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Is the Counterion Responsible for the Unusual Thermodynamic Behaviour of the Aqueous Solutions of Gemini Bispyridinium Surfactants?

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Abstract

Apparent and partial molar enthalpies at 298 K of the aqueous solutions of cationic gemini surfactants 1,1′-didodecyl-2,2′-trimethylenebispyridinium dichloride (12-Py(2)-3-(2)Py-12 Cl); 1,1′-didodecyl-2,2′-tetramethylenebispyridinium dichloride (12-Py(2)-4-(2)Py-12 Cl); 1,1′-didodecyl-2,2′-octamethylenebispyridinium dichloride (12-Py(2)-8-(2)Py-12 Cl); 1,1′-didodecyl-2,2′-dodecamethylenebispyridinium dichloride (12-Py(2)-12-(2)Py-12 Cl) were measured as a function of concentration and are here reported for the first time. The curve of the compound with the four carbon atoms spacer lies between those of the compound with spacer of 2 and 3 carbon atoms, not below the latter, as expected. This behaviour, we have already found for the same compounds here studied, but having methanesulfonate as counterion, is interpreted as an evidence of a conformation change of the molecule determined by stacking interactions between the two pyridinium rings, appearing at an optimum length of the spacer. The curves of apparent and molar enthalpies *vs.* concentration and surface tension measurements, here reported, show that this behaviour is independent on the counterion. On the contrary, the group contribution additivity for the counterion is respected, independently on the spacer length.

Keywords. Apparent and partial molar enthalpies; cationic gemini surfactants; 1,1′-didodecyl-2,2′-trimethylenebispyridinium dichloride; 1,1′-didodecyl-2,2′-tetramethylenebispyridinium dichloride; 1,1′-didodecyl-2,2′-octamethylenebispyridinium dichloride; 1,1′-didodecyl-2,2′-dodecamethylenebispyridinium dichloride; micellization enthalpy, group contribution.

Briefs. Apparent and partial molar enthalpies at 298 K of the aqueous solutions of cationic gemini surfactants 1,1′-didodecyl-2,2′-trimethylenebispyridinium dichloride (12-Py(2)-3-(2)Py-12 Cl); 1,1′-didodecyl-2,2′-tetramethylenebispyridinium dichloride (12-Py(2)-4-(2)Py-12 Cl); 1,1′-didodecyl-2,2′-octamethylenebispyridinium dichloride (12-Py(2)-8-(2)Py-12 Cl); 1,1′-didodecyl-2,2′-dodecamethylenebispyridinium dichloride (12-Py(2)-12-(2)Py-12 Cl) have been measured as a function of concentration, in order to confirm the lack of methylene group additivity with respect to the enthalpic properties of the solutions, when it is added in the spacer, already found in the case of methansulfonates. The data obtained support the hypothesis of a conformation change dependent on the spacer length, but independent on the counterion.

Introduction

It has been proved that *gemini* surfactants - i.e. surfactants in which at least two identical moieties are bound together by a spacer at the polar head level - show practical advantages over the monomeric ones owing to their increased surface activity, lower critical micelle concentration (CMC), and useful viscoelastic properties [1-4]. Moreover, the cationic *gemini* surfactants show very interesting potentialities in pharmaceutical field. In fact, they have been proposed as non-covalent functionalization agents for carbon nanotubes-based formulations for drug delivery [5] and as non viral vectors in gene therapy [6-9], owing their multiple positive charges, suitable for binding and compacting DNA, and their superior surface activity. We are for some time collecting chemico physical, particularly thermodynamic, and biological data about homologous series of cationic *gemini* surfactants with the idea of correlating in a quantitative way their structure with their biological activity, particularly gene delivery ability [9-14]. In this perspective, synthetic vectors present the advantage that their constituent parts can be quite easily modified, thereby facilitating the elucidation of structure-activity relationships. Following this idea we designed and synthesized new gemini compounds having, as polar head, two pyridinium groups, bridged together by an aliphatic chain [10], in the assumption that the aromatic rings bearing the positive charges could facilitate the interaction with the DNA. We have already measured as a function of concentration the apparent and partial molar enthalpies of these compounds having the methansulfonate as counterion and we were amazed by their very peculiar behaviour as a function of the spacer length, never found before in the literature, not allowing for the determination of a $–CH_2–$ group contribution when this group is added to the spacer [13]. We interpreted this surprising behaviour as evidence of a conformation change of the molecule caused by stacking interactions between the two pyridinium rings, mediated by the counterion and appearing at an optimum length of the spacer. The question arises if the counterion plays some role in determining this unexpected behaviour. In fact, our previous studies [15-16] have shown the strong influence of the counterions on the energetic of surfactant solutions. In order to answer this question, we synthesized the same family of compounds, having chlorides as counterions, whose solution thermodynamics is reported in the present paper.

