Supplementary information for:-

"Mixing scheme of the aqueous solution of tetrabutylphosphonium trifluoroacetate in the water-rich region"

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1. Calculation of the apparent excess partial molar volumes

For binary systems of ionic liquid (IL) and water, the molar volume are divided into the ideal part, V^{ideal}_{m}, and the excess part, V^{E}_{m}, as,

$$V_m = V^{ideal}_{m} + V^{E}_{m} = \left\{V^{*}_{IL}x_{IL} + V^{*}_{W}\left(1 - x_{IL}\right)\right\} + V^{E}_{m}. \qquad \text{(S-1)}$$

V^{ideal}_{m} can be calculated using the molar volumes of pure liquid IL, V^{*}_{IL}, and water, V^{*}_{W}, and the mole fraction of IL, x_{IL}, and it is linear to x_{IL}.

However, for the aqueous solution of $[P_{4,4,4,4}]CF_3COO$, pure $[P_{4,4,4,4}]CF_3COO$ is a solid at room temperature and it is not possible to obtain V^{*}_{IL}. We, therefore, define the "apparent" ideal molar volume of the present system, $V^{ideal}_{m,ap}$, using the data set at x_{IL}= 0.000 and at 0.079, assuming that $V^{ideal}_{m,ap}$ passes through the V_m value at the uppermost data point, x_{IL} = 0.079. Hence,

$$V_{m,ap}^{ideal}(x_{IL}) = x_{IL} \cdot \frac{V_{m(x_{IL}=0.079)} - V_W^*}{0.079} + V_W^*, \tag{S-2}$$

and the "apparent" molar volume of "pure liquid $[P_{4,4,4,4}]CF_3COO$" at x_{IL}= 1 is expressed as,

$$V_{IL,ap}^{*} = \frac{V_{m(x_{IL}=0.079)} - V_W^*}{0.079} + V_W^*. \tag{S-3}$$

According to the equation (S-1), the "apparent" excess molar volume is then written as,

$$V_{m,ap}^{E}(x_{IL}) = V_m(x_{IL}) - V_{m,ap}^{ideal}(x_{IL}). \tag{S-4}$$

Figure S1-1 shows the apparent excess molar volumes, $V_{m,ap}^{E}$, at 25 ºC. In this concentration region $V_{m,ap}^{E}$ shows negative value and concave downward. The smooth curve was drawn through all the data points using a flexible ruler as the solid line in the figure.

Then the apparent excess partial molar volume of IL, $V_{IL,ap}^{E}$, is calculated as,

$$V_{IL,ap}^{E} = (1 - x_{IL})\left(\frac{\partial V_{m,ap}^{E}}{\partial x_{IL}}\right) + V_{m,ap}^{E}. \tag{S-5}$$

We differentiated $V_{m,ap}^{E}$ graphically using the smooth curve by reading the values off the smooth curve at every 0.001 mole fraction of $[P_{4,4,4,4}]CF_3COO$ and calculate partial molar volume of $[P_{4,4,4,4}]CF_3COO$ as,

$$V_{IL,ap}^{E} = (1 - x_{IL})\left(\frac{\Delta V_{m,ap}^{E}}{\Delta x_{IL}}\right) + V_{m,ap}^{E}. \tag{S-6}$$

$\Delta V_{m,ap}^{E}$ indicates the amount of change of $V_{m,ap}^{E}$ at Δx_{IL}= 0.001 intervals. The apparent excess partial molar volume of water, $V_{W,ap}^{E}$, is calculated by the same manner.

