T as all data are at 298.15 K. | 11 |
| Figure S11. Deviations of the VLE calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + LiCl). Deviations are not plotted against T as all data are at 333.15 K. | 11 |
| Figure S12. Deviations of the density calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + LiCl). | 11 |
| Figure S13. Deviations of the MIAC calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + RbCl). Deviations are not plotted against T as all data are at 298.15 K. | 12 |

| | |
|---|----|
| Figure S14. Deviations of the MIAC calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + NaF). Deviations are not plotted against T as all data are at 298.15 K. | 12 |
| Figure S15. Deviations of the VLE calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + NaBr). Deviations are not plotted against T as all data are at 298.15 K..... | 12 |
| Figure S16. Deviations of the density calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + NaBr). | 13 |
| Figure S17. Deviations of the MIAC calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + NaCl). | 13 |
| Figure S18. Deviations of the VLE calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + NaCl). | 14 |
| Figure S19. Deviations of the density calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + NaCl). | 14 |
| Figure S20. Deviations of the MIAC calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + KCl). Deviations are not plotted against T as all data are at 298.15 K..... | 15 |
| Figure S21. Deviations of the VLE calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + KCl). | 15 |
| Figure S22. Deviations of the density calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + KCl). | 16 |
| Figure S23. Deviations of the MIAC calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + CsCl). Deviations are not plotted against T as all data are at 298.15 K. | 16 |
| Figure S24. Deviations of the density calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + CsCl). | 17 |
| Figure S25. Deviations of the MIAC calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + NaF). Deviations are not plotted against T as all data are at 298.15 K. | 17 |
| Figure S26. Deviations of the VLE calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + KBr). Deviations are not plotted against T as all data are within a very small range close to 355 K. | 17 |
| Figure S27. Deviations of the density calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + KBr). Deviations are not plotted against T as all data are at 298.15 K. | 18 |
| Figure S28. Deviations of the VLE calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + NaI). Deviations are not plotted against T as all data are at 298.15 K. | 18 |
| Figure S29. Deviations of the density calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + NaI). | 18 |
| Figure S30. Deviations of the VLE calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + KI). Deviations are not plotted against T and x_{alcohol0} as all data are within a very small range close to 355 K and at $x_{\text{alcohol0}} = 0.309$ | 19 |
| Figure S31. Deviations of the density calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + KI). | 19 |
| Figure S32. Contributions to (a) $\ln \gamma_{\pm}$, (b) $\ln \gamma_w$, and (c) $\ln \gamma_{\text{alc}}$ of the terms (association, MSA, Born, and others) of ePPC-SAFT combined with RSP-1 for (water + methanol + NaCl) at 298.15 K and 0.1 MPa. The symbols and lines are in gradient colors for salt-free alcohol mole fraction (0%, 20%, 40%, 60%, 80%, 100%), with the higher alcohol compositions in lighter interior colors. | 20 |
| Figure S33. Contributions to (a) $\ln \gamma_{\pm}$, (b) $\ln \gamma_w$, and (c) $\ln \gamma_{\text{alc}}$ of the terms (association, MSA, Born, and others) of ePPC-SAFT combined with RSP-3 for (water + methanol + NaCl) at 298.15 K and 0.1 MPa. The symbols and lines are in gradient colors for salt-free alcohol mole fraction (0%, 20%, 40%, 60%, 80%, 100%), with the higher alcohol compositions in lighter interior colors. | 21 |
| Figure S34. Contributions to (a) $\ln \gamma_{\pm}$, (b) $\ln \gamma_w$, and (c) $\ln \gamma_{\text{alc}}$ of the terms (association, MSA, Born, and others) of ePPC-SAFT combined with RSP-4 for (water + methanol + NaCl) at 298.15 K and 0.1 MPa. The symbols and lines are in gradient colors for salt-free alcohol mole fraction (0%, 20%, 40%, 60%, 80%, 100%), with the higher alcohol compositions in lighter interior colors. | 22 |

| | |
|--|----|
| Table S1. Ion-specific pseudo-unary parameters and binary interaction parameters of the ePPC-SAFT model with constant water RSP for the aqueous alkali chloride solutions. The parameters that are preset (not regressed) are marked as bold and italic..... | 3 |
| Table S2. Average absolute percentage deviations (AAPDs) and maximum absolute percentage deviations (MAPDs) for MIAC, VLE, and density of aqueous alkali chloride solutions calculated using the ePPC-SAFT with constant water RSP from experimental data..... | 3 |
| Table S3. Summary density experimental datasets of mixed-solvent electrolyte solutions used in the parameterization. | 3 |
| Table S4. Deviations of MIAC, VLE, and density calculated using the ePPC-SAFT model with the 4 RSP models. The numbers outside the parenthesis are AAPDs and AAADs. The numbers in the parenthesis are maximum absolute percentage deviations (MAPDs) and maximum absolute absolute deviations (MAADs). The MIAC, VLE p, and density deviations are in percentage. The VLE y absolute deviations are absolute deviations multiplied by 100. | 7 |
| Table S5. Summary of the (alcohol + salt) MIAC and osmotic coefficient (OC) datasets used in the comparisons..... | 22 |

Table S1. Ion-specific pseudo-unary parameters and binary interaction parameters of the ePPC-SAFT model with constant water RSP for the aqueous alkali chloride solutions. The parameters that are preset (not regressed) are marked as bold and italic.

| | N_{site} | $\sigma_{\text{Pauling}} (\text{\AA})^a$ | r_{HS} | r_{MSA} | ϵ^{AB}/k (K) | β^{AB}^b | $\sigma_{\text{Born}} (\text{\AA})^c$ | $w_{\text{cat-ani}}$ |
|-----------------|-------------------|--|-----------------|------------------|------------------------------|-----------------------|---------------------------------------|----------------------|
| Na ⁺ | 7 | 1.9 | 0.9642 | 2.000 | 1777 | 0.044394 | 3.235 | 0.6406 |
| K ⁺ | 7 | 2.66 | 0.9642 | 1.569 | 988.5 | 0.044394 | 3.897 | 0.9288 |
| Rb ⁺ | 7 | 2.96 | 0.9642 | 1.341 | 1145 | 0.044394 | 4.169 | 0.9092 |
| Cs ⁺ | 7 | 3.38 | 0.9642 | 1.000 | 1208 | 0.044394 | 4.482 | 0.8406 |
| Cl ⁻ | 6 | 3.62 | 0.9642 | 1.254 | 1225 | 0.044394 | 4.512 | - |

Note: ^a The diameter values are obtained from Ref [1].

^b The parameters are set constant to the values of water.

^c The Born diameter are calculated using the Gibbs energy of solvation [2] using the procedure introduced in our previous work [3].

Table S2. Average absolute percentage deviations (AAPDs) and maximum absolute percentage deviations (MAPDs) for MIAC, VLE, and density of aqueous alkali chloride solutions calculated using the ePPC-SAFT with constant water RSP from experimental data.

| Water + | MIAC | | VLE | | Density | |
|---------|----------|----------|----------|----------|----------|----------|
| | AAPD (%) | MAPD (%) | AAPD (%) | MAPD (%) | AAPD (%) | MAPD (%) |
| NaCl | 1.0 | 5.8 | 1.0 | 2.1 | 0.53 | 2.9 |
| KCl | 1.4 | 3.8 | 1.5 | 3.3 | 0.26 | 1.5 |
| RbCl | 0.75 | 1.2 | 1.2 | 3.5 | 0.30 | 1.5 |
| CsCl | 1.3 | 6.2 | 1.2 | 5.4 | 0.67 | 3.4 |

Table S3. Summary density experimental datasets of mixed-solvent electrolyte solutions used in the parameterization.

| | No. of datasets | No. of data points | T (K) | Reference |
|-------------------------|-----------------|--------------------|-----------------|-----------|
| Water + Methanol + NaCl | 4 | 173 | 288.15 ~ 328.15 | [4–7] |
| Water + Methanol + KCl | 2 | 20 | 283.15 ~ 328.15 | [4,8] |
| Water + Methanol + NaBr | 1 | 112 | 288.15 ~ 318.15 | [9] |
| Water + Methanol + LiCl | 1 | 81 | 298.15 ~ 308.15 | [10] |
| Water + Ethanol + NaCl | 2 | 82 | 298.15 ~ 313.15 | [11,12] |
| Water + Ethanol + KCl | 3 | 69 | 298.15 ~ 313.15 | [11–13] |

| | | | | |
|------------------------|---|----|-----------------|---------|
| Water + Ethanol + CsCl | 1 | 50 | 298.15 ~ 308.15 | [14] |
| Water + Ethanol + KBr | 1 | 10 | 298.15 | [11] |
| Water + Ethanol + NaI | 1 | 33 | 293.15 ~ 303.15 | [15] |
| Water + Ethanol + KI | 2 | 22 | 298.15 ~ 313.15 | [11,16] |

In the Supplementary Material, RSP-1 refers to RSP-TVn in the main text, RSP-2 refers to RSP-TVn-Alc, RSP-3 refers to RSP-TVn-Ion, and RSP-4 refers to RSP-TVn-AlcIon. We prefer this simplified naming system.

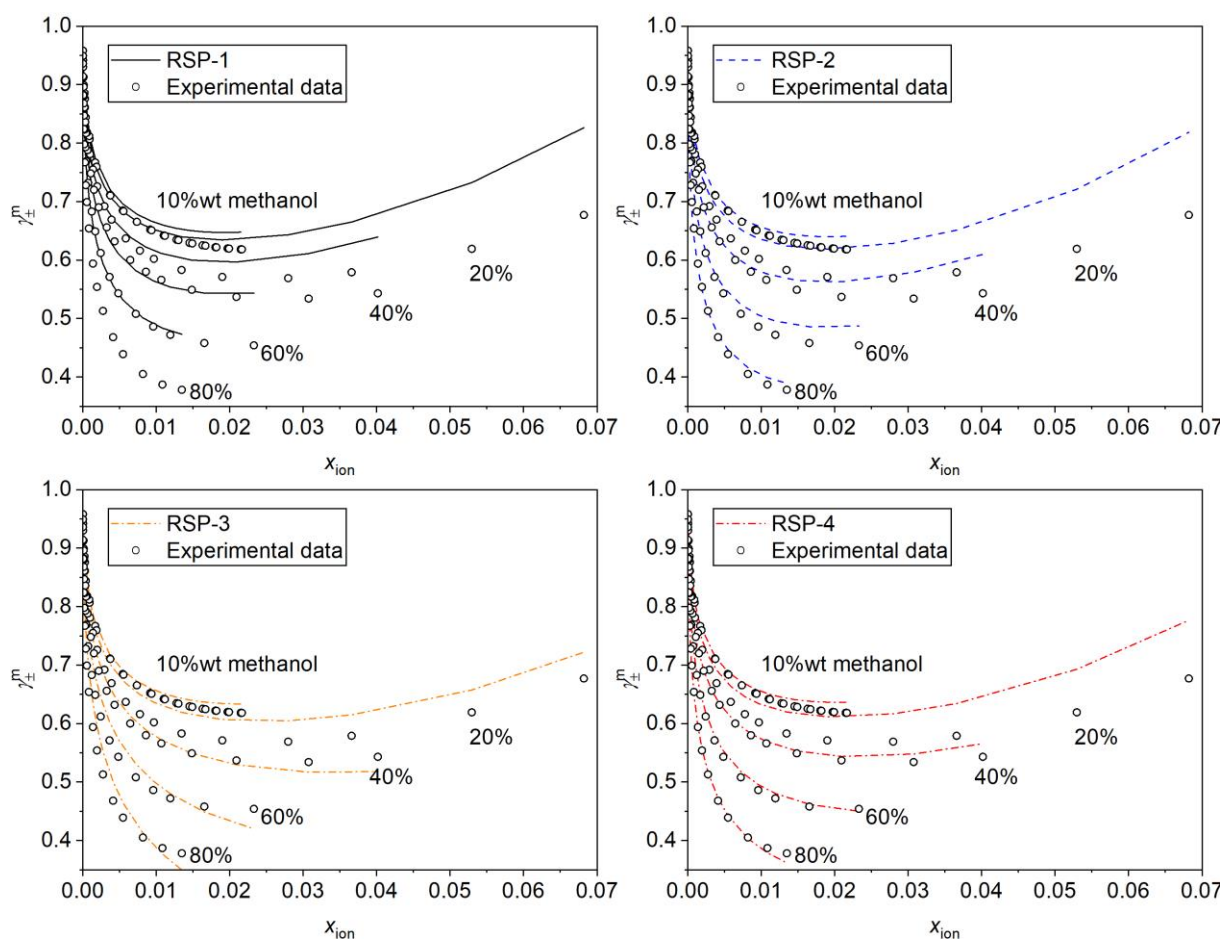


Figure S1. Comparisons of MIAC of (water + methanol + NaCl) calculated using the ePPC-SAFT with the 4 RSP models at 298.15 K and 0.1 MPa and experimental data. Literature of the experimental data is as listed and explained in Section 2.2 and Ref [17].

