

Supporting Information for “Phase Behavior of Poly(ethylene oxide) in Room Temperature Ionic Liquids: A Molecular Simulation and Deep Neural Network Study”

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S1. SAPT-UA force field parameters

The total nonbonded interaction energy in SAPT-UA force field is given by

$$E_{tot} = \sum_{i,j} \frac{q_i q_j}{r_{ij}} + \sum_{i,j} \left(A_{ij}^{tot} \exp(-B_{ij} r_{ij}) - \sum_{n=6,8,10,12} f_{n,ij} \frac{C_n^{ij}}{r_{ij}^n} \right) \quad (1)$$

where r_{ij} is the distance between i and j particles, $A_{ij}^{tot} = A_{ij}^{exch} + A_{ij}^{elec} + A_{ij}^{ind} + A_{ij}^{dhf}$, and $f_{n,ij}$ is Tang-Toennies damping function.[?]

Table S1: The partial charges of united atom types of [EMIM], [EMMIM], and [BMMIM] cations. See Fig. 1 for atomtype names.

Atom type	[EMIM]	[EMMIM]	[BMMIM]
N	-0.6754	-0.6772	-0.5945
CM	-	0.2527	0.2439
C1	0.3040	0.3630	0.3366
C2	0.6944	0.3271	0.2604
C3	0.5165	0.5165	0.4886
C4	0.4585	0.4585	0.4608
C5	-	-	-0.0053
CE	0.0734	0.0734	0.0728

Table S2: SAPT-UA force fields of atom types for the nonbonded interaction potential in Eq. 1. As for B values in , we use 39.061 \AA^{-1} for N atom type and otherwise, 34.384 \AA^{-1} for other atom types. Note that A_i 's are in kJ/mol and C_n are in $\text{kJ}/(\text{mol}\text{\AA}^{-n})$

Atom type	A_{exch}	A_{elec}	A_{ind}	A_{dhf}
N	252624.4	102233.5	0.0	17537.3
C1, C2	869803	253355	0.0	94498.0
CM, C3, CE	2620353	765461	43780	144620
C4, C5	3038134	922261.5	65333	188853

Atom type	C_6	C_8	C_{10}	C_{12}
N	1018.7	6246.0	92197.5	676941.7
C1, C2	2211.4	24830.1	149571	295630
CM, C3	3893.1	43280.5	430425	3438615
C4	2186.6	16556.1	309338	2831947
C5	2937.7	42270.1	566233	6097084
CE	5165.3	67458.1	848542	8569083

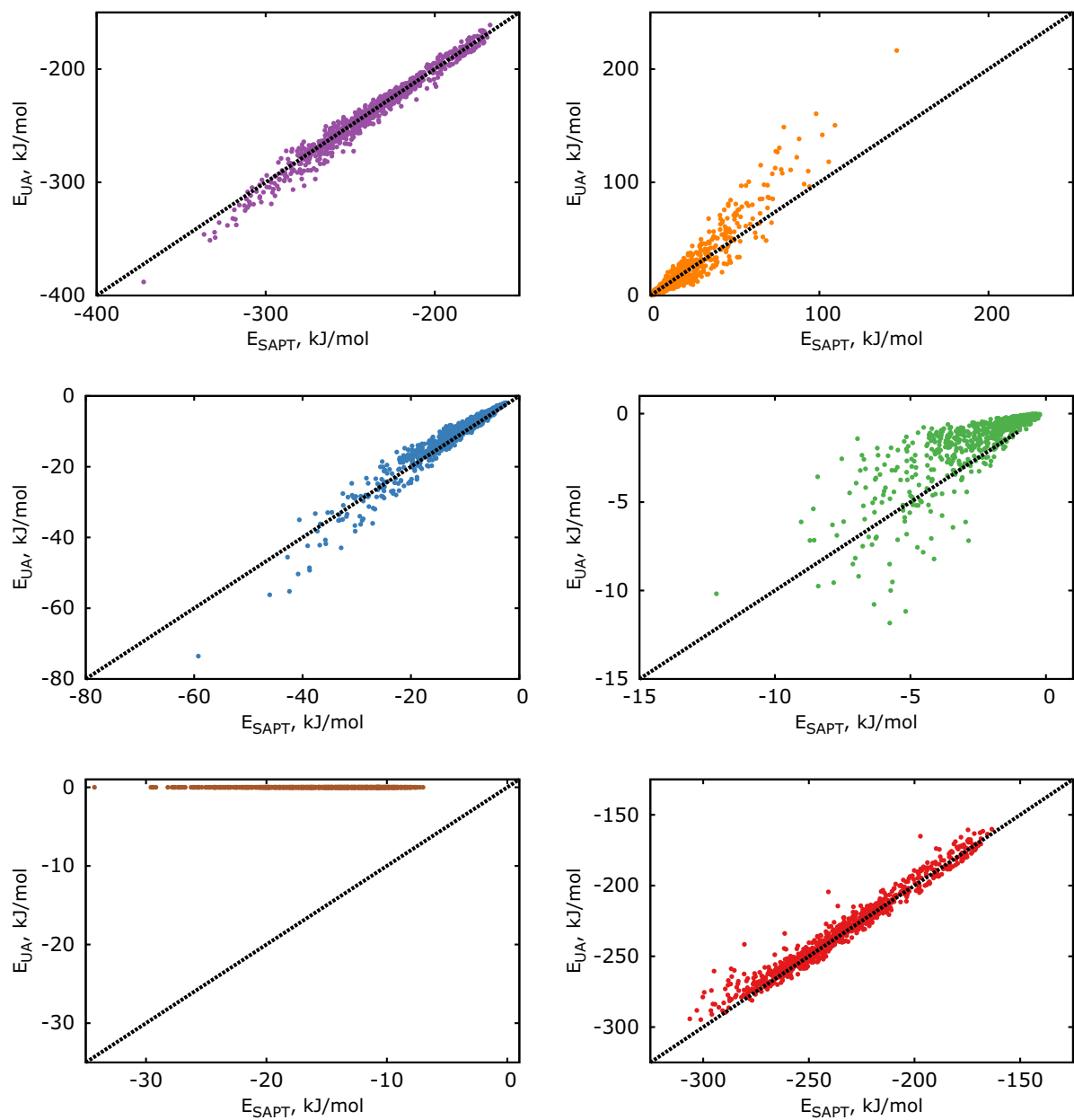


Figure S1: SAPT(PBE0) fits for [BMMIM][BF₄] dimer. From top to bottom, left to right: electrostatic, exchange, dispersion, dhf, induction, and sum of all energy components excluding induction. Note that UA model has zero induction energy because of lack of drude charge.

