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Temperature and Length Scale Dependence of Tetraalkylammonium Ion Solvation in Water, Formamide, and Ethylene Glycol

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ABSTRACT: This paper focuses on the temperature and length scale dependence of solvation of familiar hydrophobic solutes: tetraalkylammonium ions in highly associated solvents with H-bond networks. Standard enthalpies and heat capacities of solution of symmetrical tetraalkylammonium bromides in formamide (FA) and ethylene glycol $(C_2H_4(OH)_2)$ have been computed using experimental $\Delta H^m(sol)$ values and compared with previously reported enthalpies and heat capacities in pure water. Heat capacities of hydration are found to be large, positive, and increase almost linearly up to tetrapentylammonium bromide. Hydration of tetrahexyl- and tetraheptylammonium bromides is accompanied by much smaller heat capacity changes than would be expected from the length scale dependence observed. The same behavior reveals enthalpies and heat capacities of solute transfer from FA and $C_2H_4(OH)_2$ to water. The results obtained rather indicate that solvation of large tetraalkylammonium ions containing more than twenty carbon atoms is accompanied by much less water orientational ordering than for solutes of a moderate size. It results in smaller fluctuations in the water—water pair energy in a hydration shell and consequently reduces the heat capacity of hydration. The comparison of tetraalkylammonium ion behavior in water and the nonaqueous solvents studied shows that the length scale dependence of solvophobic solvation is strongly pronounced in water but not in nonaqueous media.
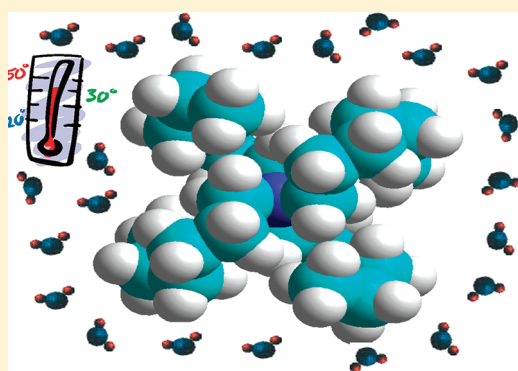
INTRODUCTION

Hydrophobic hydration and hydrophobic interaction play a major role in various important chemical phenomena such as formation of gas clathrates, molecular recognition, formation of micelles and bilayer membranes, etc.[1−5] These water-induced effects have, however, a multifaceted nature[2−5] that depends strongly upon a solute size. Recent theoretical and experimental studies have highlighted the principal difference between hydration of small and large apolar species.[2−5] Accommodation of hydrophobic units of a moderate size creates excluded volume without disrupting water structure, because water—water hydrogen bonding simply goes around the solute.[3,4] In contrast, large hydrophobic objects appear to disrupt strongly the H-bond network of water, inducing depletion of solvent density near the apolar surface.[3,4]

Hydration of apolar solutes of a moderate size is accompanied by large and positive heat capacity changes.[2,5−7] Several mechanisms have been proposed to explain this remarkable fact (see, for example, refs 2, 5, and 7) and, although they are based on different principles, most of them suggest that the main source of large and positive $\Delta C_p^\circ(hyd)$ values lies in increasing the solvent heat capacity in a solute hydration shell. In the series of publications of Sharp with co-workers (see refs 6 and 7 and references therein) it has been shown that large and positive heat capacities of hydration primarily arise from increasing the relative amount of shorter and more linear H-bonds in hydration shells in comparison with the bulk solvent and decreasing the population

of water molecules with longer and less linear H-bonds. As the number of apolar groups in the solute molecule rises, the population of water molecules forming such low angle H-bonds increases, inducing the strengthening of energy fluctuations in a hydration shell and, as a result, the increase of the heat capacity of hydration.[6] At small length scales these heat capacity changes reveal almost linear dependence with the solute size (see, for example, Figure 1). Accommodation of an extended hydrophobic surface in water should cause the partial loss of hydrogen bonding,[3,4] which induces decreasing the low angle/separation pair population near the solute. Hydration of such species is also accompanied by positive heat capacity changes which, however, should be smaller than one could expect from the length scale dependence for small hydrophobic objects.

