Density and Surface Tension of Ionic Liquid $[C_2mim][PF_3(CF_2CF_3)_3]$ and Prediction of Properties $[C_nmim][PF_3(CF_2CF_3)_3]$ ($n = 1, 3, 4, 5, 6$)

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The density and surface tension of the air- and water-stable hydrophobic ionic liquid (IL) 1-ethyl-3-methylimizazolium tris(pentafluoroethyl) trifluorophosphate (CAS Registry No.: 377739-43-0; $[C_2mim][PF_3(CF_2CF_3)_3]$) were measured in the range of $T = (283.15$ to $338.15)$ K. The other physicochemical properties of the IL $[C_2mim][PF_3(CF_2CF_3)_3]$ at 298.15 K were estimated in terms of empirical and semiempirical equations, as well as the interstice model theory. These properties include molecular volume, standard molar entropy, lattice energy, the parachor, molar enthalpy of vaporization, interstice volume, thermal expansion coefficient, interstice fraction, and so forth. Then, the physicochemical properties of the ILs $[C_nmim][PF_3(CF_2CF_3)_3]$ ($n = 1, 3, 4, 5, 6$) family were predicted in terms of the estimated values of molecular volume and the parachor.

Introduction

Ionic liquids (ILs) as organic salts show low melting points and exhibit good solvation, coordination, and nonvolatility properties, so both industrial and scientific communities were advertising to them for broad ranges of applications as green solvents. Particularly, the air- and water-stable hydrophobic ILs were attracting the attention of people in each domain. Actually, most ILs are hydrophilic, so 1-alkyl-3-methylimidazolium hexafluorophosphates (C_nmimPF_6) were attracting serious concern as an air- and water-stable hydrophobic compound.[1−3] The properties were reported in succession when the air- and water-stable hydrophobic compounds were synthesized.[4−8] Recently, a new type of IL, $[C_2mim][PF_3(CF_2CF_3)_3]$, was synthesized by Merck Co. This is also an air- and water-stable hydrophobic IL. So, the study on properties of this type of IL is significant in many concerned fields.

In view of the above fact, the density and surface tension of the IL $[C_2mim][PF_3(CF_2CF_3)_3]$ were measured from (283.15 to 338.15) K. Standard molar entropy and lattice energy were estimated in terms of the Glasser's theory;[9] the parachor was estimated. The value of molar enthalpy of vaporization was estimated in terms of Kabo's empirical equation;[10] the interstice model theory[11,12] put forward by Yang et al. was used for estimating the interstice properties of the IL $[C_2mim][PF_3(CF_2CF_3)_3]$. Then, the physicochemical properties of the homologue of $[C_nmim][PF_3(CF_2CF_3)_3]$ ($n = 1, 3, 4, 5, 6$) were predicted in terms of the molecular volume and parachor.

Experimental Section

Chemicals. The IL $[C_2mim][PF_3(CF_2CF_3)_3]$ was supplied by Merck KGaA (batch: S9588301). The real purity of the IL was determined to be 0.9967 ± 0.0014 by adiabatic calorimetric study according to the van't Hoff equation. The concerned thermodynamic research of the IL will be published in the future by other authors. The mass fraction of the water was less than 10^{-4}. The halides were less than 10^{-4}. Because the IL is an air- and water-stable hydrophobic compound, it was measured in the air without further purification.

Measurement of the Density and Surface Tension. The density of the IL $[C_2mim][PF_3(CF_2CF_3)_3]$ was measured with an Anton Paar DMA 4500 oscillating U-tube densitometer which can provide automatic viscosity calibration and measurements. The density values were recorded once every 5 K from [(283.15 to 338.15) ± 0.01] K. The temperature was regulated to ± 0.01 K with a thermostat. The densitometer was calibrated with dry air and double-distilled freshly degassed water before the measurements of the IL sample and gave an uncertainty of $\pm\ 0.00002\ \mathrm{g\cdot cm^{-3}}$.