2. Graphical differentiation using a flexible ruler

To obtain the next higher order derivative quantities, graphical differentiation using a flexible ruler was applied on the measured data as shown in Figure S1-1. The advantage of graphical differentiation for the differential thermodynamics in dilute region was discussed extensively elesewhere.[1–3] The fact that B-spline method is not able to reflect inflection points of data has been discribed.[2,3]

Conventionally, such a fitting function as the Redlich-Kister polynomial[4] is used to raise the order of derivative by a step. It is known as one of the popular fitting functions of excess quantities for binary systems written as,

$$V_m^E(x) = x(1-x)\sum_{i=0}^{n} A_i(2x-1)^i, \tag{S-7}$$

where x is mole fraction of a solute, A_i's are the fitted polynomial coefficients and n is its degree. Figure S1-2 shows the obtained fitting curves by a flexible ruler (dotted line) and the Redlich-Kister polynomial of n= 2 (solid line). On increasing to n=3, the fitting curve became wavy, and the case of n= 2 seems most appropriate. As shown in Figure S1-2, the inflection point apparent around at x_{IL}= 0.03 along the dotted curve is not reproduced on the solid curve obtained by latter. Thus, equation (S-7) is not suitable for the present mole fraction range.

Numerical differentiation is another method which reflects the experimental fact perfectly and model-free. For this purpose, the quality of all the data points with small increments ought to be very high with at the least 4 significant figures. In the previous study[5], we successfully obtained the third derivative quantities with at least 3 significant figures by numerical differentiation. When the data contain a sporadic error as for the present case apparent at about x_{IL} = 0.055 in Fig. S1-1, the numerical method cannot be used, otherwise devastating error will be introduced. In such cases, we have to use human judgement and draw a smooth curve through all the data points by the aid of a flexible ruler.

References

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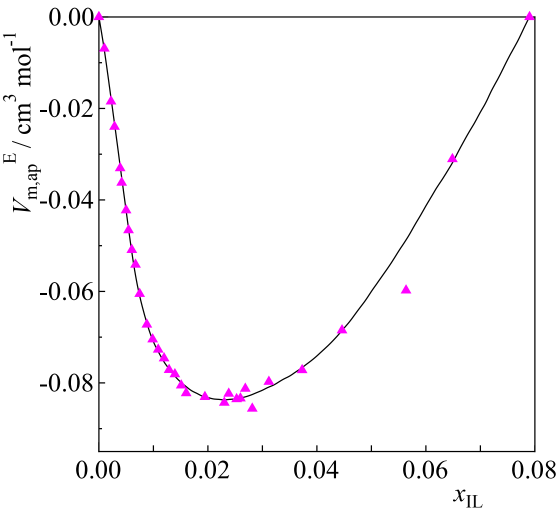

Figure S1-1 The apparent excess molar volume of the aqueous solution of $[P_{4,4,4,4}]CF_3COO$, $V_{m,ap}^{E}$, at 25 ºC against x_{IL}. The uncertainty is estimated as ± 0.002 cm^3 mol^{-1}. There is a sporadically bad point at about x_{IL} = 0.06, which was ignored. The solid curve is a smooth curve drawn with a flexible ruler.

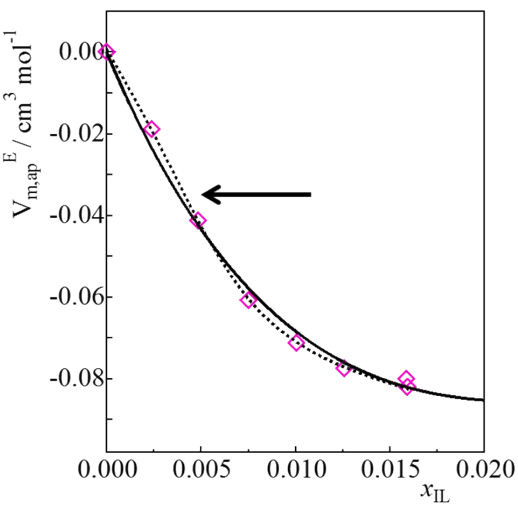

Figure S1-2 The smooth curves fitted on the plots of the measured apparent excess partial molar volume, $V^{E}_{m,ap}$, at 25 ºC. The uncertainty for these data points is estimated as ± 0.002 cm^3 mol^{-1}. The solid curve was obtained by Redlich-Kister polynomial with n= 2 and the dotted line was drawn manually using a flexible ruler.