Recently,[8,9] we have studied the length scale dependence of hydration and solute—solute interactions for familiar hydrophobic solutes: tetraalkylammonium ions in water and water—amide solutions. At small length scales, both heat capacities of solution and enthalpic parameters of the solute—amide pair interactions are found to increase almost linearly with a cation size. However, heat capacities of tetrahexyl- and tetraheptylammonium bromides per the solute surface area are smaller than those for Bu_4NBr and Pen_4NBr (Figure 1).[9] Almost identical behavior
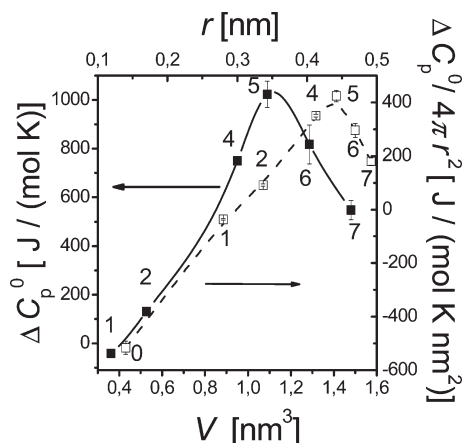
Figure 1. Length scale dependence of standard heat capacities of a solution of tetraalkylammonium bromides in water at 328 K. Left-hand scale = heat capacities vs the cation volume computed ab initio (■); right-hand scale = heat capacities per the solute surface area as a function of the cation van der Waals radius (□).[8,9] Digits on the curves from here on denote the number of carbon atoms in the cation alkyl chain (0 = NH_4Br, 1 = Me_4NBr, etc.). Lines = splain functions.

reveals enthalpic parameters of the tetraalkylammonium bromide—FA interaction.[8] The results obtained have been attributed to the mechanism of hydration of large hydrophobic species whose hydration shells are less ordered than for units of a moderate size.

In this paper we extend the analysis of the length scale dependence of solvophobic solvation and study the tetraalkylammonium ion behavior in liquid FA and $C_2H_4(OH)_2$. Both nonaqueous solvents are highly associated liquids whose H-bond networks are similar to some extent to the network in liquid water (see refs 10—13 and references therein). Consequently, one could expect that solvation of hydrophobic tetraalkylammonium ions in water, FA and $C_2H_4(OH)_2$ may reveal common features. This study provides such an analysis comparing the length scale dependence of thermal properties of tetraalkylammonium bromide solutions in water and nonaqueous solvents.

■ EXPERIMENTAL SECTION

FA (Panreac, > 98%) was dried with 4 Å molecular sieves and then distilled under reduced pressure at 348 K. $C_2H_4(OH)_2$ (Aldrich, >99.5%) was stored under 4 Å molecular sieves and then used as supplied. The residual amount of water in both solvents determined according to Karl Fisher titration was smaller than 0.02 mass %. Et_4NBr and Bu_4NBr (Merck, >99%) were recrystallized from methanol (Merck) and then dried in a vacuum at 343—348 K for several days. Hex_4NBr and Hep_4NBr (Aldrich, > 99%) were dried in a vacuum at 313—318 K for several days with a trap with liquid nitrogen and then used without further purification. Calorimetric measurements were carried out with automated ampule calorimeters described in detail previously.[8,14]

■ RESULTS

The experimental enthalpies of solution $\Delta H^m(sol)$ of Et_4NBr, Bu_4NBr, Hex_4NBr, and Hep_4NBr in FA and $C_2H_4(OH)_2$ have been obtained in the range of electrolyte molalities of 0.001—0.02 mol/kg. The standard enthalpies of solution $\Delta H^\circ(sol)$ given

Table 1. Standard Enthalpies of Solution $\Delta H^\circ(sol)$ in kJ/mol for Tetraalkylammonium Bromides in Formamide at 298—338 K[a]

T/K	Bu$_4$NBr	Hex$_4$NBr	Hep$_4$NBr
298.15	17.59 ± 0.06[b]	9.25 ± 0.08[b]	45.38 ± 0.05
313.15	20.17 ± 0.05[b]	12.29 ± 0.03[b]	46.67 ± 0.08
328.15		15.16 ± 0.04	48.19 ± 0.06
338.15		17.18 ± 0.09	48.90 ± 0.04

[a] Errors represent from here on the twice standard deviation. [b] Recalculated from the previously reported $\Delta H^m(sol)$ values.[15]

Table 2. Standard Enthalpies of Solution $\Delta H^\circ(sol)$ in kJ/mol for Tetraalkylammonium Bromides in Ethylene Glycol at 298.15—338.15 K