Using the tensiometer (DP-AW type produced by Sang Li Electronic Co.) of the forced bubble method, the surface tension of the double-distilled freshly degassed water was measured in range of [(283.15 to 338.15) ± 0.05] K, which is in good agreement with the literature,[13] and the experimental error is $\pm\ 0.1\ \mathrm{mJ\cdot m^{-2}}$. The temperature was controlled with a thermostat. The surface tension of the IL $[C_2mim][PF_3(CF_2CF_3)_3]$ was measured with the same method. Each data point of the surface tension is the average value of five measurements. The uncertainties of the measurement are in the range of $\pm\ 0.2\ \mathrm{mJ\cdot m^{-2}}$.

The experimental measured values of density and surface tension of the IL $[C_2mim][PF_3(CF_2CF_3)_3]$ are listed in Table 1.

Results and Discussion

Volumetric and Surface Properties. The molecular weights of the ILs $[C_nmim][PF_3(CF_2CF_3)_3]$ ($n = 1, 2, 3, 4, 5, 6$) are listed in Table 2.

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Table 1. Experimental Values of Density, ρ, and Surface Tension, γ, of the IL $[C_2mim][PF_3(CF_2CF_3)_3]$ from (283.15 to 338.15) K

T/K	283.15	288.15	293.15	298.15	303.15	308.15
$\rho/g\cdot cm^{-3}$	1.72705	1.72113	1.71517	1.70926	1.70332	1.69740
$\gamma/mJ\cdot m^{-2}$	35.3	35.1	34.9	34.8	34.6	34.4
T/K	313.15	318.15	323.15	328.15	333.15	338.15
$\rho/g\cdot cm^{-3}$	1.69150	1.68562	1.67975	1.67388	1.66804	1.66221
$\gamma/mJ\cdot m^{-2}$	34.2	34.1	34.0	33.8	33.6	33.4

Table 2. Estimated and Predicted Values of Physicochemical Properties of IL $[C_nmim][PF_3(CF_2CF_3)_3]$ (n = 1, 2, 3, 4, 5, 6) at 298.15 K

properties	$[C_1mim]$ $[PF_3(CF_2CF_3)_3]^a$	$[C_2mim]$ $[PF_3(CF_2CF_3)_3]^b$	$[C_3mim]$ $[PF_3(CF_2CF_3)_3]^a$	$[C_4mim]$ $[PF_3(CF_2CF_3)_3]^a$	$[C_5mim]$ $[PF_3(CF_2CF_3)_3]^a$	$[C_6mim]$ $[PF_3(CF_2CF_3)_3]^a$
$M/g\cdot mol^{-1}$	542.15	556.18	570.20	584.23	598.26	612.29
V_m/nm^3	0.5130	0.5405	0.5680	0.5955	0.6230	0.6505
$\rho/g\cdot cm^{-3}$	1.75552	1.70926^c	1.66756	1.62962	1.59516	1.56356
$S^0/J\cdot K^{-1}\cdot mol^{-1}$	669.0	703.3	737.5	771.8	806.1	840.3
$U_{pot}/kJ\cdot mol^{-1}$	397	392	387	383	379	375
$V/cm^{-3}\cdot mol^{-1}$	308.8	325.4	341.9	358.5	375.0	391.6
p	757.8	792.1	826.4	860.7	895.0	929.3
$\Delta_l^g H_m^0/kJ\cdot mol^{-1}$	161.9	157.8	160.3	161.1	162.0	163.1
$10^{24}\ \upsilon/cm^3$	25.93	27.63	28.48	29.65	30.75	31.78
$\sum\upsilon/cm^3$	31.22	33.33	34.29	35.70	37.03	38.26
$10^2\ \sum\upsilon/V$	10.11	10.22	10.29	9.96	9.87	9.77
$10^4\ \alpha/K^{-1}$		6.96^c				
$10^4\ \alpha/K^{-1}$	5.10	5.14	5.04	5.00	4.96	4.91
$\gamma\cdot 10^3/N\cdot m^{-1}$	36.3	34.8^c	34.1	33.2	32.4	31.7

[a] Data in the column were predicted values. [b] Data in the column were estimated values. [c] Experimental data.