S2. Thermophysical properties: density and excess molar volume

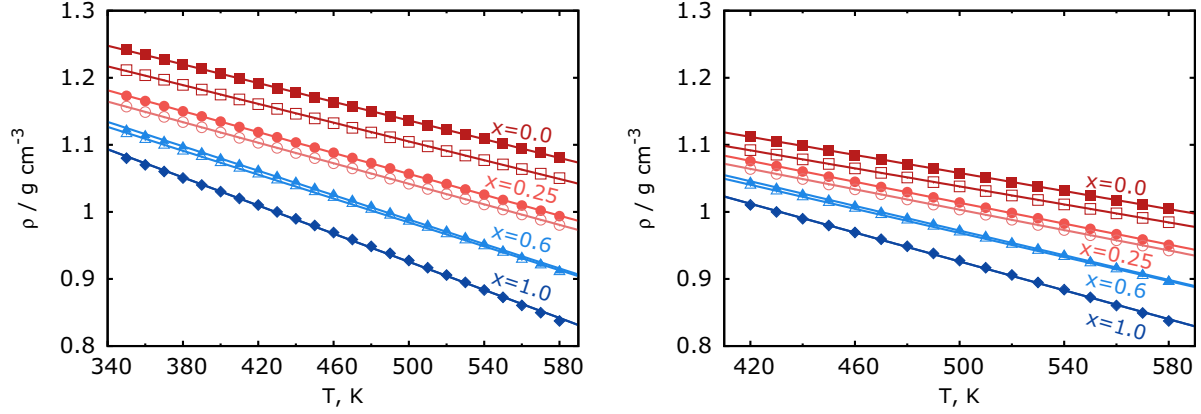


Figure S2: Variation of density for (left) PEO/[EMIM][BF₄] and PEO/[EMMIM][BF₄] and (right) PEO/[BMIM][BF₄] and PEO/[BMMIM][BF₄] mixtures for several mole fractions of PEOs, x 's, and the studied temperature range. Note that filled and empty symbols represent [C_nMIM] and [C_nMMIM] cations in mixtures, respectively. The solid lines represent a fit to the equation $\rho = \rho_0 + aT$.

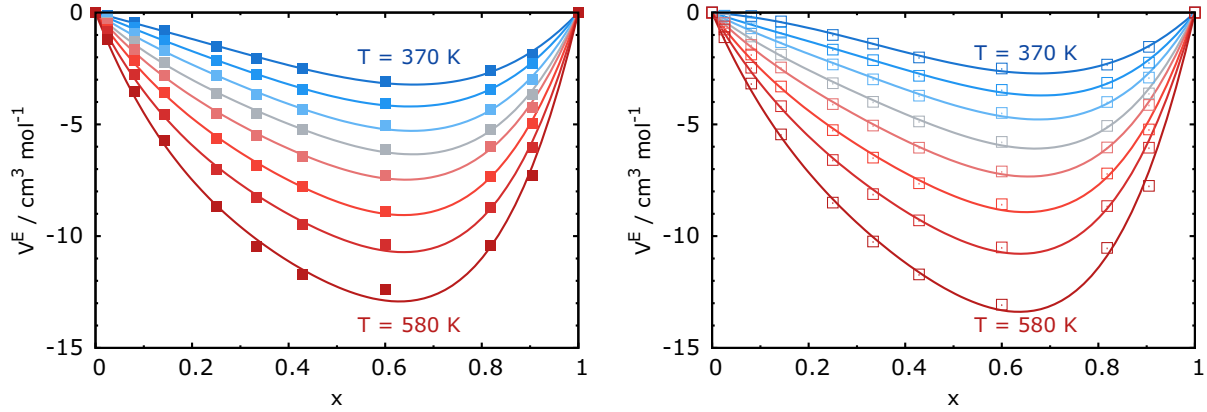


Figure S3: Variation of molar excess volume of (left) PEO/[EMIM][BF₄] and (right) PEO/[EMMIM][BF₄] mixtures as a function of mole fraction of PEOs. The color of lines represents temperature from 370 K to 580 K with interval 30 K. Solid and dashed curves show fits according to the Redlich-Kister equation.

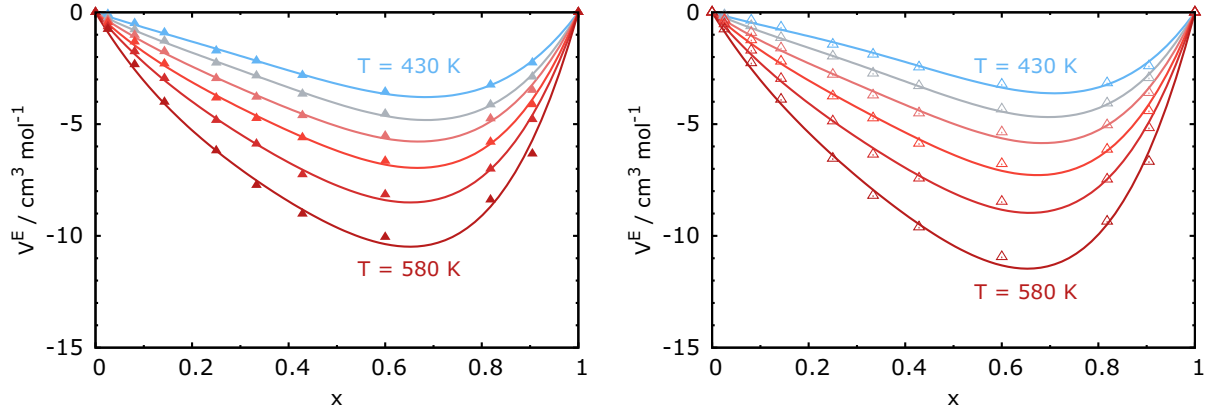


Figure S4: Variation of molar excess volume of (left) PEO/[BMIM][BF₄] and (right) PEO/[BMMIM][BF₄] mixtures as a function of mole fraction of PEOs. The color of lines represents temperature from 430 K to 580 K with interval 30 K. Solid and dashed curves show fits according to the Redlich-Kister equation.