T/K	Et$_4$NBr	Bu$_4$NBr
298.15	21.31 ± 0.07[a]	28.98 ± 0.04[a]
313.15	21.78 ± 0.09[a]	30.18 ± 0.11[a]
328.15	21.90 ± 0.11	31.72 ± 0.08
338.15	22.02 ± 0.05	32.52 ± 0.07
	Hex$_4$NBr	Hep$_4$NBr
298.15	21.76 ± 0.04[a]	58.31 ± 0.11
313.15	23.17 ± 0.06[a]	58.00 ± 0.09
318.15	23.75 ± 0.05	
328.15	24.79 ± 0.09	58.04 ± 0.19
338.15	26.42 ± 0.15	57.85 ± 0.15

[a] Recalculated from the previously reported $\Delta H^m(sol)$ values.[15]

in Tables 1 and 2 reflect the result of four or more measurements in both FA and $C_2H_4(OH)_2$. These values have been calculated from the following relationship: $\Delta H^\circ(sol) = \Delta H^m(sol) + \Delta H^{m\rightarrow\circ}(dil)$, where the enthalpies of dilution $\Delta H^{m\rightarrow\circ}(dil)$ are estimated as in our previous studies.[8,14−16] For liquid FA the enthalpies of dilution are found to be only few tens of joules per mole, whereas for ethylene glycol the correction to an infinite dilution is significantly larger, being 400—1500 J/mol.

■ DISCUSSION

A. Length Scale Dependence of Tetraalkylammonium Bromide Hydration. Figure 1 shows the length scale dependence of heat capacities of tetraalkylammonium bromide solution in water at 328 K.[9] The $\Delta C_p^\circ(sol)/4\pi r^2$ values are seen to increase almost linearly with the cation van der Waals radii up to tetrapentylammonium bromide. A further rise of the solute size induces decreasing heat capacity, which has been attributed to the weakening of energy fluctuations in the solute hydration shell due to the decrease of the relative amount of low angle/separation water pair configurations.[9] However, at least two problems may arise.

First, it is not quite clear how correctly van der Waals radii reflect real packing of cation alkyl chains, especially, for large tetraalkylammonium ions containing more than twenty carbon atoms. Because there are not reliable ways to estimate accurately the size of large tetraalkylammonium ions in a liquid phase we have optimized their structures in terms of the 3-21 G* basis and then computed cation volumes. Figure 1 clearly shows that although computed cation volumes are larger than van der Waals ones, the curve $\Delta C_p^\circ(sol) - f(V)$ also passes through the maximum.

The second problem dealing with correct calculation of the heat capacities of hydration for tetraalkylammonium ions appears to be more complex. In fact, to compute heat capacities of hydration from the $\Delta C_p^\circ(\text{sol})$ values we should know heat capacities of ions in a gas phase $C_p^\circ(\text{g})$ and heat capacity of pure solid salt $C_p(\text{s})$:

$$\Delta C_p^\circ(\text{hyd}) = \Delta C_p^\circ(\text{sol}) + C_p(\text{s}) - C_p^\circ(\text{g}) \quad (1)$$

The second term in eq 1 is easily measurable with differential scanning calorimetry. However, the $C_p^\circ(\text{g})$ values cannot be estimated accurately for multiatom tetraalkylammonium ions because the complete set of vibrational frequencies as well as the barrier height to internal rotation is unavailable, which does not allow us to compute a vibrational contribution. The $\Delta C_p^\circ(\text{hyd})$ values at 298 K reported by Abraham and Marcus[17] have been obtained with the additivity-of-group approach using the experimental $C_p^\circ(\text{g})$ value for the tetramethylammonium ion and the methylene group contribution from uncharged compounds. The length scale dependence of these quantities is found to be almost identical to the dependence for the heat capacities of solution.[9] Moreover, for this homological series the $C_p(\text{s}) - C_p^\circ(\text{g})$ difference is within 40−90 J/(mol K) at 298 K, indicating that for Pr_4NBr, Bu_4NBr, and especially, Pen_4NBr the $\Delta C_p^\circ(\text{hyd})$ values are almost identical to heat capacities of solution. We have assumed that this approximation should be valid for larger cations at 328 K and used the $\Delta C_p^\circ(\text{sol})$ values for the comparative analysis. Figure 1 clearly shows that the heat capacity decrease for Hex_4NBr and Hep_4NBr is significantly larger than the $C_p(\text{s}) - C_p^\circ(\text{g})$ difference above. Because the large and positive $\Delta C_p^\circ(\text{hyd})$ values are highly correlated with water orientational ordering in a solute hydration shell,[6,7] we may state that Hex_4N^+ and Hep_4N^+ ions induce much smaller increase of the low angle/separation population in their nearest vicinity than cations of a moderate size.