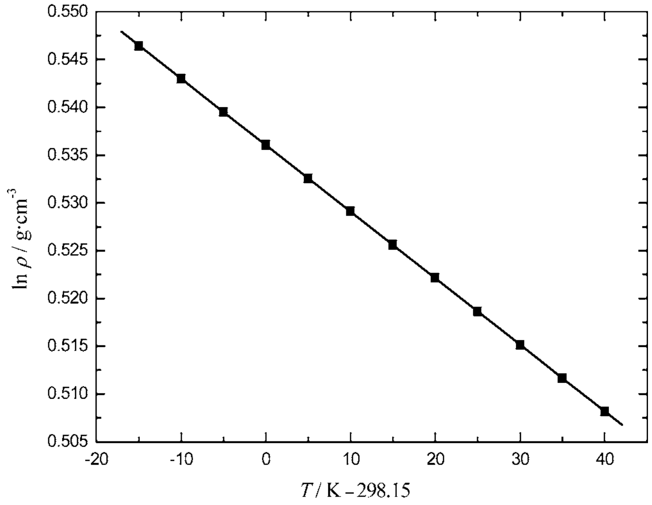

Figure 1. Plot of ln ρ vs T/K − 298.15 of the IL $[C_2mim][PF_3(CF_2CF_3)_3]$.

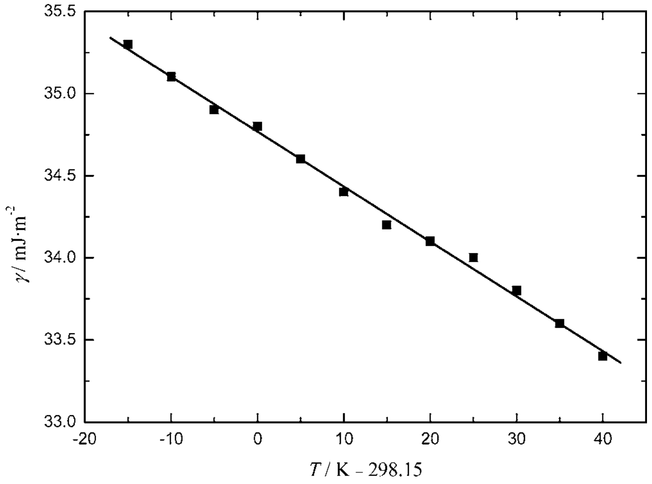

Figure 2. Plot of γ vs T/K − 298.15 of the IL $[C_2mim][PF_3(CF_2CF_3)_3]$.

By plotting the ln ρ against (T − 298.15) K, a straight line can be obtained (see Figure 1), and the empirical equation is:

$$\ln \rho/g\cdot cm^{-3} = b - \alpha(T/K - 298.15) \qquad (1)$$

where b is an empirical constant and the negative value of the slope, $\alpha = -(\partial \ln \rho/\partial(T - 298.15))_p$, is the thermal expansion coefficient of the IL. The correlation coefficient is $R = 0.99999$, the standard deviation $s = 3.0\cdot 10^{-5}\ g\cdot cm^{-3}$, $b = 0.53603$, and the thermal expansion coefficient of the IL is $\alpha = 6.96\cdot 10^{-4}\ K^{-1}$ at 298.15 K, respectively.

By plotting the values of γ obtained from the experiment against (T − 298.15) K, a linear equation was obtained (see Figure 2). The correlation coefficient is $R = 0.998$, and the standard deviation is $0.04\ mJ\cdot m^{-2}$. From Figure 2, the surface entropy, $S_a = -(\partial\gamma/\partial(T - 298.15))_p = 33.4\cdot 10^{-3}\ mJ\cdot K^{-1}\cdot m^{-2}$, can be obtained at 298.15 K. Additionally, the surface energy can be estimated by the experimental value of the surface tension at 298.15 K: $E_a = \gamma - T(\partial\gamma/\partial(T - 298.15))_p = 44.8\ mJ\cdot m^{-2}$. Compared with the fused salts and organic liquids, for example, $146\ mJ\cdot m^{-2}$ for $NaNO_3$[14], $67\ mJ\cdot m^{-2}$ for benzene, and $51.1\ mJ\cdot m^{-2}$ for octane,[14] the value of the IL $[C_2mim][PF_3(CF_2CF_3)_3]$ is close to the organic liquids and even less than some organic liquids. This fact shows that the interaction energy between ions in $[C_2mim][PF_3(CF_2CF_3)_3]$ is less than that in fused salts.