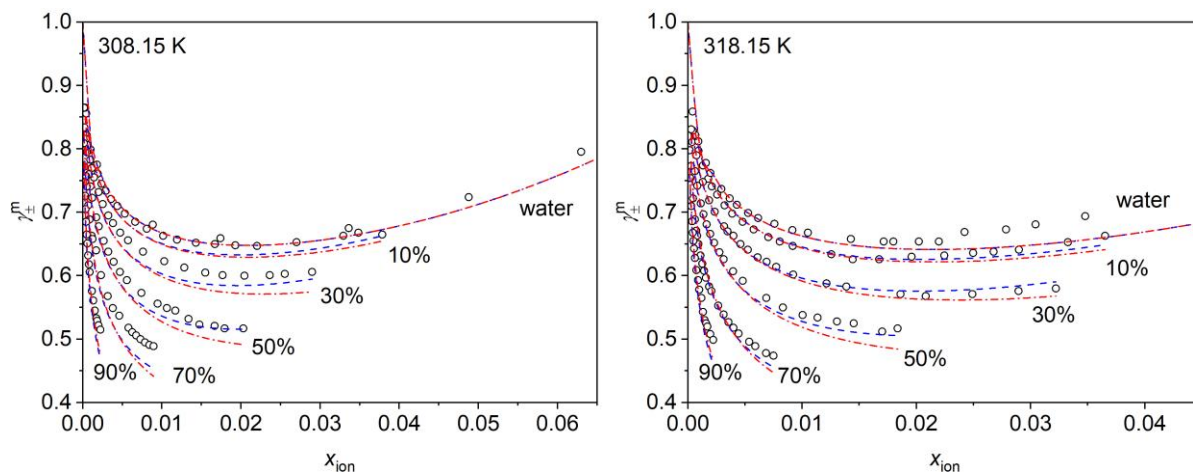


Figure S2. Comparisons of MIAC of (water + methanol + NaCl) calculated using the ePPC-SAFT with RSP-2 (blue dashed lines) and RSP-4 (red dash-dotted lines) at 308.15 K and 318.15 K and 0.1 MPa and experimental data (symbols). Literature of the experimental data is as listed and explained in Section 2.2 and Ref [17].

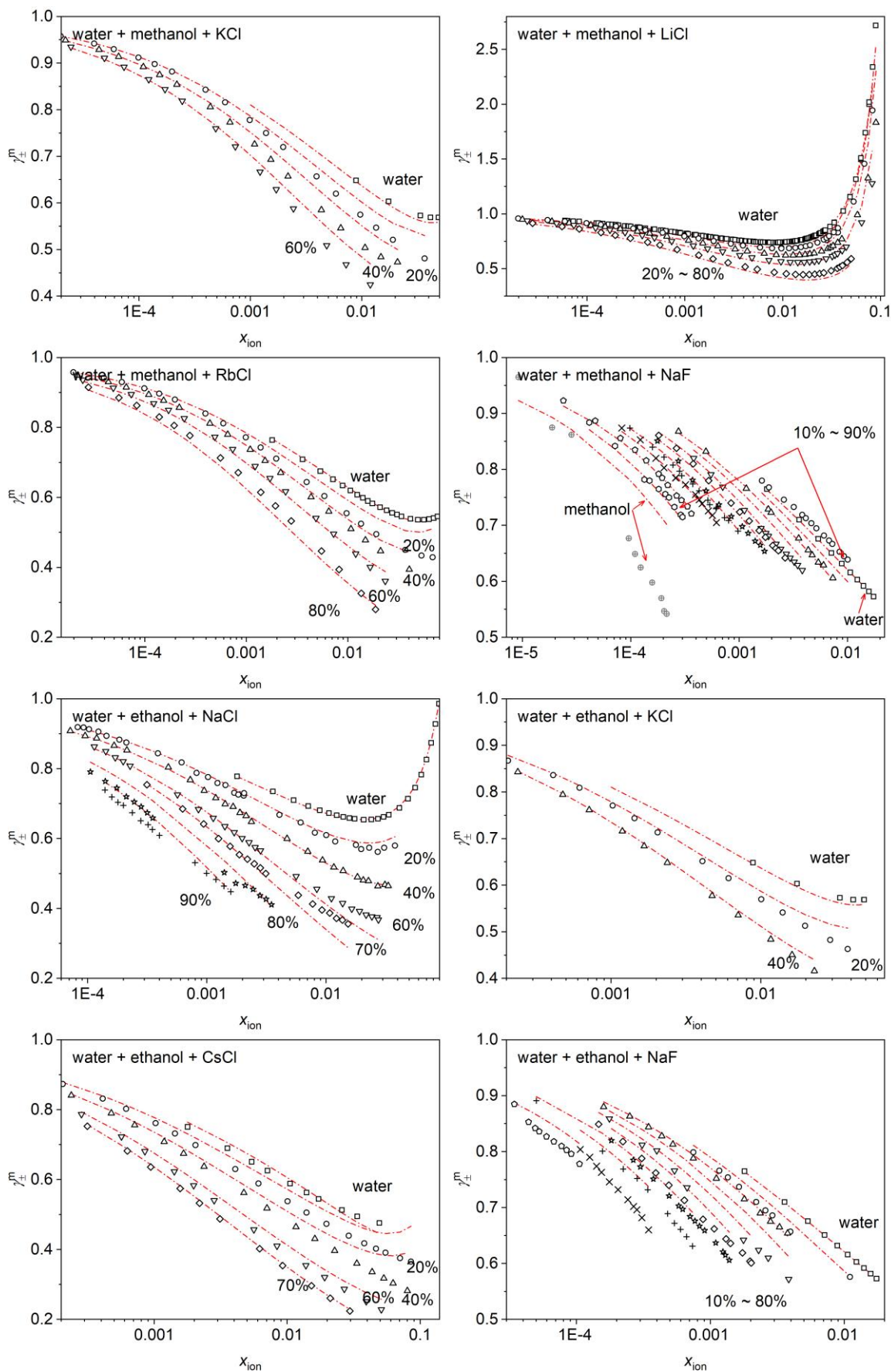


Figure S3. Comparisons of the MIAC of (water + methanol + KCl), (water + methanol + LiCl), (water + methanol + RbCl), (water + methanol + NaF), (water + ethanol + NaCl), (water + ethanol + KCl), (water + ethanol + CsCl), and (water + ethanol + NaF) calculated using the ePPC-SAFT with RSP-4 (red dash-dotted lines) at 298.15 K and 0.1 MPa and experimental data (symbols represent salt-free weight fraction of the alcohol, percentages noted in the sub-graphs). Literature of the experimental data is as listed and explained in Section 2.2 and Ref [17].

Table S4. Deviations of MIAC, VLE, and density calculated using the ePPC-SAFT model with the 4 RSP models. The numbers outside the parenthesis are AAPDs and AAADs. The numbers in the parenthesis are maximum absolute percentage deviations (MAPDs) and maximum absolute absolute deviations (MAADs). The MIAC, VLE p, and density deviations are in percentage. The VLE y absolute deviations are absolute deviations multiplied by 100.

| | MIAC | | | | VLE p | | | | VLE y | | | | Density | | | |
|---------------------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|---------------|----------------|---------------|---------------|----------------|----------------|----------------|----------------|
| | RSP-1 | RSP-2 | RSP-3 | RSP-4 | RSP-1 | RSP-2 | RSP-3 | RSP-4 | RSP-1 | RSP-2 | RSP-3 | RSP-4 | RSP-1 | RSP-2 | RSP-3 | RSP-4 |
| (water + methanol + LiCl) | 7.4 (50) | 4.2 (43) | 4.5 (30) | 3.6 (26) | 4.8 (14) | 4.5 (12) | 3.2 (17) | 3.1 (7.1) | 2.1 (5.3) | 2.0 (5.0) | 1.0 (2.3) | 1.4 (3.3) | 3.1 (4.8) | 3.1 (4.8) | 3.0 (4.7) | 3.1 (4.8) |
| (water + methanol + NaCl) | 5.1 (25) | 2.3 (21) | 2.9 (9.2) | 2.1 (15) | 2.1 (7.4) | 2.1 (9.3) | 2.3 (12) | 2.1 (10) | 1.1 (5.5) | 1.0 (4.5) | 1.0 (4.4) | 0.96 (3.7) | 1.3 (4.3) | 1.4 (4.3) | 1.3 (4.2) | 1.4 (4.3) |
| (water + methanol + KCl) | 5.3 (28) | 2.3 (12) | 3.3 (13) | 2.3 (10) | 2.4 (7.0) | 2.5 (6.1) | 3.3 (8.0) | 2.7 (6.3) | 0.71 (3.2) | 0.65 (2.4) | 1.1 (4.2) | 0.73 (2.5) | 2.8 (6.7) | 2.8 (6.7) | 2.8 (6.6) | 2.8 (6.7) |
| (water + methanol + RbCl) | 7.3 (43) | 3.7 (23) | 3.0 (14) | 2.9 (19) | | | | | | | | | | | | |
| (water + methanol + NaF) | 4.5 (7.1) | 1.8 (5.9) | 3.7 (6.3) | 1.7 (6.2) | | | | | | | | | | | | |
| (water + methanol + NaBr) | | | | | 1.8 (4.1) | 1.8 (4.1) | 2.1 (3.3) | 1.8 (3.8) | 1.2 (2.2) | 1.2 (2.3) | 0.74 (1.7) | 1.0 (1.8) | 1.7 (2.8) | 1.7 (2.8) | 1.7 (2.8) | 1.7 (2.8) |
| (water + ethanol + NaCl) | 16 (60) | 4.3 (30) | 8.8 (27) | 3.1 (19) | 2.5 (14) | 2.5 (10) | 2.6 (13) | 2.4 (8.7) | 2.7 (7.5) | 2.4 (6.0) | 2.6 (7.2) | 2.3 (5.1) | 0.88 (2.4) | 0.85 (2.4) | 0.90 (2.4) | 0.87 (2.4) |
| (water + ethanol + KCl) | 12 (37) | 3.4 (15) | 8.3 (20) | 2.3 (9.7) | 1.8 (4.2) | 1.5 (4.7) | 1.5 (4.5) | 1.4 (4.7) | 3.5 (6.5) | 3.7 (6.3) | 3.4 (5.8) | 3.4 (5.4) | 0.72 (5.4) | 0.70 (5.4) | 0.73 (5.3) | 0.71 (5.4) |
| (water + ethanol + CsCl) | 34 (140) | 13 (84) | 18 (53) | 6.5 (38) | | | | | | | | | 0.32 (2.7) | 0.33 (2.5) | 0.33 (2.7) | 0.32 (2.6) |
| (water + ethanol + NaF) | 11 (23) | 3.1 (7.6) | 10 (21) | 4.8 (12) | | | | | | | | | | | | |
| (water + ethanol + KBr) | | | | | 2.5 (5.5) | 2.9 (5.9) | 3.5 (6.8) | 3.4 (6.4) | 0.88 (2.9) | 1.1 (2.9) | 1.3 (4.5) | 1.3 (4.0) | 1.2 (1.7) | 1.2 (1.7) | 1.1 (1.7) | 1.2 (1.7) |
| (water + ethanol + NaI) | | | | | 2.7 (4.3) | 3.7 (6.4) | 4.3 (12) | 3.1 (8.6) | 3.2 (6.2) | 3.2 (6.0) | 2.8 (5.6) | 2.2 (3.9) | 0.20 (0.68) | 0.21 (0.67) | 0.20 (0.68) | 0.20 (0.68) |
| (water + ethanol + KI) | | | | | 1.8 (2.7) | 2.4 (3.1) | 2.0 (3.0) | 2.2 (3.3) | 0.54 (1.0) | 0.33 (0.62) | 2.1 (5.6) | 1.9 (5.1) | 1.1 (3.4) | 0.85 (3.0) | 1.4 (3.7) | 1.1 (3.4) |
| Average | 11 | 4.2 | 6.9 | 3.3 | 2.5 | 2.7 | 2.8 | 2.5 | 1.8 | 1.7 | 1.8 | 1.7 | 1.3 | 1.3 | 1.3 | 1.3 |

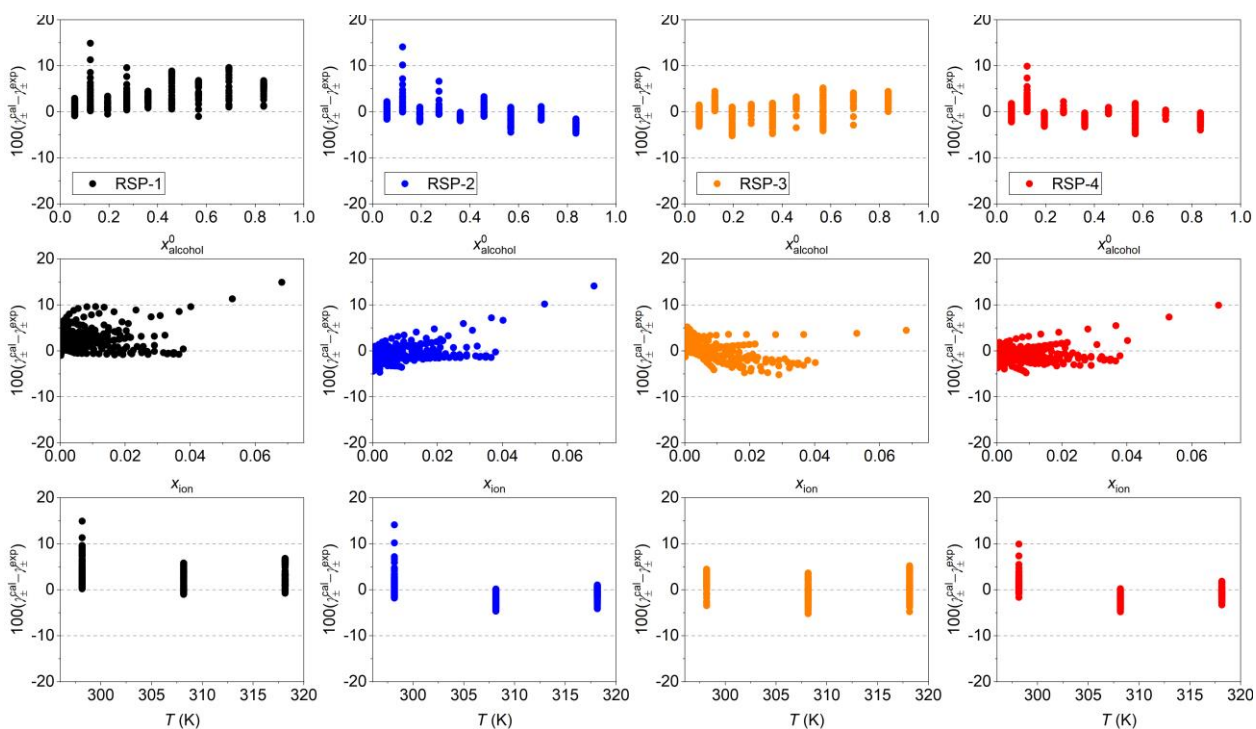


Figure S4. Deviations of the MIAC calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + NaCl).

