Electronic Supplementary Information

Effect of cation alkyl chain length on density and diffusion in dialkylpyrrolidinium bis(mandelato)borate ionic liquids

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Table S1. Mean and “fractional” diffusion coefficients (x10^{-12} m^2/s) of [C_nC_1Pyrr][BMB] in the temperature range 313-373 K. Fractional diffusion coefficients for samples with *n* = 10 and 14 obtained after CORE analysis[26] of the corresponding diffusion decays.

n / T, K	313	323	333	343	353	373
4			0.5 ± 0.03	0.9 ± 0.03	1.8 ± 0.1	6.2 ± 0.1
5			1.0 ± 0.03	0.95 ± 0.03	1.7 ± 0.1	8.7 ± 0.1
6			0.7 ± 0.03	0.99 ± 0.03	1.9 ± 0.1	5.8 ± 0.1
7			0.4 ± 0.03	0.78 ± 0.03	1.6 ± 0.1	5.5 ± 0.1
8			0.7 ± 0.03	1.3 ± 0.03	2.6 ± 0.1	8.9 ± 0.1
10 mean “fast” “slow”		2.6 ± 0.1 4.9 ± 0.1 0.25 ± 0.02	2.4 ± 0.1 4.8 ± 0.1 0.36 ± 0.02	1.6 ± 0.1 5.4 ± 0.1 0.86	2.1 ± 0.1 5.8 ± 0.1 1.8 ± 0.1	8.5 ± 0.1
14 mean “fast” “slow”	4.5 ± 0.1 6.9 ± 0.1 0.24 ± 0.02	5.4 ± 0.1 7.7 ± 0.1 0.32 ± 0.02	6.6 ± 0.1 9.9 ± 0.1 0.46 ± 0.02	7.1 ± 0.1 12.5 ± 0.1 0.98 ± 0.02	6.8 ± 0.1 16 ± 0.1 1.85 ± 0.02	7.7 ± 0.1

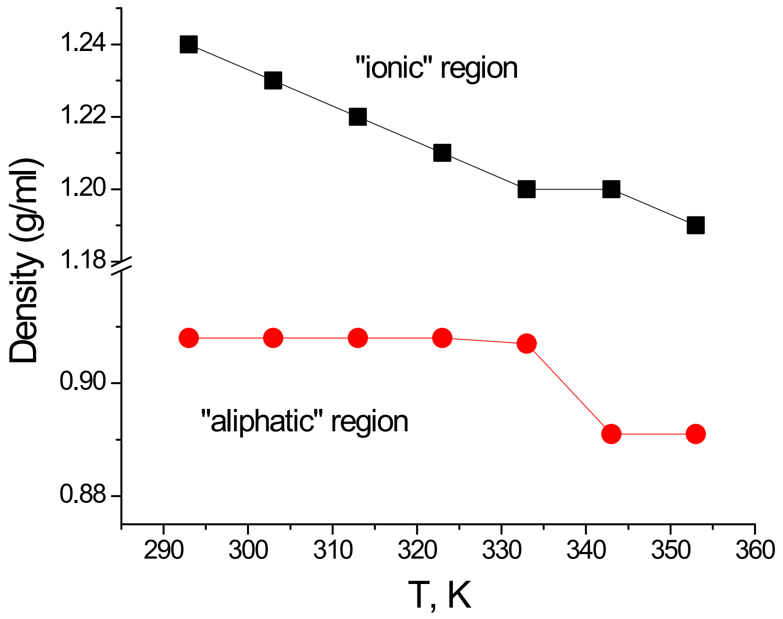

Figure S1. Densities of “ionic” and “aliphatic” regions of studied ILs as a function of temperature (data from Table 1).

A more complicated model was also applied to describe the experimental data presented in Figure 4. It was proposed that the density of the hydrocarbon regions may depend on the length of the long hydrocarbon chains of the cations. This phenomenon was taken into account using an equation for the volume occupied by one CH_2 group:

$$V_{CH2}(n) = V_{CH2\_0}(1-\alpha \cdot n)$$

where a factor $\alpha \cdot n$ was introduced to simulate either descending or ascending trend of the V_{CH2_0}, which is the free volume of CH_2 and CH_3 segments in long alkyl chains of cations independent on *n*, used in Eq.(5).

Therefore, Eq. (5) can be modified as follows, Eq. (S1):

$$\rho = \frac{m_{NC} + n \cdot m_{CH2}}{V_{NC} + n \cdot (V_{CH2\_0}(1-\alpha \cdot n))} . \tag{S1}$$

Results of best fits for this model are shown in Fig. S2.