The molecular volume, V_m, can be calculated from experimental density using the following equation:

$$V_m(298.15\ K)/nm^3 = M/(N\rho) \qquad (2)$$

where M is molar mass, ρ, density, and N, Avogadro's constant. The calculated value is listed in Table 2.

According to Glasser's theory,[9] the standard molar entropy can be estimated from the equation:

$$S^0(298.15\ K)/J\cdot K^{-1}\cdot mol^{-1} = 1246.5(V_m/nm^3) + 29.5 \qquad (3)$$

where V_m is the molecular volume. The estimated value is listed in Table 2.

The surface tension, γ, has a relationship with the temperature in terms of the Eötvös equation:[14]

$$\gamma V^{2/3} = k(T_c - T) \qquad (4)$$

where V is the molar volume of the liquid, T_c, critical temperature, and k, an empirical constant.

By plotting the $\gamma V^{2/3}$ against T, a straight line was obtained (see Figure 3). From the plot, the values of $k = 0.8 \cdot 10^{-7}\ \mathrm{J \cdot K^{-1}}$ and $T_c = 2290$ K were obtained, respectively. For the majority of organic liquids, $k \approx 2.1 \cdot 10^{-7}\ \mathrm{J \cdot K^{-1}}$, but for fused salts, $k = 0.4 \cdot 10^{-7}\ \mathrm{J \cdot K^{-1}}$ for fused NaCl.[14] So, the present polarity of the IL [C_2mim][$PF_3(CF_2CF_3)_3$] may be regarded as more similar to those of the fused salts in terms of the value of the k.

The lattice energy, U_{POT}, was estimated according to the following equation:[9]

$$U_{POT}(298.15\ \mathrm{K})/\mathrm{kJ \cdot mol^{-1}} = 1981.2(\rho/M)^{1/3} + 103.8 \qquad (5)$$

where M is molar mass and ρ, density. The estimated data are listed in Table 2.

The contribution per methylene ($-CH_2-$) group to the molecular volume is 0.0272 $\mathrm{nm^3}$ for [$C_n$mim][BF_4],[9] 0.0282 $\mathrm{nm^3}$ for [$C_n$mim][NTf_2],[9] 0.0270 $\mathrm{nm^3}$ for [$C_n$mim][$AlCl_4$],[15] and 0.0278 $\mathrm{nm^3}$ for [$C_n$mim][Ala].[16] Because of the similar values of the contribution per $-CH_2-$ to the molecular volume, the group of methylene in the alkyl chains of the imidazolium-based ILs can be considered to have the same chemical environment. Then, the mean value of the contribution can be calculated to be 0.0275 $\mathrm{nm^3}$, and the physicochemical properties (density, standard entropy, lattice energy) of the homologues of [$C_n$mim][$PF_3(CF_2CF_3)_3$] (n = 1, 3, 4, 5, 6) can be predicted. All of the predicted data are listed in Table 2.

From Table 2, the contribution per methylene group to standard entropy, S^0(298.15 K), can be calculated to be 34.3 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. The above calculated value is in good agreement with the literature values of 35.1 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for [$C_n$mim][NTf_2],[9] 33.9 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for [$C_n$mim][BF_4],[9] 33.7 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for [$C_n$mim][$AlCl_4$],[15] and 34.6 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for [$C_n$mim][Ala].[16] According to the contribution per methylene group to standard entropy in the family with different anions, it can be concluded that the contribution of the methylene group to standard entropy is approximately equivalent for imidazolium-based ILs.

Parachors and Molar Enthalpy of Vaporization. The parachor, P, was estimated from the following equation:

$$P(298.15\ \mathrm{K}) = (M\gamma^{1/4})/\rho \qquad (6)$$

where M is molar mass, ρ, density, and γ, surface tension. The estimated data are listed in Table 2.