B. Temperature Dependence of the Enthalpies of Solution in Nonaqueous Solvents. To give a deeper insight into the length scale dependence of hydrophobicity, we compare the tetraalkylammonium ion behavior in water and highly associated nonaqueous solvents: formamide and ethylene glycol. Using the $\Delta H^\circ(\text{sol})$ values for Me_4NBr and Bu_4NBr given elsewhere,[15,18,19] as well as the enthalpies of solution presented in Table 1, we have found that the enthalpies of tetraalkylammonium bromide solution in FA are linear functions of the temperature:

$$\Delta H^\circ(\text{sol})(\text{Me}_4\text{NBr}) = 24.07(0.04) + 0.015(0.001)\cdot(T - 328.15)$$
$$s_f = 0.05 \text{ kJ/mol} \quad (2)$$

$$\Delta H^\circ(\text{sol})(\text{Bu}_4\text{NBr}) = 22.45(0.10) + 0.163(0.003)\cdot(T - 328.15)$$
$$s_f = 0.14 \text{ kJ/mol} \quad (3)$$

$$\Delta H^\circ(\text{sol})(\text{Hex}_4\text{NBr}) = 15.20(0.03) + 0.198(0.003)\cdot(T - 328.15)$$
$$s_f = 0.05 \text{ kJ/mol} \quad (4)$$

$$\Delta H^\circ(\text{sol})(\text{Hep}_4\text{NBr}) = 48.07(0.06) + 0.090(0.003)\cdot(T - 328.15)$$
$$s_f = 0.10 \text{ kJ/mol} \quad (5)$$

where values in brackets from here on represent the standard deviation and s_f is the standard deviation of the fit.

For ethylene glycol solutions the $\Delta H^\circ(\text{sol}) - f(T)$ curves in the temperature range 298−338 K are found to fit very well to the following equations:

$$\Delta H^\circ(\text{sol})(\text{Et}_4\text{NBr}) = 15.38(0.02) + 0.00781(0.006)$$
$$\cdot(T - 328.15) - 0.5\cdot8.9\cdot10^{-4}(4\cdot10^{-4})$$
$$\cdot[(T - 328.15)^2]$$
$$s_f = 0.05 \text{ kJ/mol} \quad (6)$$

$$\Delta H^\circ(\text{sol})(\text{Bu}_4\text{NBr})$$
$$= 31.64(0.06) + 0.091(0.003)\cdot(T - 328.15)$$
$$s_f = 0.10 \text{ kJ/mol} \quad (7)$$

$$\Delta H^\circ(\text{sol})(\text{Hex}_4\text{NBr}) = 24.93(0.06) + 0.134(0.007)$$
$$\cdot(T - 328.15) - 0.5\cdot0.00192(6\cdot10^{-4})$$
$$\cdot[(T - 328.15)^2]$$
$$s_f = 0.11 \text{ kJ/mol} \quad (8)$$

$$\Delta H^\circ(\text{sol})(\text{Hep}_4\text{NBr})$$
$$= 57.96(0.06) + 0.009(0.003)\cdot(T - 328.15)$$
$$s_f = 0.10 \text{ kJ/mol} \quad (9)$$

Equations 2−9 show that almost for all cases the $\Delta H^\circ(\text{sol})$ values increase rather linearly with the temperature, which is very similar to the behavior of tetraalkylammonium bromides in water.[9,16] However, for nonaqueous solvents the slope of the $\Delta H^\circ(\text{sol}) - f(T)$ curves is significantly smaller.

C. Length Scale Dependence of Enthalpies and Heat Capacities of Transfer. Figure 2a compares the length scale dependence of heat capacities of solution of tetraalkylammonium bromides in water, FA, and $\text{C}_2\text{H}_4(\text{OH})_2$ at 328 K. Most of the $\Delta C_p^\circ(\text{sol})$ values are positive and increase with the cation volume. However, in both water and nonaqueous solvents the heat capacities of Hep_4NBr solution are seen to be smaller than those for Bu_4NBr or Hex_4NBr. It is obvious that although some common features in the solute behavior in water and nonaqueous solvents exist, heat capacity changes in aqueous solutions are much larger and reveal much stronger dependence upon a solute size.