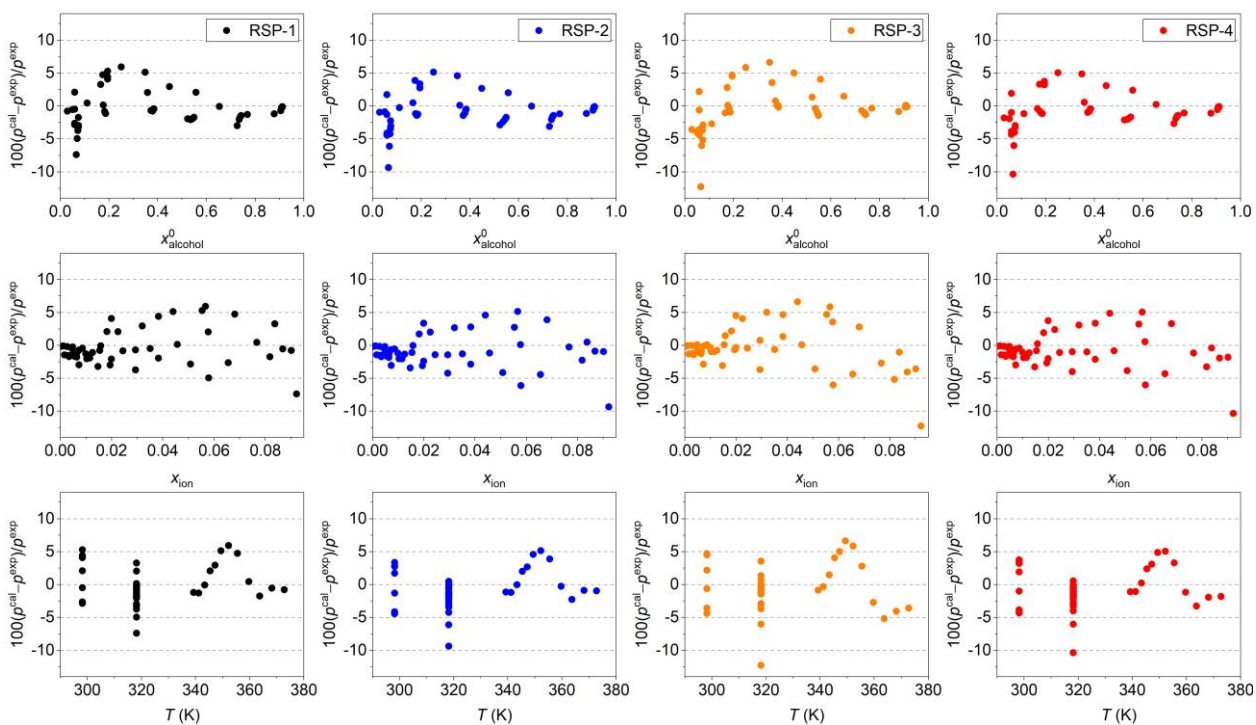


Figure S5. Deviations of the VLE pressure calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + NaCl).

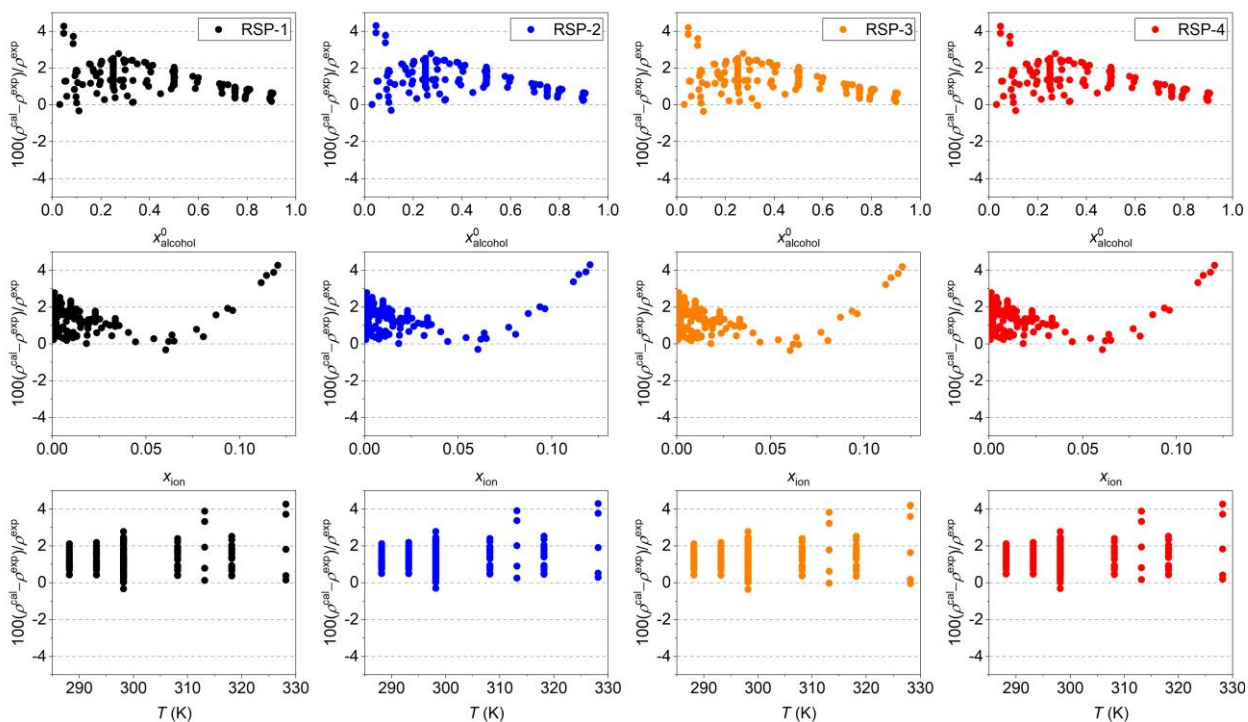


Figure S6. Deviations of the density calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + NaCl).

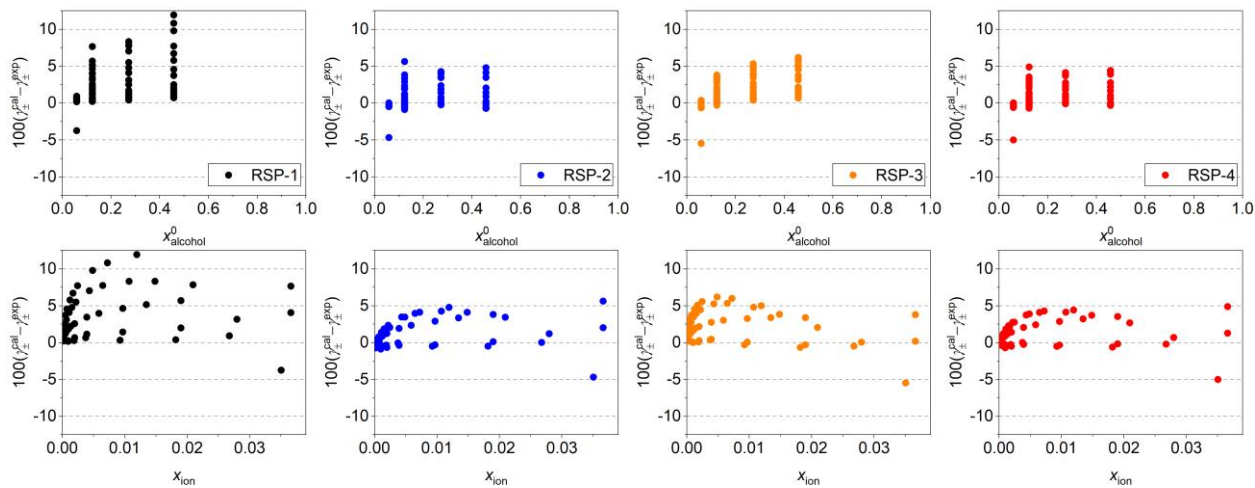


Figure S7. Deviations of the MIAC calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + KCl). Deviations are not plotted against T as all data are at 298.15 K.

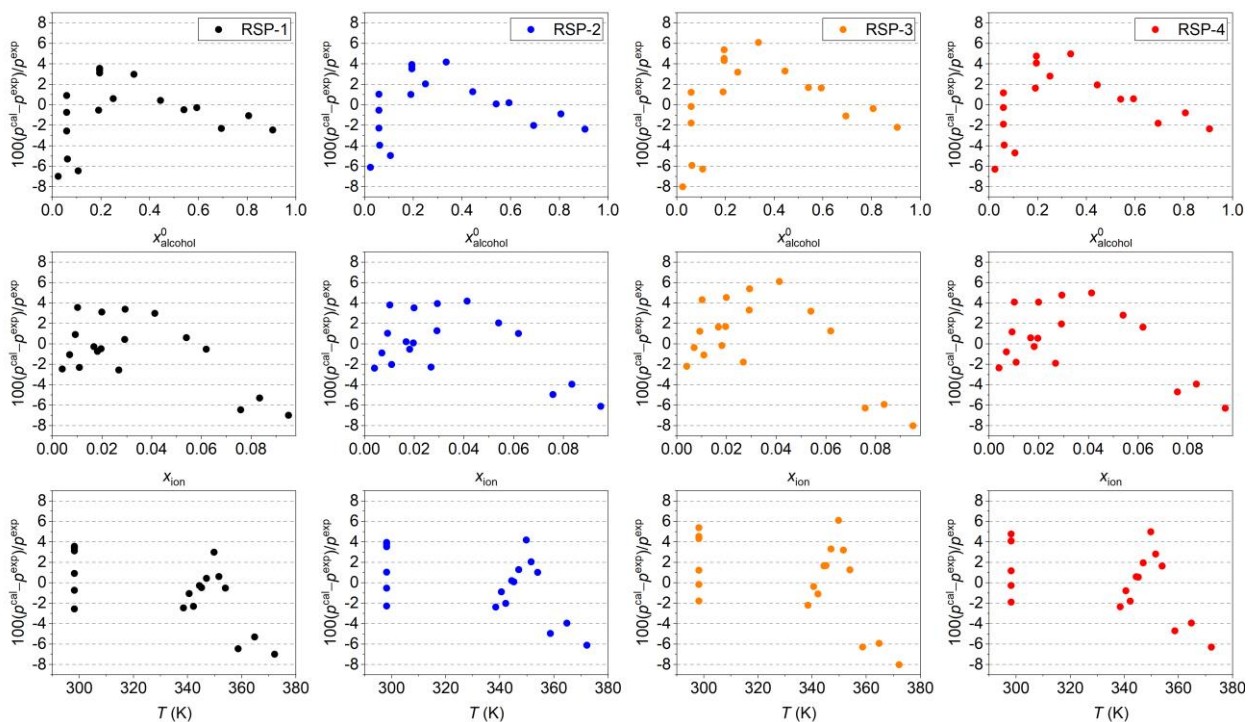


Figure S8. Deviations of the VLE calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + KCl). Deviations are not plotted against T as all data are at 298.15 K.

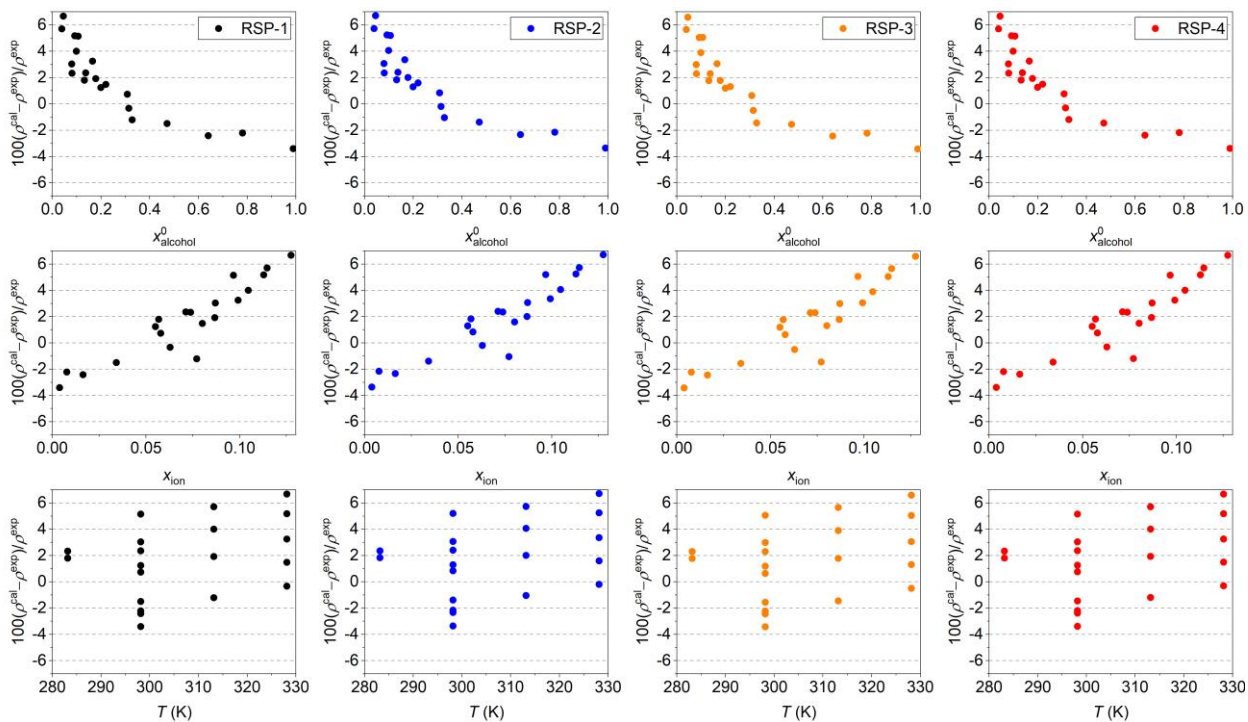


Figure S9. Deviations of the density calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + KCl). Deviations are not plotted against T as all data are at 298.15 K.