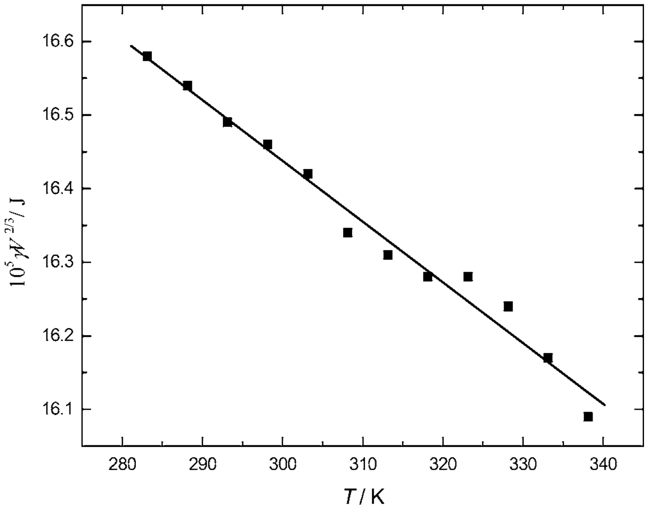

Figure 3. Plot of $\gamma V^{2/3}$ vs T/K of IL [C_2mim][$PF_3(CF_2CF_3)_3$].

According to the literature,[15,16] the contribution per methylene ($-CH_2-$) to parachor is 31.1 for [$C_n$mim][$AlCl_4$] and 37.5 for [$C_n$mim][Ala]. An average value of the contribution can be calculated to be 34.3. So, the average value can be used to predict the parachor of the ILs [$C_n$mim][$PF_3(CF_2CF_3)_3$] (n = 1, 3, 4, 5, 6). The values are listed in Table 2.

The value of the molar enthalpy of vaporization was estimated in terms of Kabo's empirical equation:[10]

$$\Delta_l^g H_m^0(298.15\ \mathrm{K})/\mathrm{kJ \cdot mol^{-1}} = 0.01121(\gamma V^{2/3} N^{1/3}) + 2.4 \qquad (7)$$

where V is molar volume, γ, surface tension, and N, Avogadro's constant. The estimated value of the molar enthalpy of vaporization is listed in Table 2.

According to eq 6, the surface tension can be calculated from the predicted density and parachor. The molar enthalpy of vaporization, $\Delta_l^g H_m^0$, can be obtained from predicted density and surface tension. The data are listed in Table 2.

Interstice Model Theory. According to the interstice model[11,12] the interstice volume, v, can be estimated by classical statistical mechanics at 298.15 K:

$$v = 0.6791(k_B T/\gamma)^{3/2} \qquad (8)$$

where k_B is Boltzmann's constant, T, the thermodynamic temperature, and γ, the surface tension of ILs.

The molar volume of ionic liquids, V, consists of the inherent volume, V_i, and the volume of the interstices; the molar volume of the interstice, $\sum \nu = 2N\nu$:[11]

$$V = V_i + 2N\nu \qquad (9)$$

If the expansion volume of IL only results from the expansion of the interstices when the temperature increases, the thermal expansion coefficient, α, can be predicted from the interstice model at 298.15 K:

$$\alpha = (1/V)(\partial V/\partial T)p = 3N\nu/VT \qquad (10)$$

All of the data obtained from estimation and prediction are listed in Table 2.

From Table 2, comparing the predicted and experimental thermal expansion coefficients of [C_2mim][$PF_3(CF_2CF_3)_3$] at 298.15 K, they differ from each other with a factor of about 26 %; the predicted values could be like reference values for the lack of experimental values at 298.15 K. It also can be seen that the estimation and prediction values of interstice fractions, $\sum v/V$, are in the range of (9 to 11) % for all ILs [$C_n$mim][$PF_3(CF_2CF_3)_3$] (n = 1, 2, 3, 4, 5, 6) at 298.15 K; these values are in good agreement with the values of volume expansion resulting in the process from a solid to a liquid state for the majority of materials which exhibit (10 to 15) %. This means that the interstice model is reasonable, and the interstice model theory can be applied to calculate the thermal expansion coefficient of imidazolium-based ILs.