S3. Polymer conformations: radius of gyration and end-to-end distance of poly(ethylene oxide)

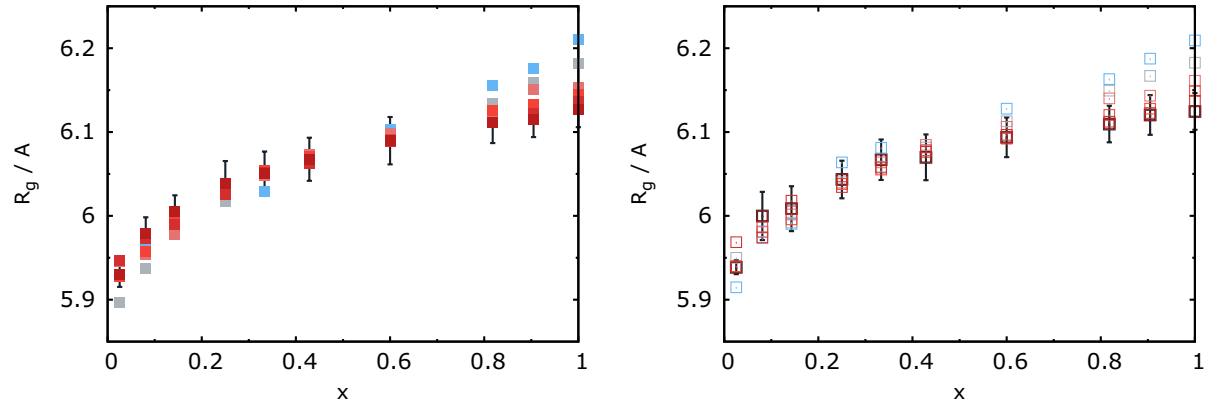


Figure S5: Variation of radius of gyration of (left) PEO/[EMIM][BF₄] and (right) PEO/[EMMIM][BF₄] mixtures as a function of mole fraction of PEOs. The color of lines represents temperature from 370 K to 580 K with interval 30 K, which is the same as Fig. S3. The y-error bar (black) is the standard deviation at 580 K (red).

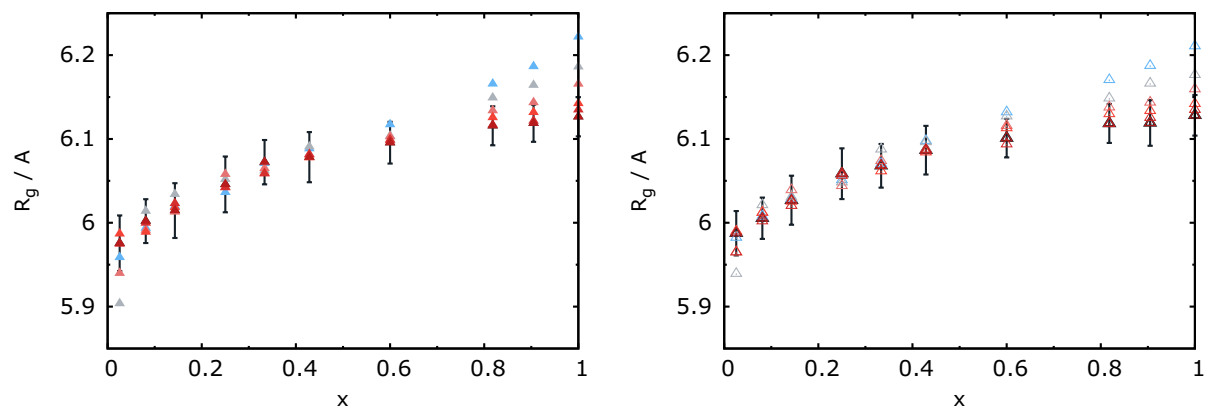


Figure S6: Variation of radius of gyration of (left) PEO/[BMIM][BF₄] and (right) PEO/[BMMIM][BF₄] mixtures as a function of mole fraction of PEOs. The color of lines represents temperature from 430 K to 580 K with interval 30 K, which is the same as Fig. S4. The y-error bar (black) is the standard deviation at 580 K (red).

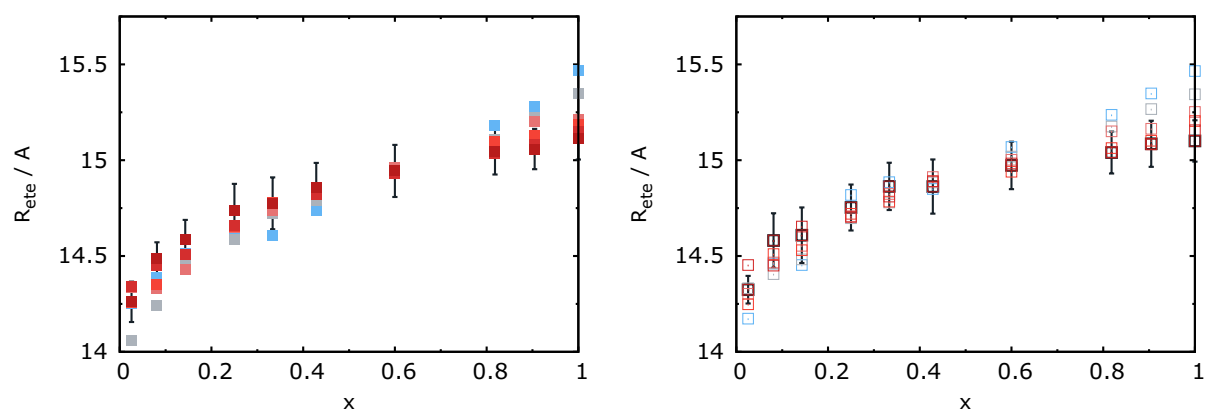


Figure S7: Variation of end-to-end distance of (left) PEO/[EMIM][BF₄] and (right) PEO/[EMMIM][BF₄] mixtures as a function of mole fraction of PEOs. The color of lines represents temperature from 370 K to 580 K with interval 30 K, which is the same as Fig. S3. The y-error bar (black) is the standard deviation at 580 K (red).