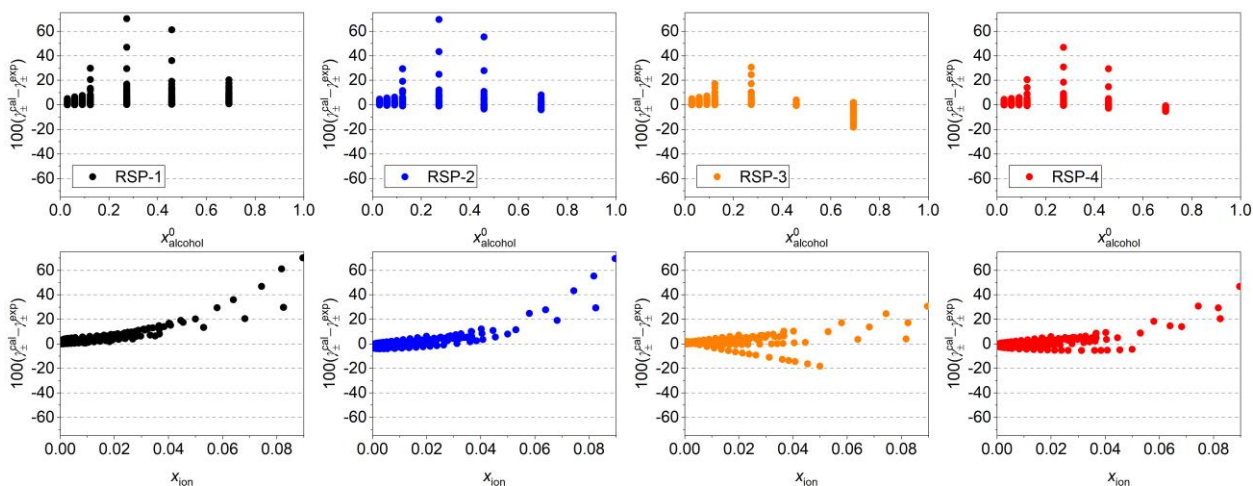


Figure S10. Deviations of the MIAC calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + LiCl). Deviations are not plotted against T as all data are at 298.15 K.

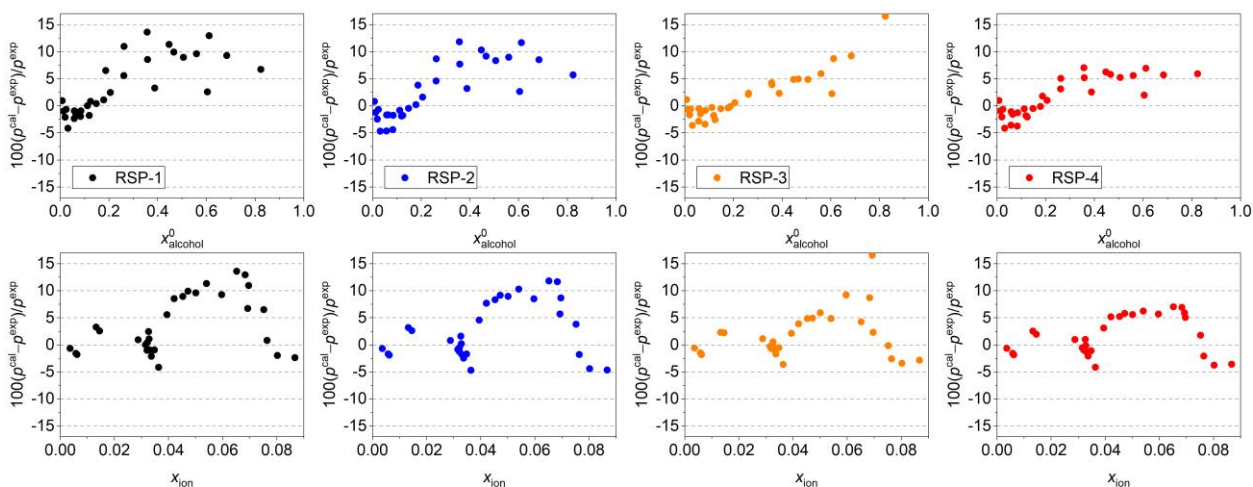


Figure S11. Deviations of the VLE calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + LiCl). Deviations are not plotted against T as all data are at 333.15 K.

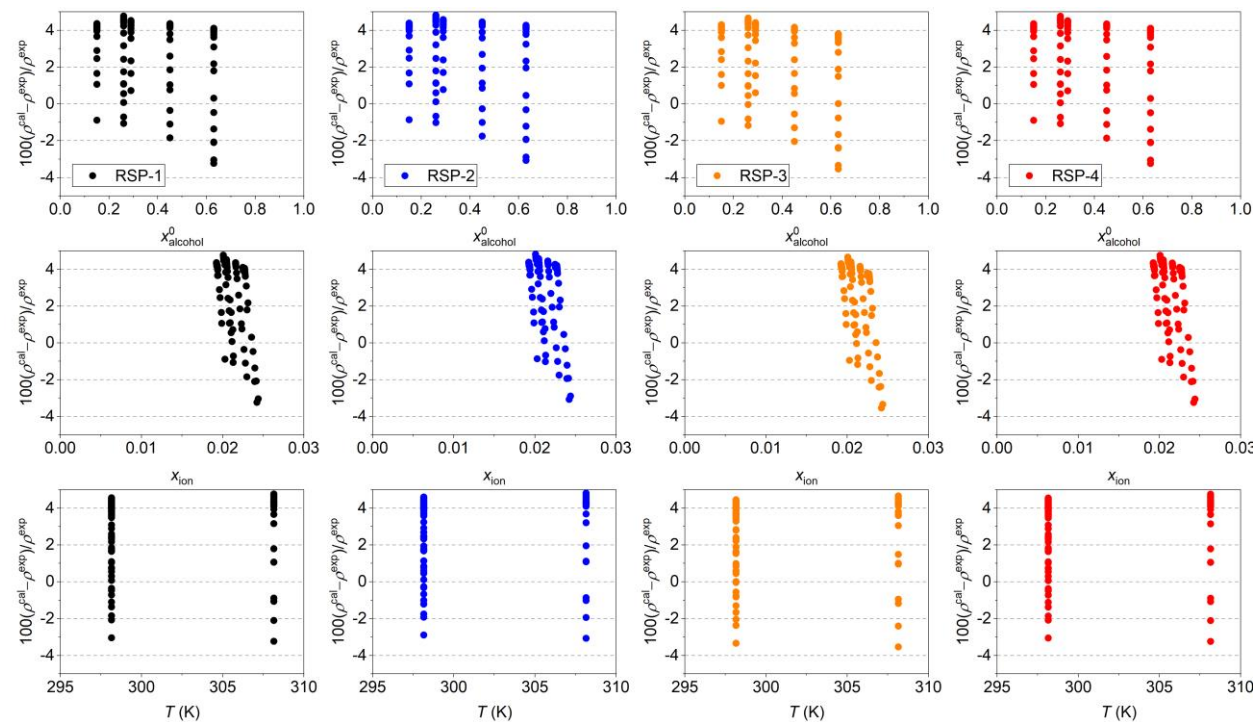


Figure S12. Deviations of the density calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + LiCl).

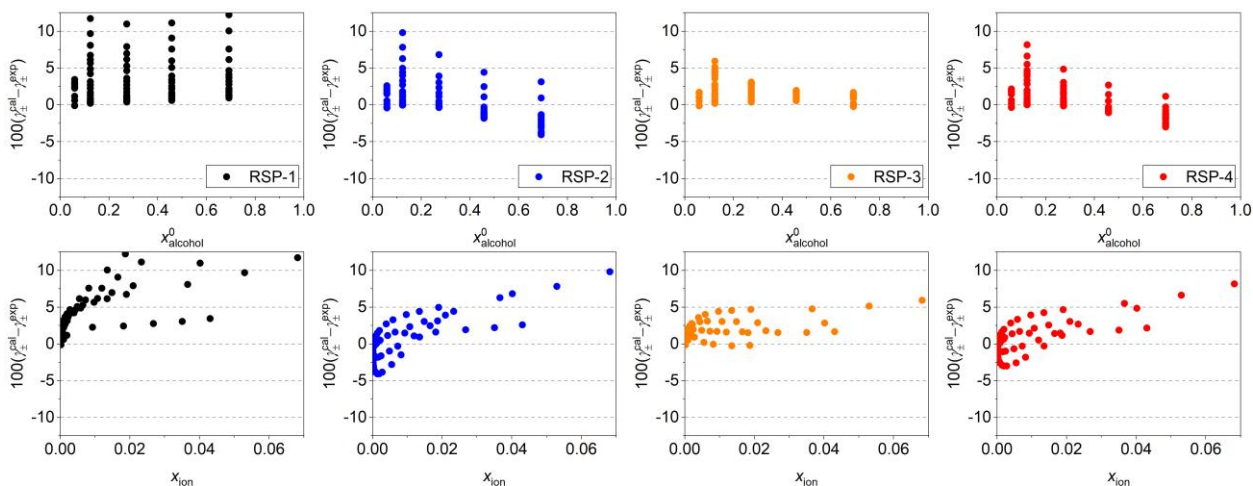


Figure S13. Deviations of the MIAC calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + RbCl). Deviations are not plotted against T as all data are at 298.15 K.

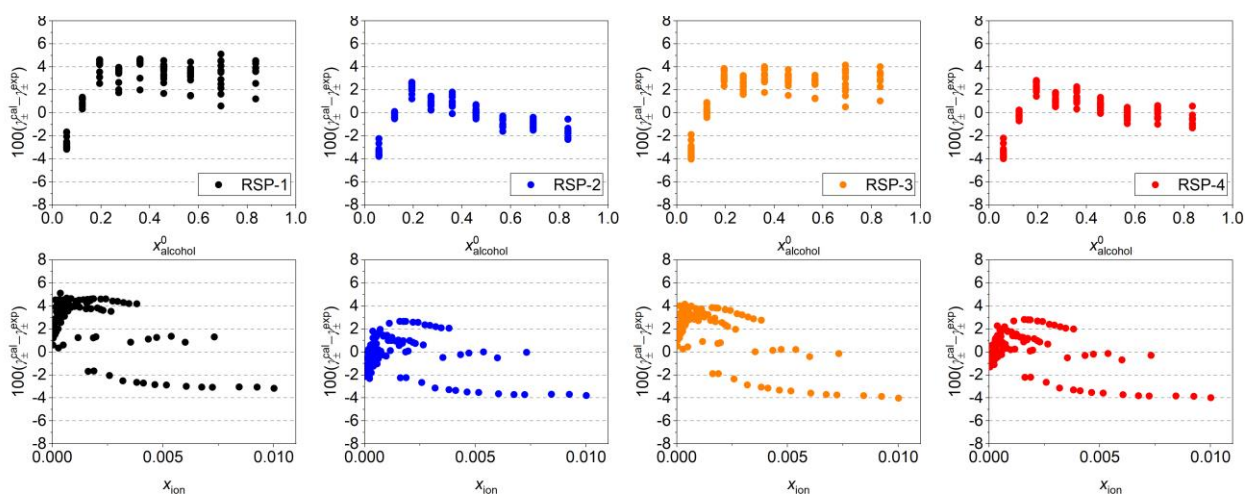


Figure S14. Deviations of the MIAC calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + NaF). Deviations are not plotted against T as all data are at 298.15 K.

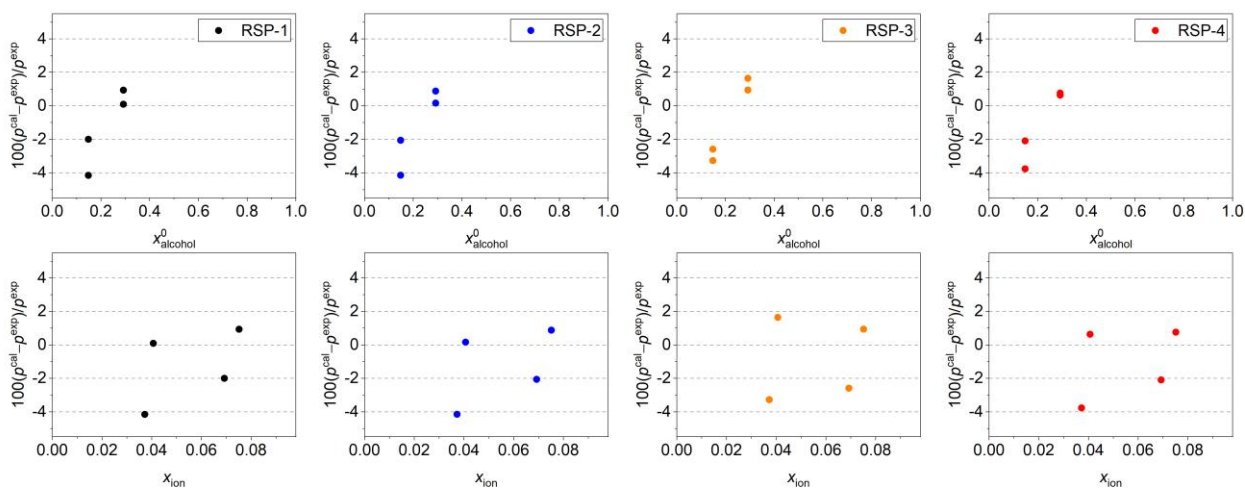


Figure S15. Deviations of the VLE calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + NaBr). Deviations are not plotted against T as all data are at 298.15 K.