Figure 2b illustrates enthalpies and heat capacities of the solute transfer from nonaqueous solvents to water. The standard transfer functions reflecting the difference of solute solvation in aqueous and nonaqueous media do not contain the contribution from the solute−solute interactions in a condensed state, and the Br^- contributions are identical for the given homological series. Figure 2b shows that solvation of Et_4NBr and Bu_4NBr is more exothermic in water than in nonaqueous solvents, the methylene group increment to the enthalpy of transfer being negative. However, transfer of Hex_4NBr and Hep_4NBr is much less favorable. For both nonaqueous solvent enthalpies of tetraheptylammonium bromide transfer become positive indicating that the methylene group increment changes its sign.

The $\Delta C_p^\circ(t)$ values shown in Figure 2b reveal the same tendencies as heat capacities of solution given in Figure 1. For both cases the curves $\Delta C_p^\circ(t) - f(V)$ pass through the maxima, indicating that transfer of Hex_4N^+ and Hep_4N^+ ions is accompanied by much smaller heat capacity changes than would be expected from the length scale dependence for the solutes of a moderate size. Therefore, we may state that the $C_p(\text{s}) - C_p^\circ(\text{g})$ difference is small in comparison with heat capacities of hydration for both small and large tetraalkylammonium cations. This

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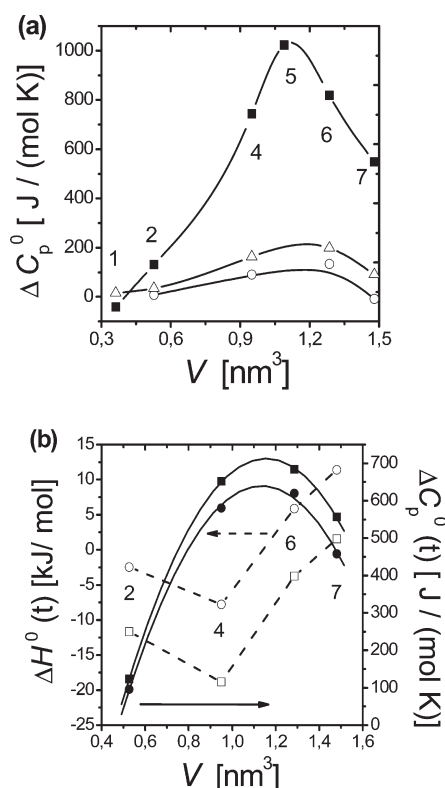
Figure 2. (a) Length scale dependence of standard heat capacities of a solution of tetraalkylammonium bromides in water (■), formamide (△), and ethylene glycol (○) at 328 K. Lines = splain functions. (b) Length scale dependence of standard enthalpies (light symbols) and heat capacities (dark symbols) of tetraalkylammonium bromides transfer from FA (●, ○) and $C_2H_4(OH)_2$ (■, □) to water at 328 K. Thermodynamic quantities for Et_4NBr in liquid FA have been estimated from the $\Delta H°(sol)$ values at 298 and 313 K[15] assuming that the heat capacity of solution is independent of the temperature.

result confirms the conclusions drawn above from the analysis of the $\Delta C_p°(sol)$ values.

CONCLUSIONS

Thus, our comparative analysis clearly indicates that hydration of tetraalkylammonium ions containing more than twenty carbon atoms differ from hydration of the cations of a moderate size. Because the maxima in Figures 1 and 2 occur at a lower solute size than for model hydrophobic objects[3,4] and tetraalkylammonium ions and water molecules attract each other via a variety of forces, it is reasonable to consider that large tetraalkylammonium cations do not still induce the significant loss of water—water hydrogen bonding in their nearest vicinity or drying. These solutes rather invoke the weakening of orientational ordering of the nearest water molecules that results in decreasing the heat capacity of hydration. This explanation appears to contradict to some extent with the findings of Zanghi and Berne,[20] which have observed still a substantial orientational ordering of the water molecules in the nearest vicinity of large hydrophobic plates at 360 K. However, they did not compare the degree of an orientational ordering for different length scales and compute the contribution from the first shell waters to the heat capacity of hydration for small and large species. Thus, in our opinion, to give a deeper insight into this problem the additional computational studies are required.

Although in nonaqueous solvents with H-bond networks (formamide and ethylene glycol) most of the $\Delta C_p°(sol)$ values are positive, the length scale dependence of these quantities is rather insignificant. It allows us to draw a tentative conclusion that the mechanism of solvation of small and large hydrophobic units in formamide and ethylene glycol should not differ strongly.