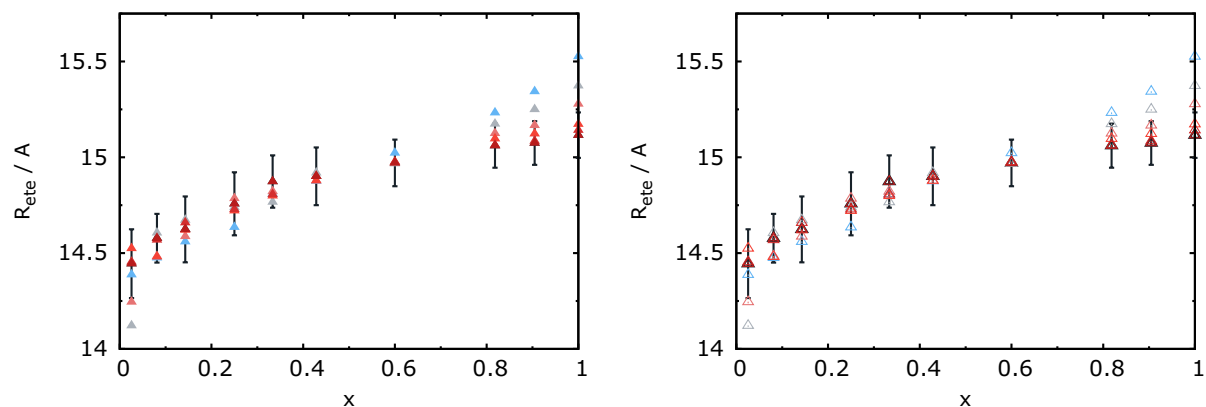


Figure S8: Variation of end-to-end distance of (left) PEO/[BMIM][BF₄] and (right) PEO/[BMMIM][BF₄] mixtures as a function of mole fraction of PEOs. The color of lines represents temperature from 430 K to 580 K with interval 30 K, which is the same as Fig. S4. The y-error bar (black) is the standard deviation at 580 K (red).

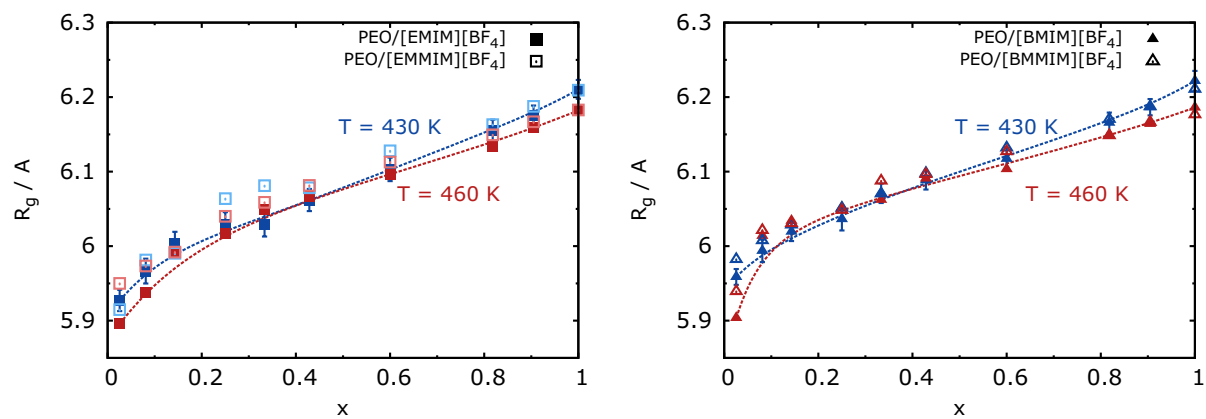


Figure S9: Plots of radius of gyration and end-to-end distance of polymers in (left) PEO/[EMIM][BF₄] and PEO/[EMMIM][BF₄] and (right) PEO/[BMIM][BF₄] and PEO/[BMMIM][BF₄] as a function of mole fraction of PEOs at 430 K and 460 K. The y-error bar is the block average error of PEO/[BMIM][BF₄] at 430 K. Dotted lines serve as eye-guide lines for PEO/[C_nMIM][BF₄] mixture.

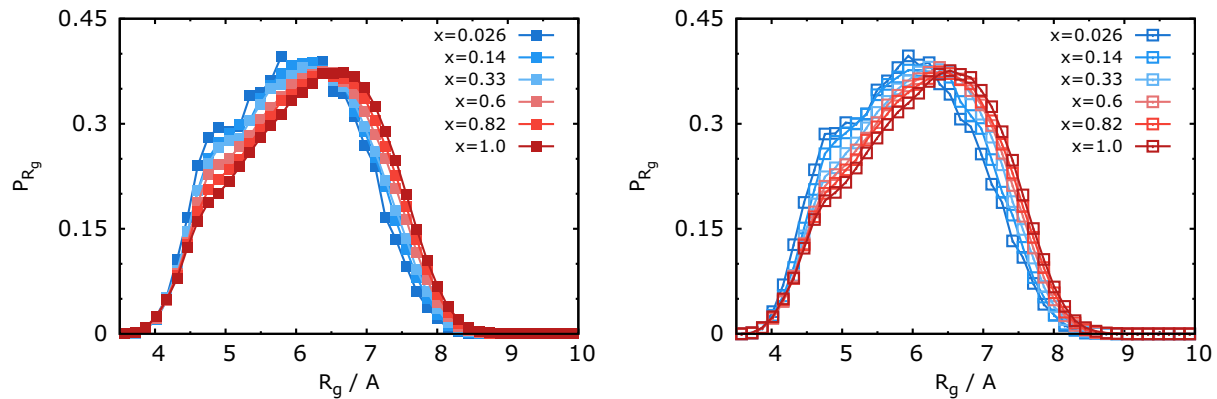


Figure S10: Probabilities of R_g of PEOs for (left) PEO/[EMIM][BF₄] and (right) PEO/[EMMIM][BF₄] as a function of mole fractions of PEOs at 430 K.