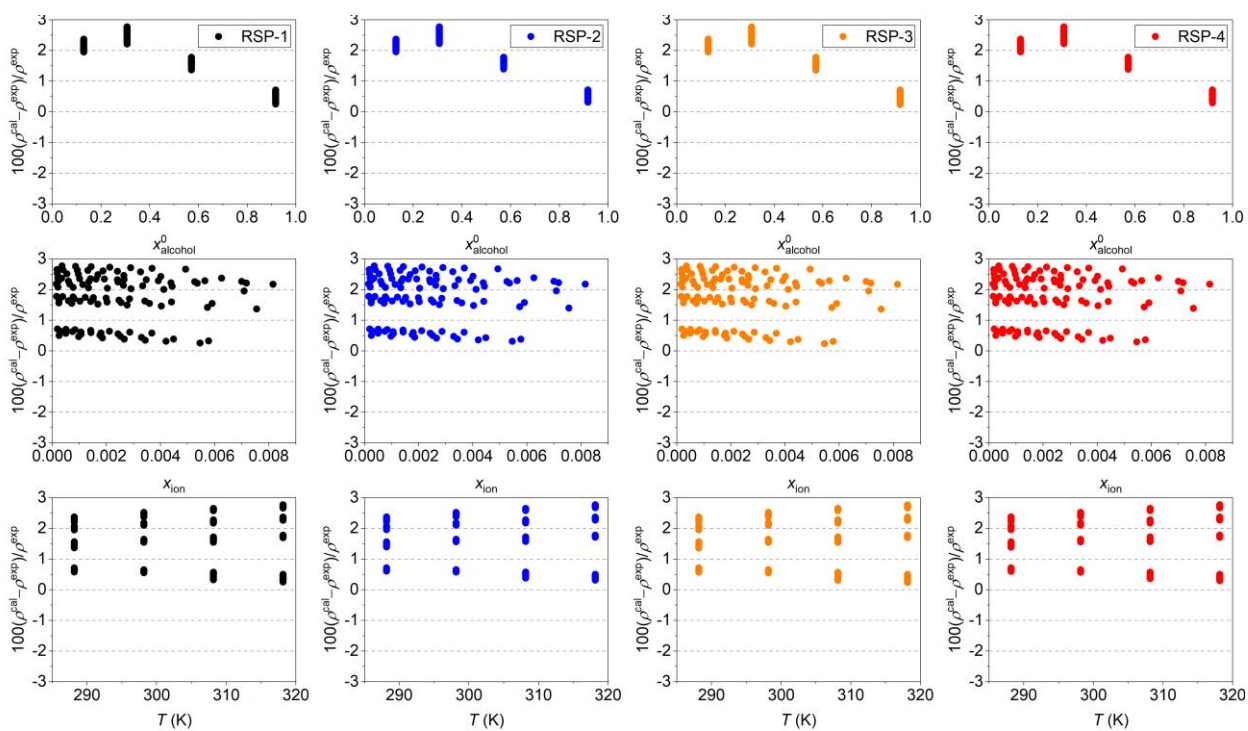


Figure S16. Deviations of the density calculated with the ePPC-SAFT using the 4 RSP models for (water + methanol + NaBr).

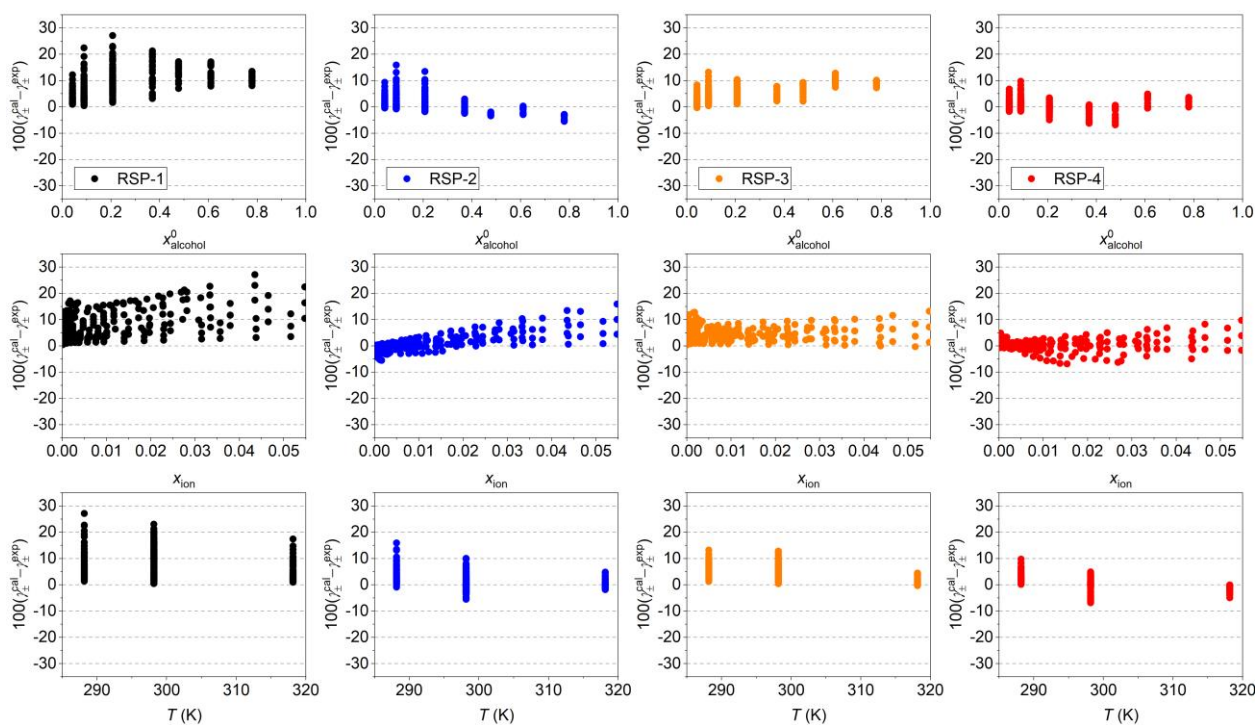


Figure S17. Deviations of the MIAC calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + NaCl).

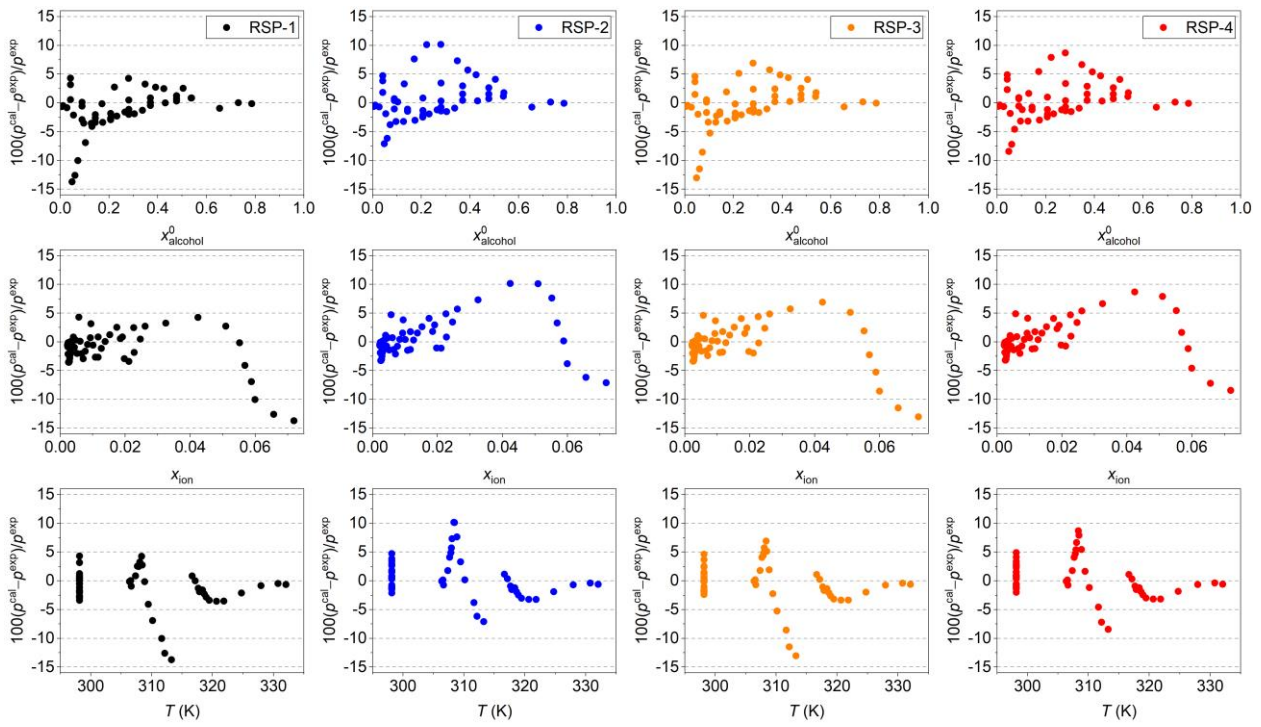


Figure S18. Deviations of the VLE calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + NaCl).

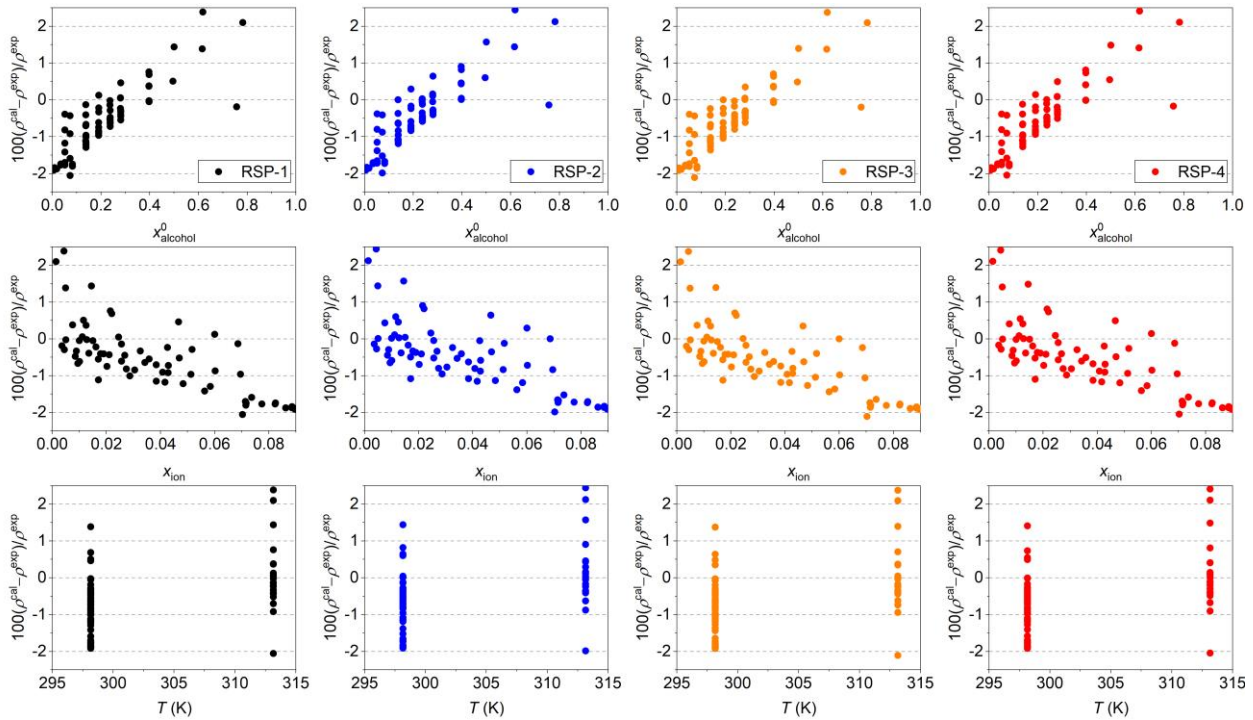


Figure S19. Deviations of the density calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + NaCl).

