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 volumes are divided into the ideal part, \( V_{\text{ideal}}^m \), and the excess part, \( V_{\text{E}}^m \), as,

\[
V_m = V_{\text{ideal}}^m + V_{\text{E}}^m = \left\{ V_{IL}^* x_{IL} + V_W^* (1 - x_{IL}) \right\} + V_{\text{E}}^m.
\]  

(S-1)

\( V_{\text{ideal}}^m \) 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 \([P_{4,4,4,4}]\text{CF}_3\text{COO}\), pure \([P_{4,4,4,4}]\text{CF}_3\text{COO}\) 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, \( V_{\text{ideal}}^{m,\text{ap}} \), using the data set at \( x_{IL} = 0.000 \) and at 0.079, assuming that \( V_{\text{ideal}}^{m,\text{ap}} \) passes through the \( V_m \) value at the uppermost
data point, $x_{IL} = 0.079$. Hence,

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

and the “apparent” molar volume of “pure liquid $[P_{4,4,4,4}]CF_{3}COO$” at $x_{IL} = 1$ is expressed as,

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

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

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

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,

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

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 $[P_{4,4,4,4}]CF_{3}COO$ and calculate partial molar volume of $[P_{4,4,4,4}]CF_{3}COO$ as,

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

$\Delta V_{m, ap}^{E}$ indicates the amount of change of $V_{m, ap}^{E}$ at $\Delta x_{IL} = 0.001$ 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 elsewhere.\textsuperscript{1–3} The fact that B-spline method is not able to reflect inflection points of data has been described.\textsuperscript{2,3}

Conventionally, such a fitting function as the Redlich-Kister polynomial\textsuperscript{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,

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

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 least 4 significant figures. In the previous study\textsuperscript{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


Figure S1-1   The apparent excess molar volume of the aqueous solution of 
\([P_{4,4,4,4}]\text{CF}_3\text{COO}, V^E_{m,ap}\), at 25 °C against \(x_{IL}\). The uncertainty is estimated as \(\pm 0.002 \text{ cm}^3\) 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, $V_{m, ap}^E$, at 25 °C. The uncertainty for these data points is estimated as $\pm 0.002 \text{ cm}^3 \text{ mol}^{-1}$. The solid curve was obtained by Redlich-Kister polynomial with $n=2$ and the dotted line was drawn manually using a flexible ruler.