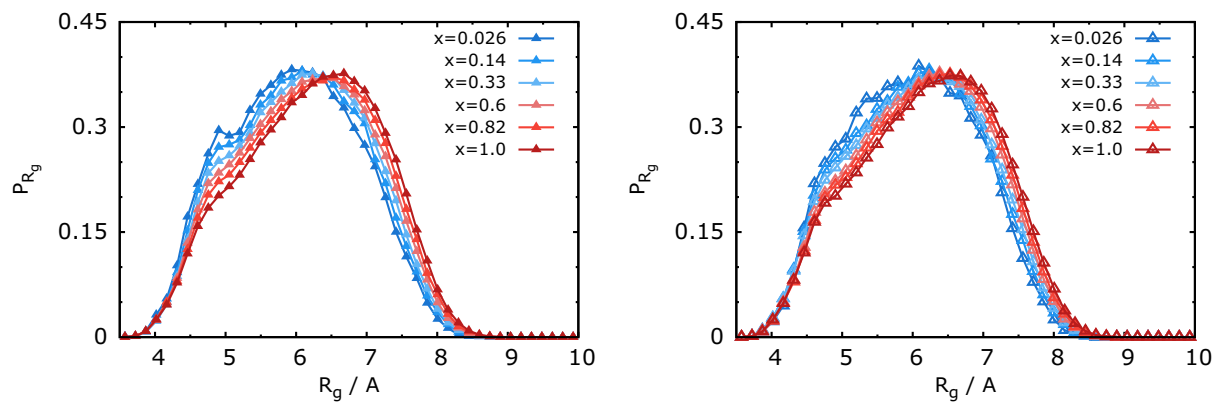


Figure S11: Probabilities of R_g of PEOs for (left) PEO/[BMIM][BF₄] and (right) PEO/[BMMIM][BF₄] as a function of mole fractions of PEOs at 430 K.

S4. Molar cohesive energy between PEO and ILs

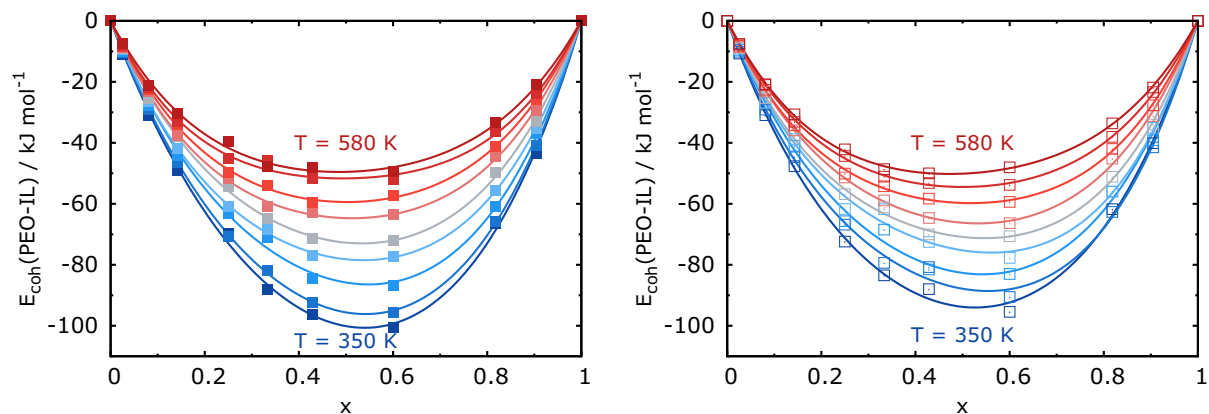


Figure S12: Variation of molar cohesive energy of (left) PEO/[EMIM][BF₄] and (right) PEO/[EMMIM][BF₄] mixtures as a function of mole fraction of PEOs. The color of lines represents temperature from 370 K to 580 K with interval 30 K, which is the same as Fig. S3.

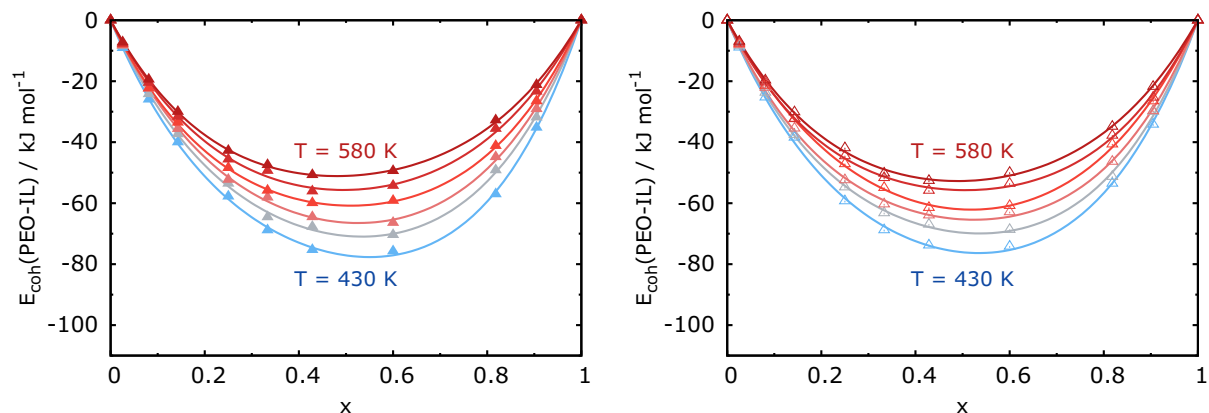


Figure S13: Variation of molar cohesive energy of (left) PEO/[BMIM][BF₄] and (right) PEO/[BMMIM][BF₄] mixtures as a function of mole fraction of PEOs. The color of lines represents temperature from 430 K to 580 K with interval 30 K, which is the same as Fig. S4.