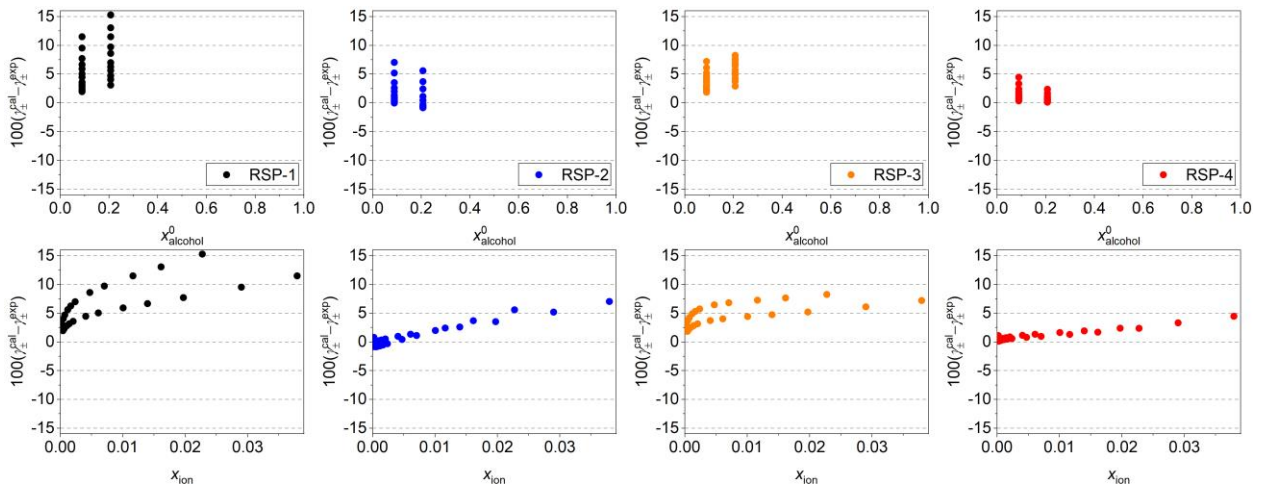


Figure S20. Deviations of the MIAC calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + KCl). Deviations are not plotted against T as all data are at 298.15 K.

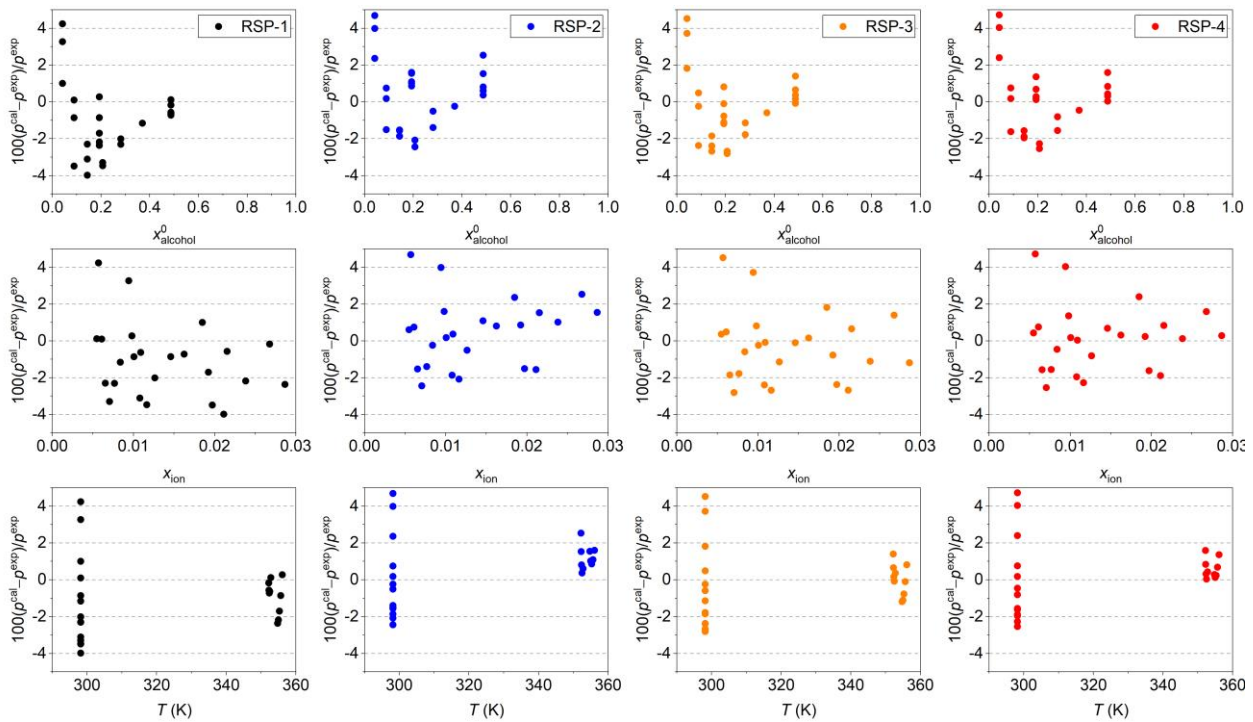


Figure S21. Deviations of the VLE calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + KCl).

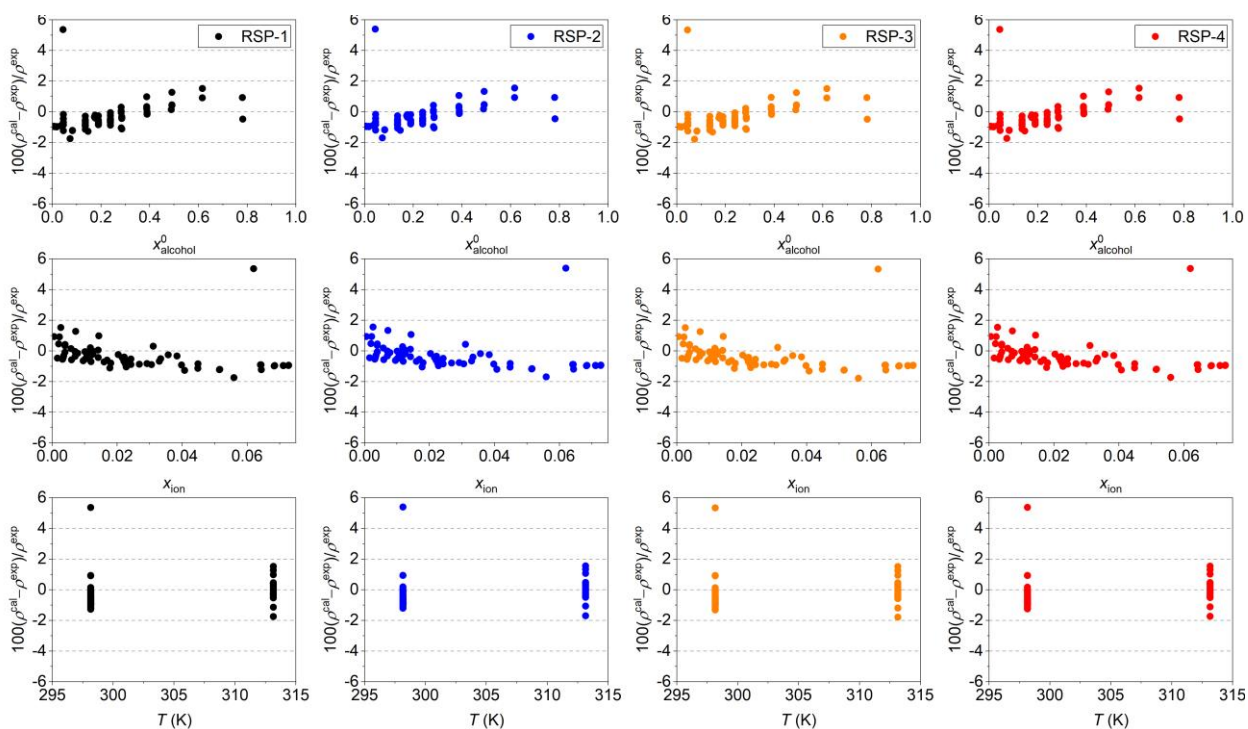


Figure S22. Deviations of the density calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + KCl).

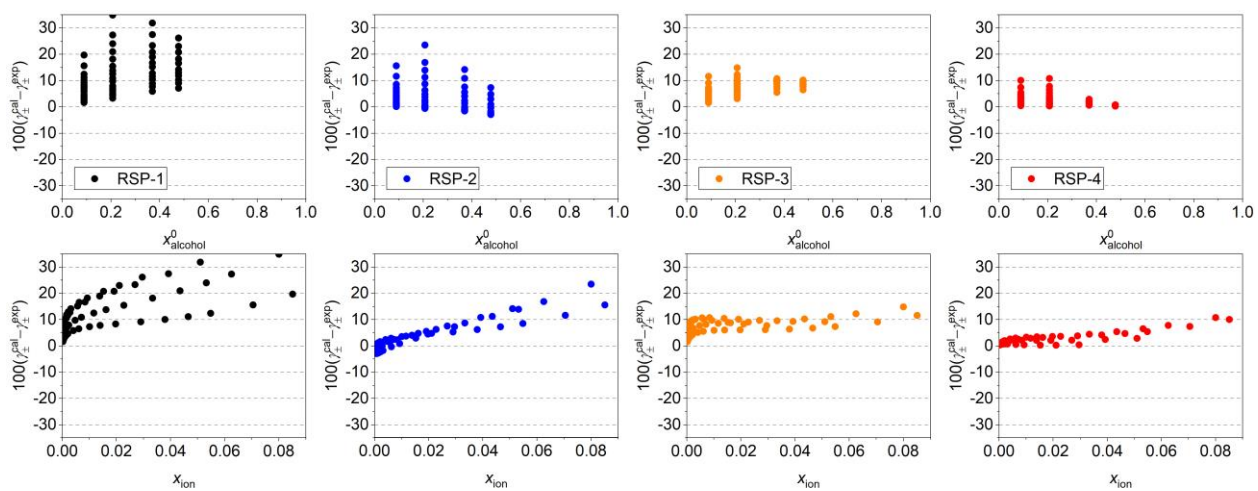


Figure S23. Deviations of the MIAC calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + CsCl). Deviations are not plotted against T as all data are at 298.15 K.

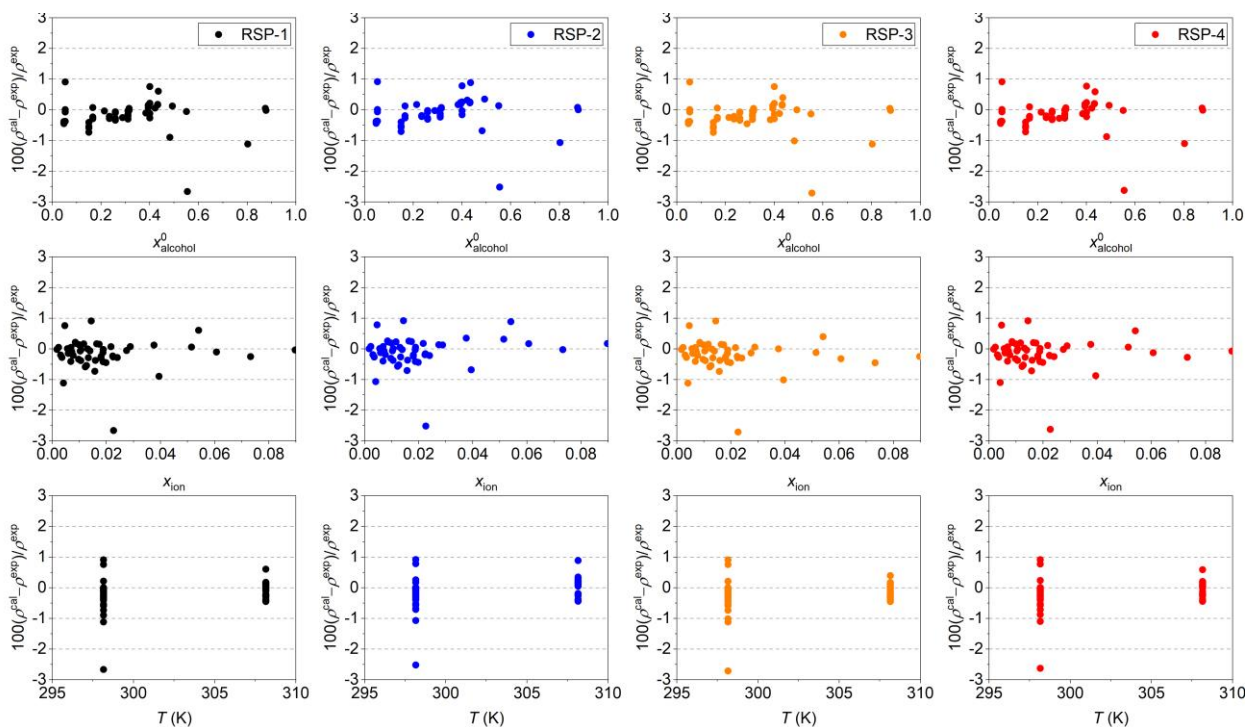


Figure S24. Deviations of the density calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + CsCl).

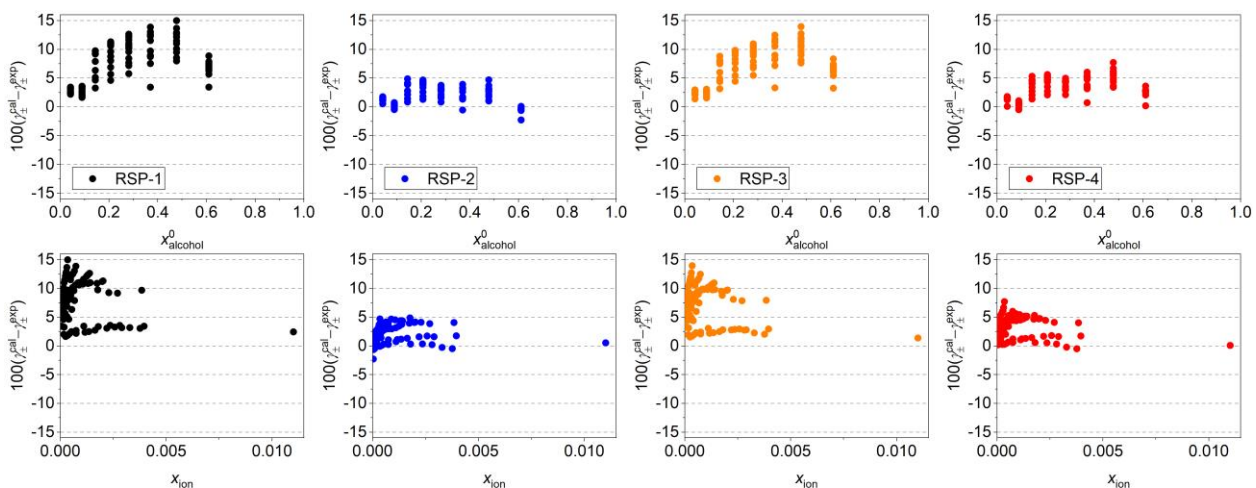


Figure S25. Deviations of the MIAC calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + NaF). Deviations are not plotted against T as all data are at 298.15 K.