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Literature Cited

(1) Fuller, J.; Carlin, R. T.; Long, H. C. D.; Haworth, D. Structure of 1-ethyl-3-methylimidazolium hexafluorophosphate: model for room temperature molten salts. *J. Chem. Soc., Chem. Commun.* **1994**, 299–300.

(2) Gordon, C. M.; Holbrey, J. D.; Kennedy, A. R.; Seddon, K. R. Ionic liquid crystals: hexafluorophosphate salts. *J. Mater. Chem.* **1998**, *8*, 2627–2636.

(3) Bonhôte, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts. *Inorg. Chem.* **1996**, *35*, 1168–1178.

(4) Restolho, J.; Serro, A. P.; Mata, J. L.; Saramago, B. Viscosity and Surface Tension of 1-Ethanol-3-methylimidazolium Tetrafluoroborate and 1-Methyl-3-octylimidazolium Tetrafluoroborate over a Wide Temperature Range. *J. Chem. Eng. Data* **2009**, *54*, 950–955.

(5) kabo, G. J.; Blokhin, A. V.; Paulechka, Y. U.; Kabo, A. G.; Shymanovich, M. P.; Magee, J. W. Thermodynamic Properties of 1-Butyl-3-methylimidazolium Hexafluorophosphate in the Condensed State. *J. Chem. Eng. Data* **2004**, *49*, 453–461.

(6) Fredlake, C. P.; Crosthwaite, J. M.; Hert, D. G.; Aki, S. N. V. K.; Brennecke, J. F. Thermophysical Properties of Imidazolium-Based Ionic Liquids. *J. Chem. Eng. Data* **2004**, *49*, 954–961.

(7) Harris, K. R.; Woolf, L. A.; Kanakubo, M. Temperature and Pressure Dependence of the Viscosity of the Ionic Liquid 1-Butyl-3-methylimidazolium Hexafluorophosphate. *J. Chem. Eng. Data* **2005**, *50*, 1777–1782.

(8) Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. Solubilities and Thermodynamic Properties of Gases in the Ionic Liquid 1-*n*-Butyl-3-methylimidazolium Hexafluorophosphate. *J. Phys. Chem. B* **2002**, *106*, 7315–7320.

(9) Glasser, L. Lattice and phase transition thermodynamics of ionic liquids. *Thermochim. Acta* **2004**, *421*, 87–93.

(10) Zaitsau, D. H.; Kabo, G. J.; Strechan, A. A.; Paulechka, Y. U.; Tschersich, A.; Verevkin, S. P.; Heintz, A. Experimental Vapor Pressures of 1-Alkyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imides and a Correlation Scheme for Estimation of Vaporization Enthalpies of Ionic Liquids. *J. Phys. Chem. A* **2006**, *110*, 7303–7306.

(11) Yang, J. Z.; Lu, X. M.; Gui, J. S.; Xu, W. G. A new theory for ionic liquids - the Interstice Model Part 1. The density and surface tension of ionic liquid EMISE. *Green Chem.* **2004**, *6*, 541–543.

(12) Zhang, Q. G.; Yang, J. Z.; Lu, X. M.; Gui, J. S.; Huang, M. Studies on an ionic liquid based on $FeCl_3$ and its properties. *Fluid Phase Equilib.* **2004**, *226*, 207–211.

(13) Lide, D. R. *Handbook of Chemistry and Physics*, 82nd ed.; CRC Press: Boca Raton, FL, 20012002.

(14) Adamson, A. W. *Physical chemistry of surfaces*, 3rd ed.; John-Wiley: New York, 1976; translated by Gu, T. R.; Science Press: Beijing, 1986.

(15) Tong, J.; Liu, Q. S.; Xu, W. G.; Fang, D. W.; Yang, J. Z. Estimation of Physicochemical Properties of Ionic Liquids 1-Alkyl-3-methylimidazolium Chloroaluminate. *J. Phys. Chem. B* **2008**, *112*, 4381–4386.

(16) Fang, D. W.; Guan, W.; Tong, J.; Wang, Z. W.; Yang, J. Z. Study on Physicochemical Properties of Ionic Liquids Based on Alanine $[C_n mim][Ala]$ ($n = 2,3,4,5,6$). *J. Phys. Chem. B* **2008**, *112* (25), 7499–7505.

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