S5. Molar coordination number of PEO oxygen atoms around single cation, N_{cont}^{high} and N_{cont}^{low}

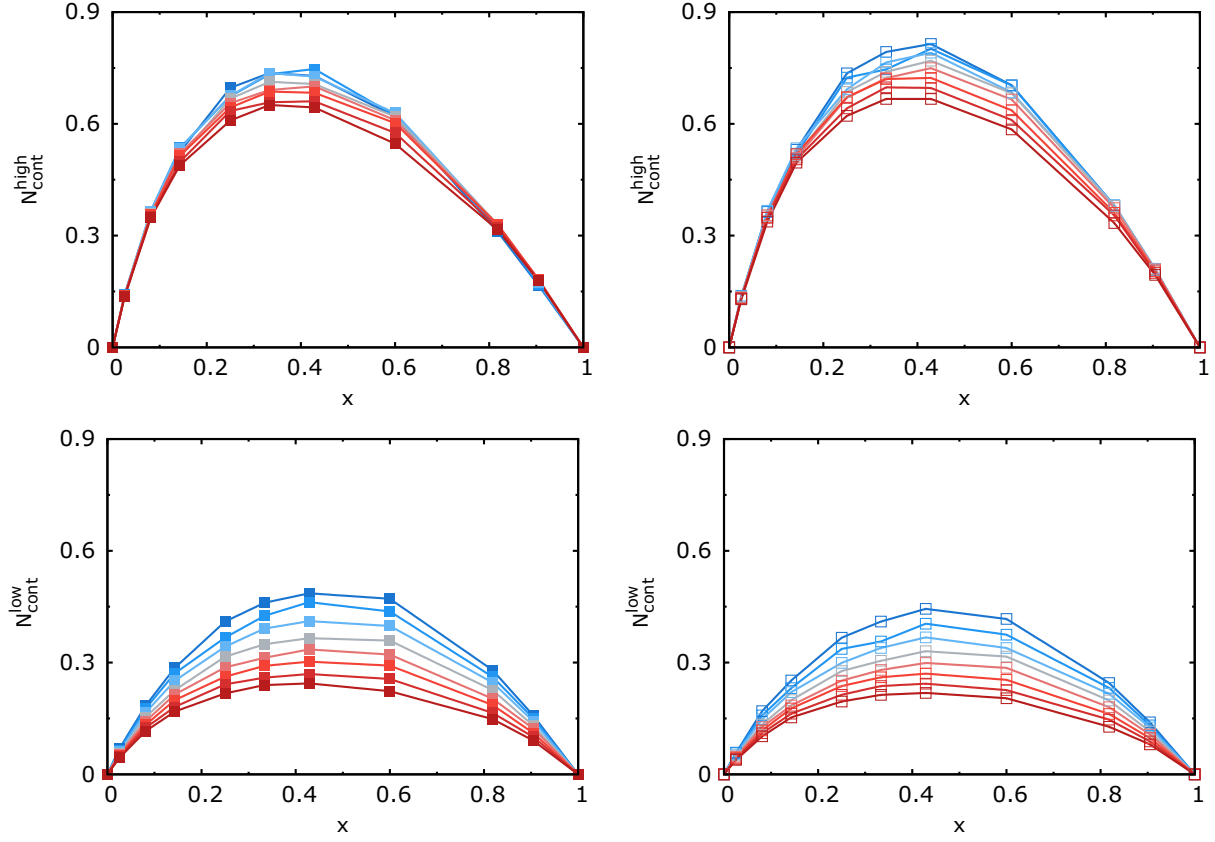


Figure S14: Variation of N_{cont} 's for (left) PEO/[EMIM][BF₄] and (right) PEO/[EMMIM][BF₄] mixture. The meaning of colors is working temperature, as shown in Fig. 3. Solid lines are the linearly interpolated lines.