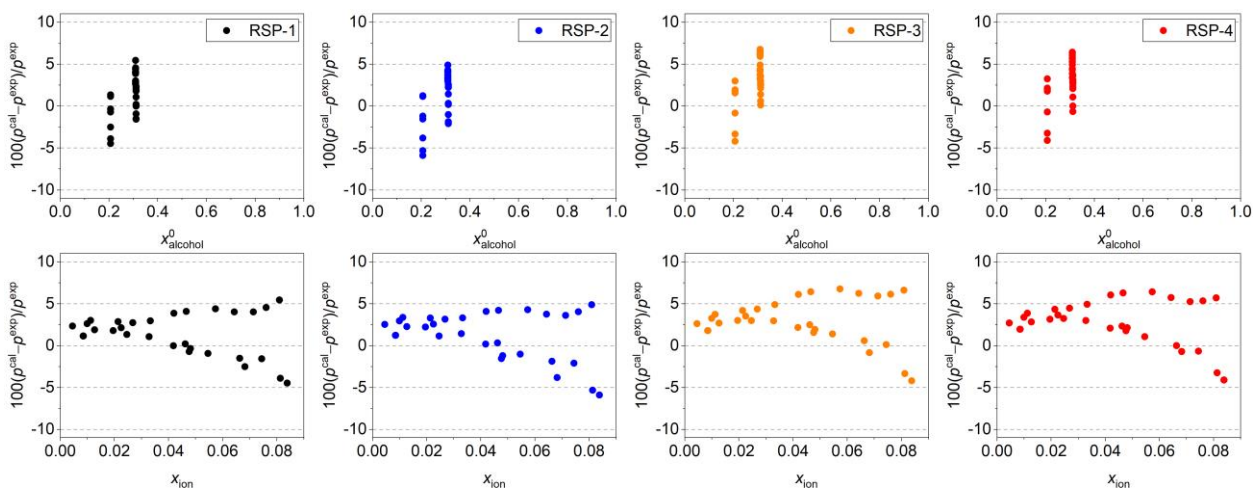


Figure S26. Deviations of the VLE calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + KBr). Deviations are not plotted against T as all data are within a very small range close to 355 K.

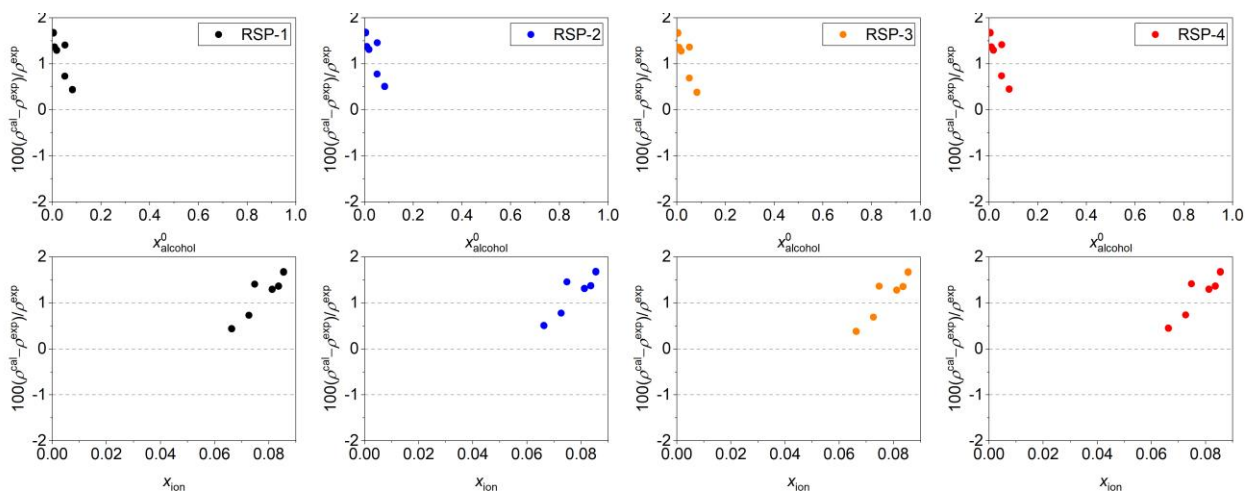


Figure S27. Deviations of the density calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + KBr). Deviations are not plotted against T as all data are at 298.15 K.

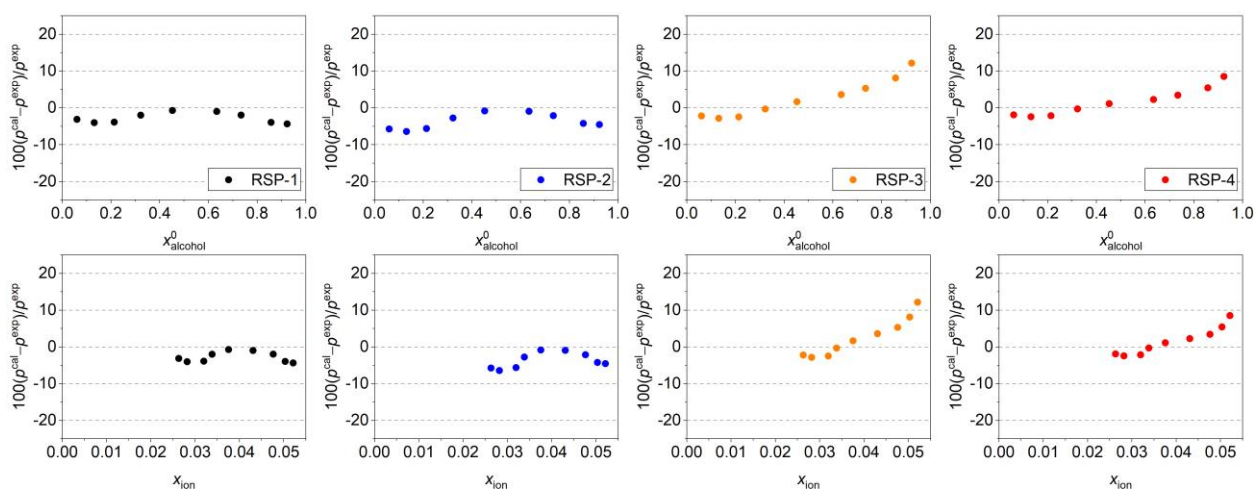


Figure S28. Deviations of the VLE calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + NaI). Deviations are not plotted against T as all data are at 298.15 K.

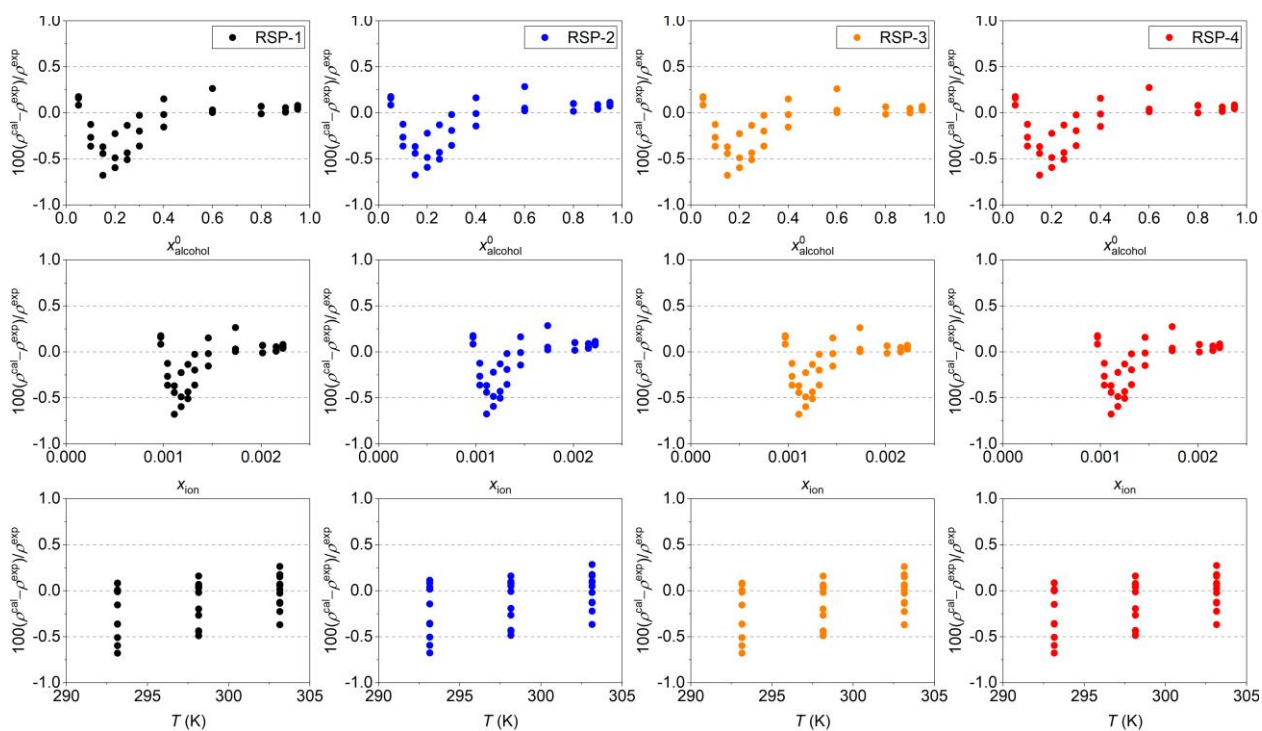


Figure S29. Deviations of the density calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + NaI).

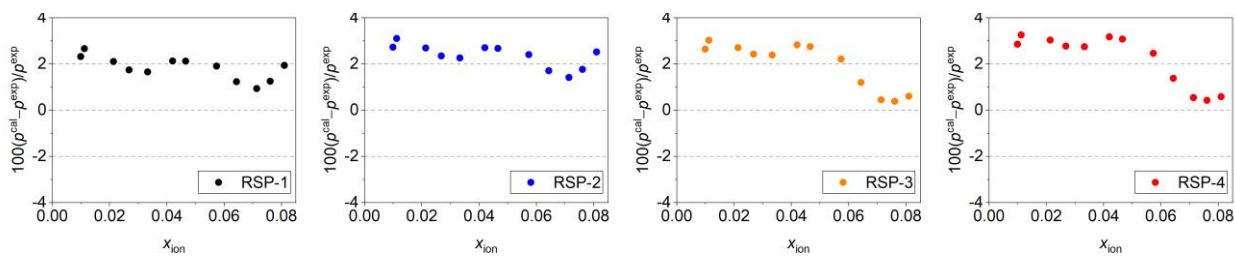


Figure S30. Deviations of the VLE calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + KI). Deviations are not plotted against T and x_{alcohol}^0 as all data are within a very small range close to 355 K and at $x_{\text{alcohol}}^0 = 0.309$.

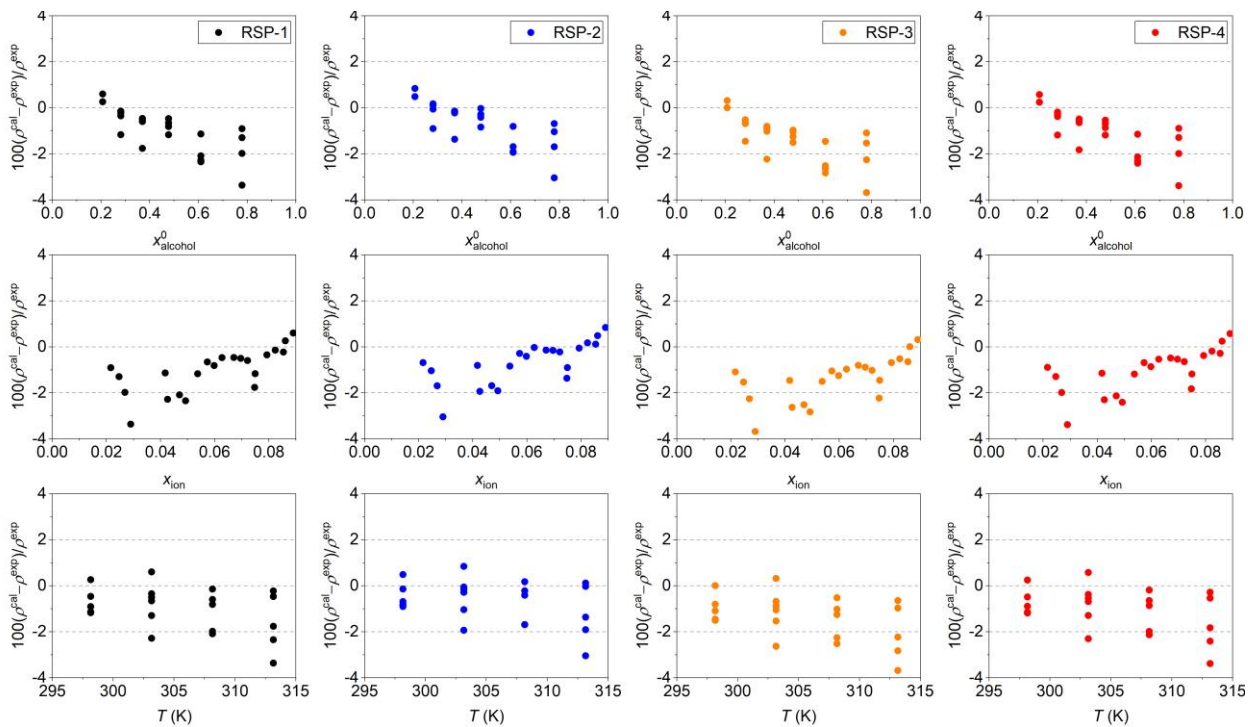


Figure S31. Deviations of the density calculated with the ePPC-SAFT using the 4 RSP models for (water + ethanol + KI).