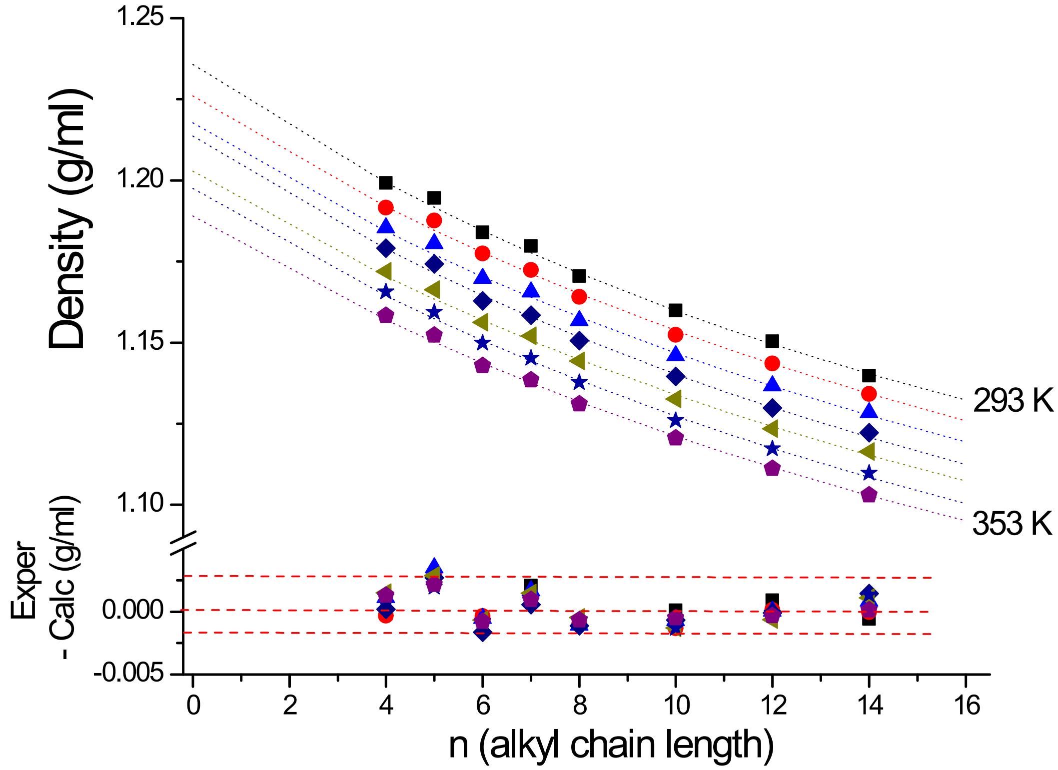

Figure S2. Densities of studied ILs as a function of number of CH_2 groups in the cation long alkyl chain, and best fits of the experimental data using Eq. (S1). Differences after subtraction of experimental and calculated data are shown in the bottom.

Table S2. Parameters of Eq. (S1) to the best fit of experimental data from Fig. S2.

T / K	**V_I / 10^{-22} ml**	**V_{al} / 10^{-22} ml**	**α**	**ρ_I / (g ml^{-1})**
293	87.80	2.57	0.004	1.24
303	88.50	2.57	0.002	1.23
313	89.10	2.57	0.002	1.22
323	89.40	2.58	0.0025	1.21
333	90.20	2.60	0.002	1.20
343	90.60	2.62	0.0022	1.20
353	91.25	2.63	0.0022	1.19

Application of this ‘complicated’ model gives almost the same differences between calculated and experimental data (see Fig. S2, bottom) as more the simple ‘additive’ model discussed in the main text. Mean-squared deviations of calculated densities (Eqs. (1) and (S1)) from the experimental densities were calculated as (see Eq. (S2):

$$\delta = \frac{\sum_{4}^{14} \left(\rho_{exper} - \rho_{calc}\right)^2}{8} \tag{S2}$$

Results of these calculations are shown in Fig. S3.

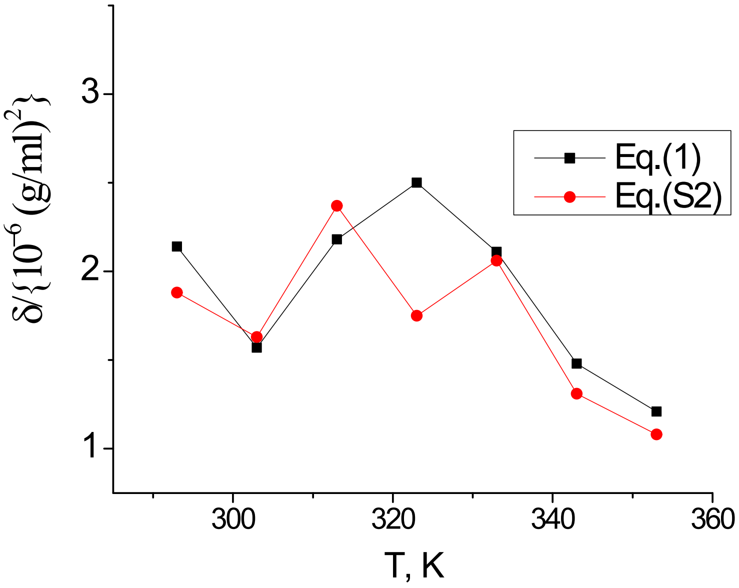

Figure S3. Mean-squared deviations of calculated and experimental densities at different temperatures as calculated using Eq. (1) and Eq. (S2).

Therefore, it can be concluded that for densities of [C$_n$C1Pyrr][BMB] ionic liquids the assumptions used in the 'additive' or 'mosaic' model are sufficient to describe the experimental dependences, obviating the need for a more complicated model.