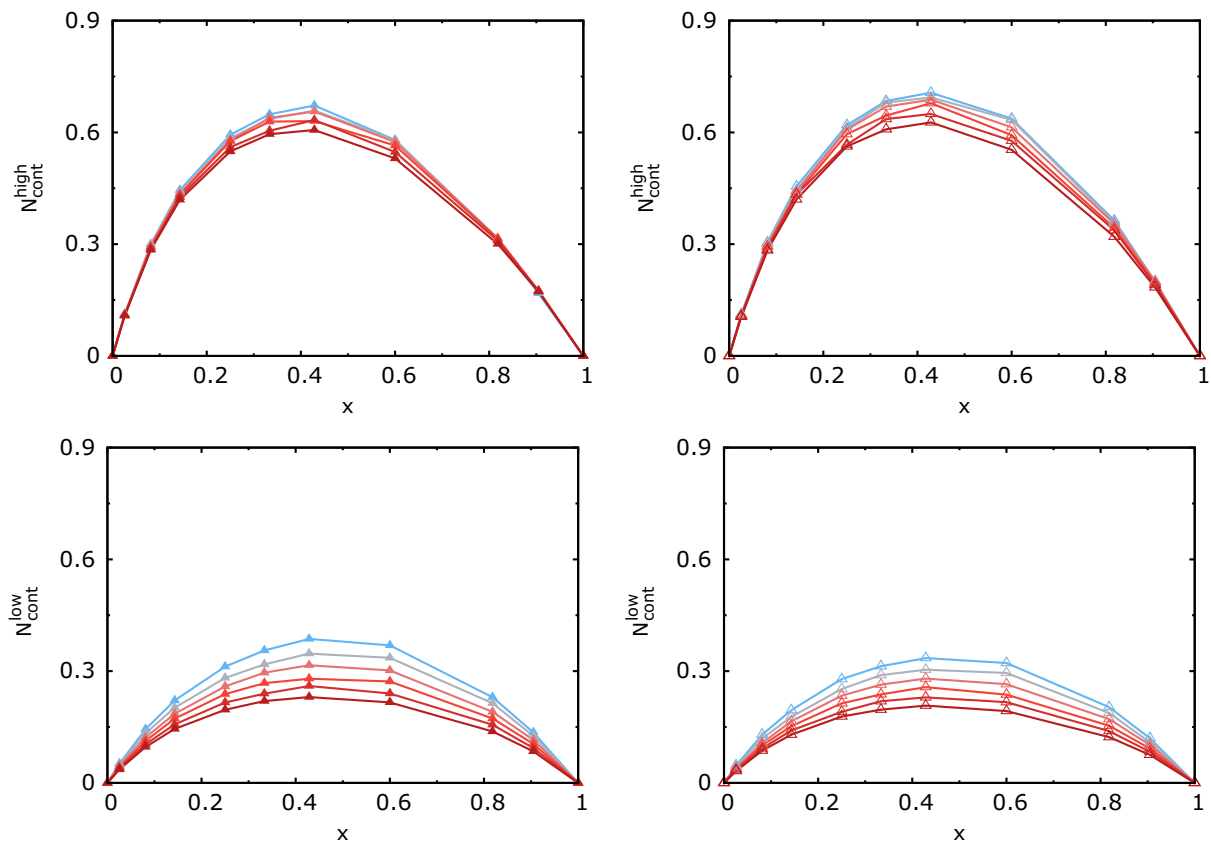


Figure S15: Variation of N_{cont} 's for (left) PEO/[BMIM][BF₄] and (right) PEO/[BMMIM][BF₄] mixture. The meaning of colors is working temperature, as shown in Fig. 4. Solid lines are the linearly interpolated lines.

S6. Deep Neural Network

As the result of training our deep neural network model, Figure 16 shows the optimized weights and biases of neurons of the first hidden layers. With large magnitude of weights, excess volume and coordination numbers is likely to activate input data to predict phases. The examples of activated data by hidden neurons are shown in Figure 17 and Figure 18. They show that distribution of intermediate scores after the first layer is converged to easily indicate its phase on output layer. It is not clear to know how the neural network works for phase prediction, but it may indicate that the first hidden layer can capture the feature of phase separation with the chosen descriptors.

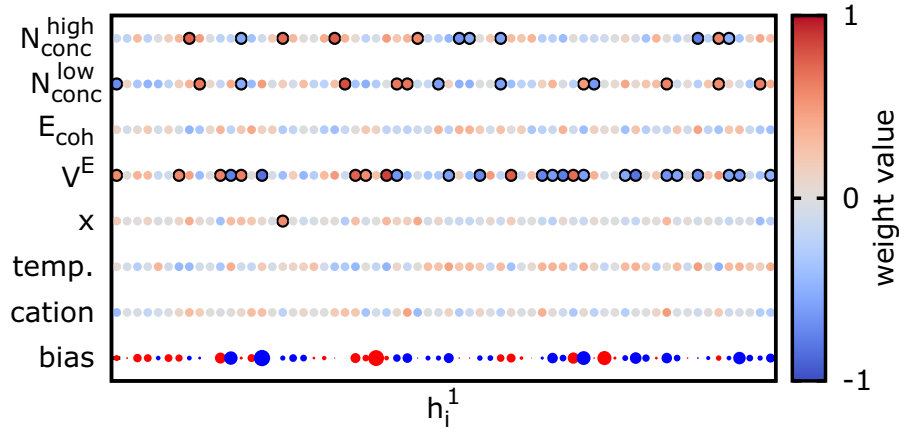


Figure S16: Pictorial figure to represent the optimized (7 x 64) weight matrix with 64 biases for the first hidden layer. The color of points represents the value of weights on color bar and black border dots are used when the absolute weight values are greater than 0.5. For bias, we use unique blue and red color for positive and negative value with variable sizes depending on the (absolute) magnitude.