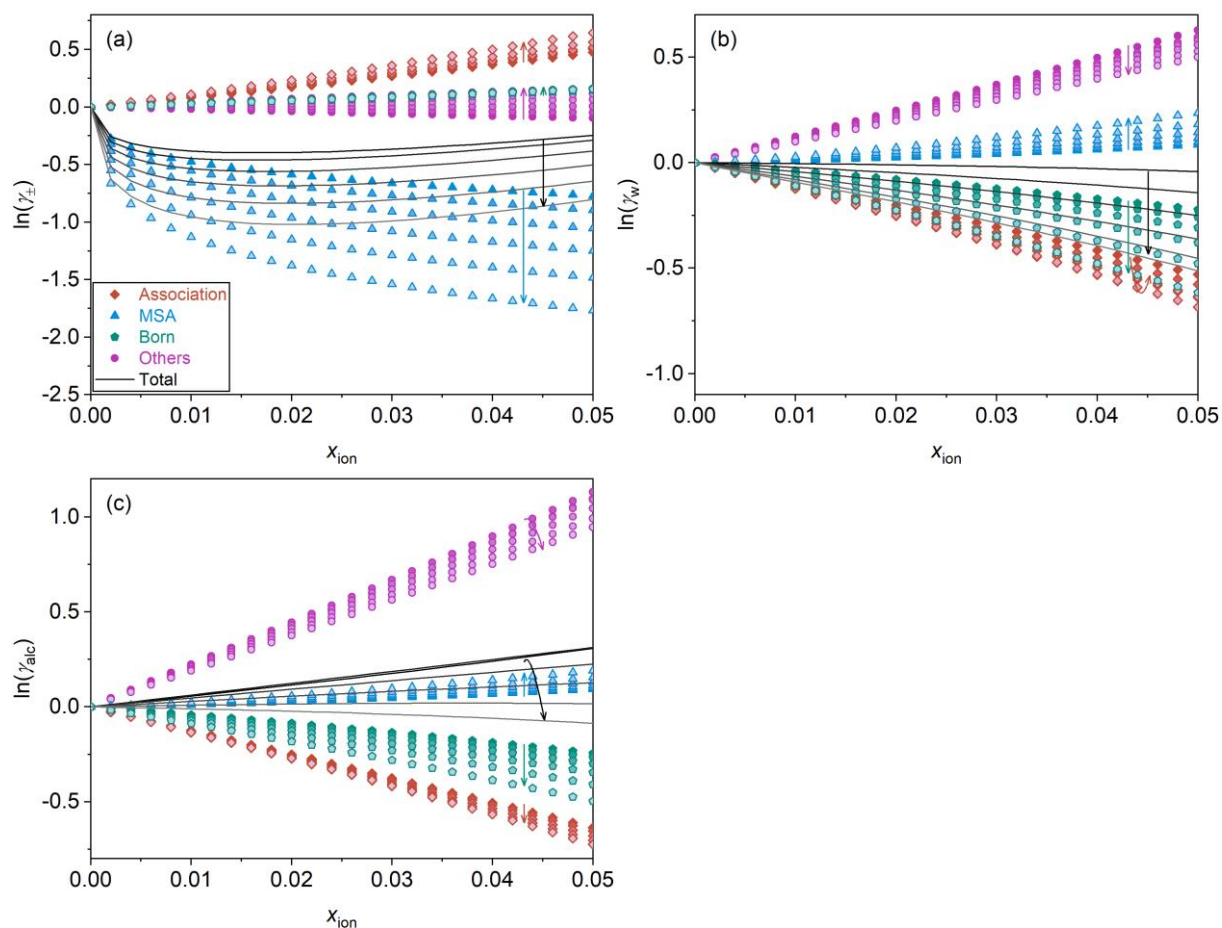


Figure S32. Contributions to (a) $\ln \gamma_{\pm}$, (b) $\ln \gamma_w$, and (c) $\ln \gamma_{alc}$ of the terms (association, MSA, Born, and others) of ePPC-SAFT combined with RSP-1 for (water + methanol + NaCl) at 298.15 K and 0.1 MPa. The symbols and lines are in gradient colors for salt-free alcohol mole fraction (0%, 20%, 40%, 60%, 80%, 100%), with the higher alcohol compositions in lighter interior colors.

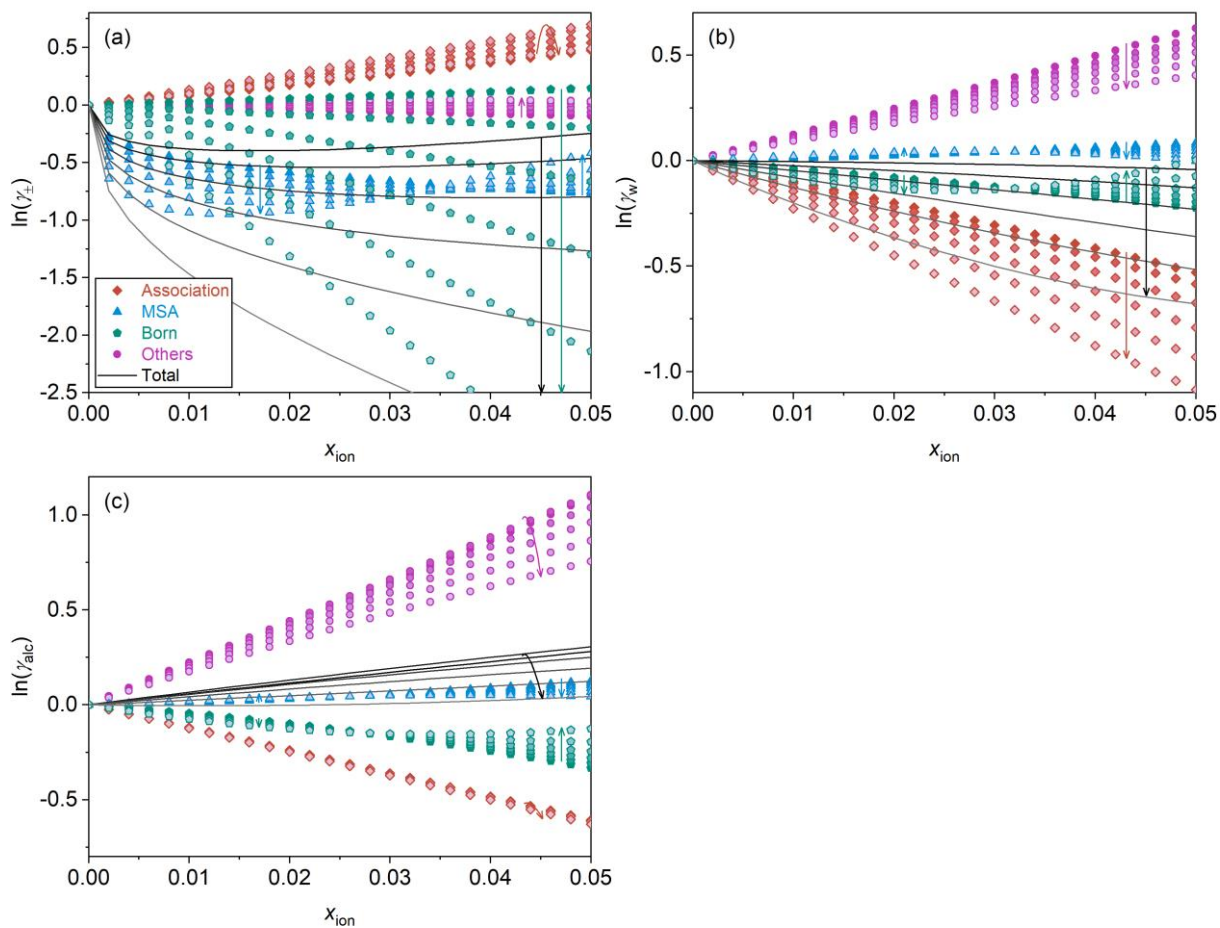


Figure S33. Contributions to (a) $\ln \gamma_{\pm}$, (b) $\ln \gamma_w$, and (c) $\ln \gamma_{alc}$ of the terms (association, MSA, Born, and others) of ePPC-SAFT combined with RSP-3 for (water + methanol + NaCl) at 298.15 K and 0.1 MPa. The symbols and lines are in gradient colors for salt-free alcohol mole fraction (0%, 20%, 40%, 60%, 80%, 100%), with the higher alcohol compositions in lighter interior colors.

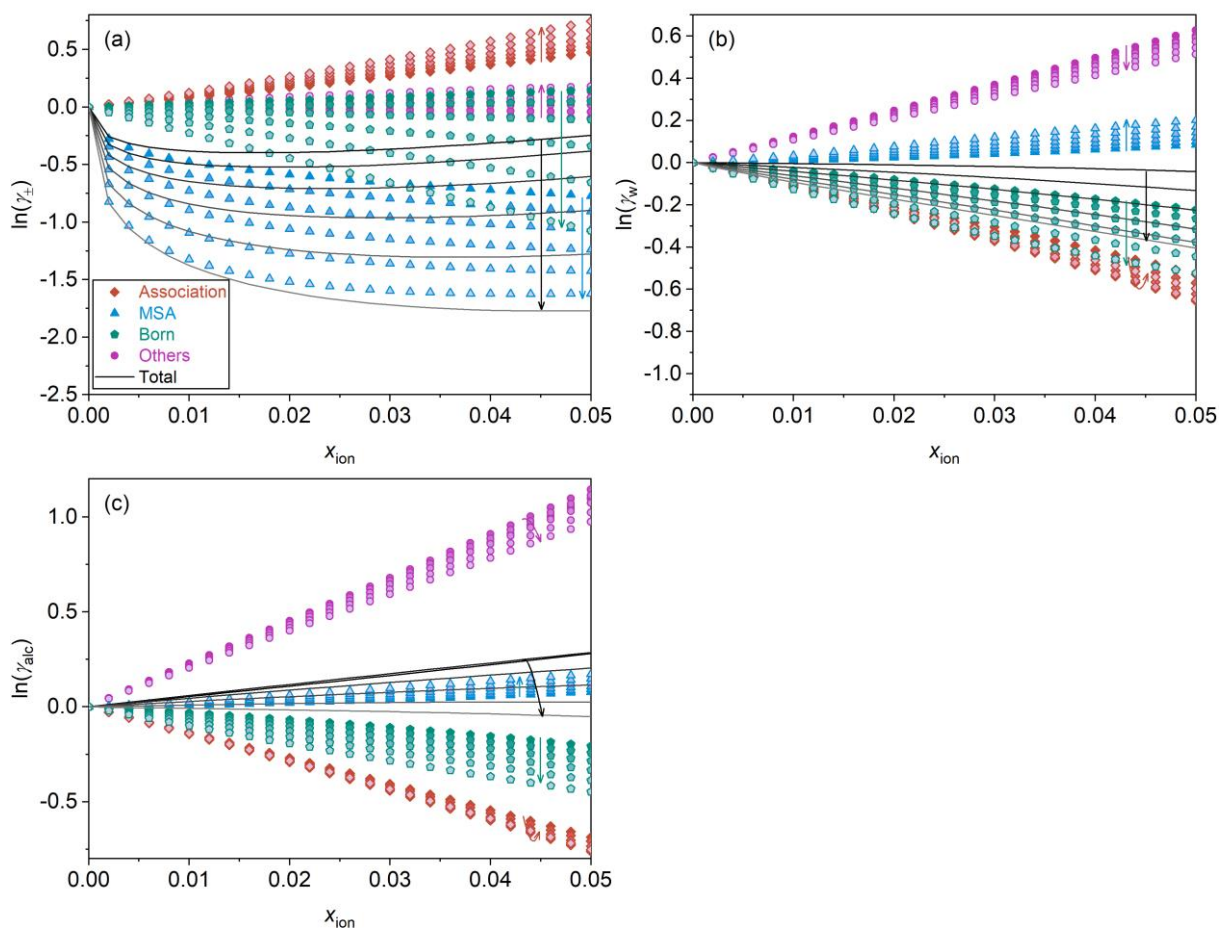


Figure S34. Contributions to (a) $\ln \gamma_{\pm}$, (b) $\ln \gamma_w$, and (c) $\ln \gamma_{\text{alc}}$ of the terms (association, MSA, Born, and others) of ePPC-SAFT combined with RSP-4 for (water + methanol + NaCl) at 298.15 K and 0.1 MPa. The symbols and lines are in gradient colors for salt-free alcohol mole fraction (0%, 20%, 40%, 60%, 80%, 100%), with the higher alcohol compositions in lighter interior colors.

Table S5. Summary of the (alcohol + salt) MIAC and osmotic coefficient (OC) datasets used in the comparisons.

| | MIAC | OC |
|-----------------|---------|---------|
| Methanol + LiCl | [18] | [19–21] |
| Methanol + NaF | [22] | |
| Methanol + NaBr | | [23,24] |
| Methanol + KCl | [25] | |
| Methanol + RbCl | [25] | |
| Ethanol + NaI | [26,27] | [28,29] |
| Ethanol + KI | | [28] |

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