The significant difference between aqueous and nonaqueous solutions may be associated with the fact that in comparison with liquid water both nonaqueous solvents at 328 K are far from liquid—vapor phase coexistence and the attractive force imbalance occurring between water and large hydrophobic objects[3] becomes much less pronounced in FA and $C_2H_4(OH)_2$. Probably at higher temperatures the crossover in the dependence of solvophobic solvation upon a solute size will appear for these highly associated nonaqueous solvents; however, it will be too far to have any biological significance.

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REFERENCES

(1) Pratt, L. R. Molecular theory of hydrophobic effects: "She is too mean to have her name repeated". *Annu. Rev. Phys. Chem.* **2002**, *53*, 1–31.

(2) Ashbaugh, H. S.; Pratt, L. R. Colloquium: scaled particle theory and the length scales of hydrophobicity. *Rev. Mod. Phys.* **2006**, *78*, 159–178.

(3) Chandler, D. Interfaces and the driving force of hydrophobic assembly. *Nature (London)* **2005**, *437*, 640–647.

(4) Chandler, D. Oil on troubled waters. *Nature (London)* **2007**, *445*, 831–832.

(5) Southall, N. T.; Dill, K. A.; Haymet, A. D. J. A view of hydrophobic effect. *J. Phys. Chem. B* **2002**, *106*, 521–533.

(6) Madan, B.; Sharp, K. Molecular origin of hydration heat capacity changes of hydrophobic solutes: perturbation of water structure around alkanes. *J. Phys. Chem. B* **1997**, *101*, 11237–11242.

(7) Gallagher, K. R.; Sharp, K. A new angle on heat capacity changes in hydrophobic solvation. *J. Am. Chem. Soc.* **2003**, *125*, 9853–9860.

(8) Kustov, A. V.; Korolev, V. P. Temperature and length scale dependence of the tetraalkylammonium ion-amide interaction. *J. Phys. Chem. B* **2008**, *112*, 2040–2044.

(9) Kustov, A. V. Hydrophobic hydration and hydrophobic interaction in tetraalkylammonium salt solutions: the cation size effect. *Russ. J. Inorg. Chem.* **2011**, *56*, 824–829.

(10) Rodnikova, M. N.; Barthel, J. Elasticity of the spatial network of hydrogen bonds in liquids and solutions. *J. Mol. Liq.* **2007**, *131–132*, 121–123.

(11) Rodnikova, M. N. A new approach to the mechanism of solvophobic interactions. *J. Mol. Liq.* **2007**, *136*, 211–213.

(12) Gao, J.; Pavelites, J. J.; Habibollazadeh, D. Simulations of liquid amides using a polarizable intermolecular potential function. *J. Phys. Chem.* **1996**, *100*, 2689–2697.

(13) Bushuev, Yu. G.; Davletbaeva, S. V.; Korolev, V. P. The influence of universal and specific interactions on structural properties of liquid formamide. *Russ. Chem. Bull.* **1999**, *48*, 2200–2210.

(14) Kustov, A. V.; Smirnova, N. L. Standard enthalpies and heat capacities of solution of urea and tetramethylurea in water. *J. Chem. Eng. Data* **2010**, *55*, 3055–3058.

(15) Korolev, V. P.; Antonova, O. A.; Smirnova, N. L.; Kustov, A. V. Thermal properties of tetraalkylammonium bromides in several solvents. *J. Therm. Anal. Calorim.* **2010**, *103*, 401–407.

(16) Kustov, A. V.; Korolev, V. P. The enthalpies and heat capacities of hydration of ammonium and tetraalkylammonium bromides. *Russ. J. Phys. Chem.* **2006**, *80*, 56–62.

(17) Abraham, M. H.; Marcus, Y. Thermodynamics of solvation of ions. Part 1. The heat capacity of hydration at 298.15 K. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 3255–3274.

(18) De Visser, C.; Somsen, G. Enthalpies of solution and heat capacities of tetra-n-butylammonium bromide in several solvents from 278 to 328 K. *J. Chem. Thermodyn.* **1973**, *5*, 147–152.

(19) De Visser, C.; Somsen, G. "Structure promotion" and "structure breaking". Heat capacities of caesium bromide, tetramethylammonium bromide and tetra-n-butylammonium bromide in several solvents from 278 to 328 K. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 1440–1447.

(20) Zanhgi, A; Berne, B. J. Temperature dependence of dimerization and dewetting of large-scale hydrophobes: a molecular dynamics study. *J. Phys. Chem. B* **2008**, *112*, 8634–8644.

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