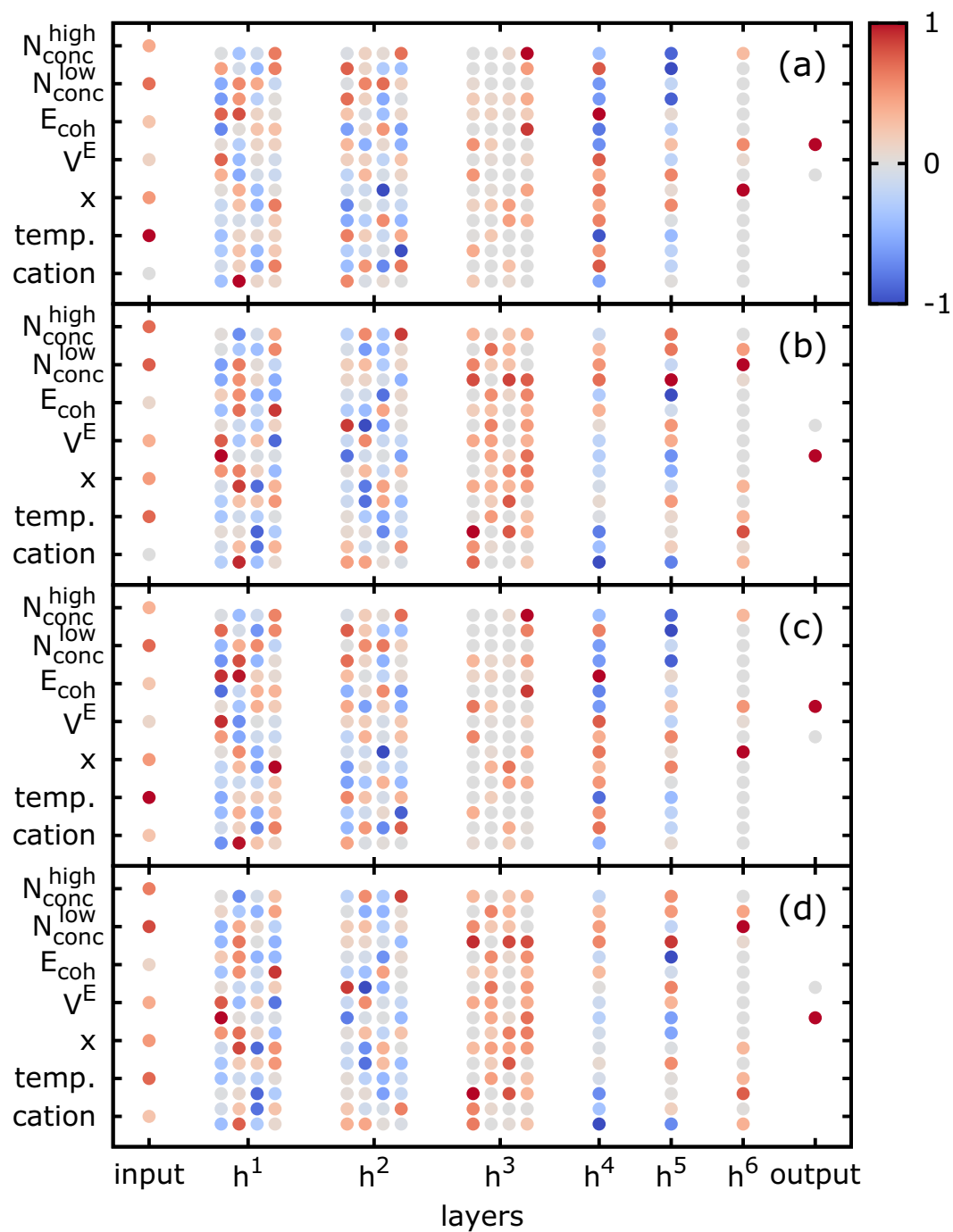


Figure S17: Pictorial figures to represent input data, intermediate scores in hidden layers, and outputs for mixing and separation phase of mixtures; for $x = 0.5$, using the input vector of 7 descriptors at (a) 580 K and (b) 420 K for of PEO/[BMIM][BF₄] and at (c) 580 K and (d) 420 K for PEO/[BMMIM][BF₄]. To easily see (intermediate) activated scores in hidden layers, we normalized scores dividing by the largest magnitude among scores in the layer.

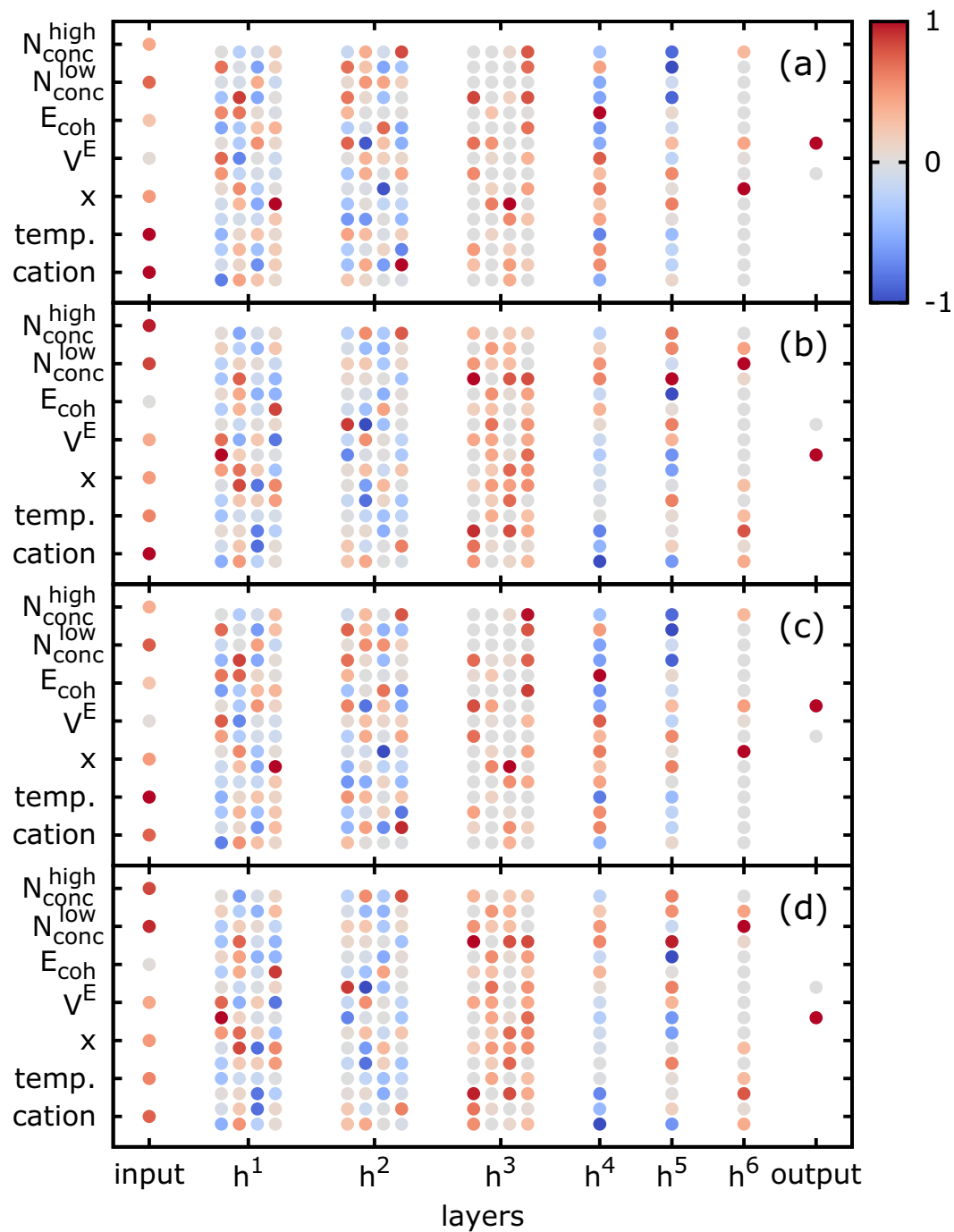


Figure S18: Pictorial figures to represent input data, intermediate scores in hidden layers, and outputs for mixing and separation phase of mixtures; for $x = 0.5$, using the input vector of 7 descriptors at (a) 580 K and (b) 350 K for of PEO/[EMIM][BF₄] and at (c) 580 K and (d) 350 K for PEO/[EMMIM][BF₄]. For details, refer the caption in Figure 17