Experimental Section

Materials

The series of bispyridinium cationic gemini surfactants under study was prepared by us, as described in ref. [10]. The compounds studied are the following: 1,1′-didodecyl-2,2′-trimethylenebispyridinium dichloride (12-Py(2)-3-(2)Py-12 Cl); 1,1′-didodecyl-2,2′-tetramethylenebispyridinium dichloride (12-Py(2)-4-(2)Py-12 Cl); 1,1′-didodecyl-2,2′-octamethylenebispyridinium dichloride (12-8-12PybisCl); 1,1′-didodecyl-2,2′-dodecamethylenebispyridinium dichloride (12-Py(2)-12-(2)Py-12 Cl).

Purity was checked by NMR, elemental analysis and TLC: eluent BAW (butanol:acetic acid:water 4:1:5-organic phase) on silica gel plate (Merck). The solutions were prepared by weight using freshly boiled bi-distilled water, stored under nitrogen. Solution concentrations are expressed as molality, m (mol kg^{-1}).

Dilution enthalpies measurements

The enthalpies of dilution were measured by means of the Thermometric TAM (flow mixing cell) microcalorimeter, equipped with 221 Nano Amplifier, at 298 and 313 K. The freshly prepared surfactant solutions, kept before injection at the experimental temperature by means of a Heto cryothermostatic bath, were diluted into the "mixing" measuring cell of the microcalorimeter in a ratio 1:1 by using CO_2-free water. The solutions and the water were injected by means of a Gilson peristaltic pump, Minipuls 2, and their flows were determined by weight.

Surface tension measurements

The surface tension, γ, was measured by using a Lauda (TE1C/3) digital tensiometer, equipped with the Du Noüy ring (Pt/Ir alloy (80/20), circumference: 60 ± 0.2 mm, wire diameter 0.4 mm, weight: 1.6 g). Sample temperature was maintained at 25.0 ± 0.1°C by using a circulating water thermostatic bath (ISCO GTR 2000 IIx). The data were corrected according to the Zuidema and Waters method [17]. The instrument was calibrated against double-distilled (and previously deionised) water, equilibrated against atmospheric CO_2, each time measurements were done. Because the dicationic gemini surfactants adsorb onto negatively charged glass surfaces, all glassware was thoroughly soaked with the solution to be measured; soaking solutions were discarded. The fresh solution was aged for several hours before surface tension measurement. Sets of measurements were taken at 15 min intervals until no significant change occurred, using a very slow ring rising velocity. These tactics ensure that the ring is completely wetted. Standard deviation of the surface tension measurements is less than 0.15 mN/m. The absence of a minimum in the γ *vs* log *c* (*c* is the concentration expressed in mol/L) plot in the post-cmc region showed that there was very little or no surface active impurity present in the final products.

Results

The experimental data were expressed in terms of apparent and partial molar quantities of the solute, as usual in solution thermodynamics, assuming infinite dilution as the reference state. Apparent and partial molar quantities were obtained from the experimental data using methods stated in detail elsewhere [11-16, 18].

For the sake of clarity, we recall that, with reference to the state of infinite dilution, the molar enthalpy of dilution, ΔH_d, is given by:

$$\Delta H_d = L_{\Phi,f} - L_{\Phi,i} \qquad (1)$$

where L_Φ is the apparent relative molar enthalpy and the indexes *f* and *i* stand for the final (after dilution) and initial (before dilution) concentrations, respectively.

For ionic surfactant in the premicellar region, the apparent relative molar enthalpy can be expressed by means of a polynomial of $m^{½}$. Stopping the serial expansion at the third term we obtain:

$$L_\Phi = A_L m^{½} + B_L m + C_L m^{3/2} \qquad (2)$$

where A_L is the limiting Debye-Hückel slope for relative enthalpies accounting for the long range electrostatic solute-solute interactions. Parameters B_L and C_L are obtained from the experimental points in the premicellar region by a least squares curve fitting.

In the micellar region, the apparent molar enthalpies are evaluated by means of eq. (1) and, when a value of L_Φ *vs. m* not experimentally measured is needed, by graphical interpolation.

The partial molar enthalpies L_2 are determined by drawing the best curve for the apparent molar enthalpies *vs. m* and then by calculating the partial molar quantities as $\Delta(mL_\Phi)/\Delta m$ from points interpolated at regular intervals.

Tables with all the experimental data are available as supporting information. Apparent and partial molar enthalpies *vs. m* for the compounds under investigation, obtained as above described, are shown in figures 1 and 2, respectively.

Surface Tension Measurements

The surface tension measurements (γ *vs.* log *c*) are reported in Table 1 and shown in Figure 3. By using the Gibbs adsorption equation (3) [19, 20], several parameters were determined from the γ *vs.* log *c* plots: (i) the critical micelle concentration (cmc), taken as the concentrations at the point of intersection of the two linear portions of the γ *vs.* log *c* plots; (ii) the maximum surface excess concentration Γ_{max} [mol cm^{-2}]; (iii) the area per molecule at the interface A_{min} [nm^2] from equation (4); (iv) the efficiency in surface tension reduction, measured by C_{20}, i.e. the molar surfactant concentration required to reduce the surface tension of the solvent by 20 mN/m [21]; (v) the effectiveness of the surface tension reduction, measured by the surface tension at the cmc, γ_{cmc}; (vi) the cmc/C_{20} ratio, i.e. the measure of the tendency to form micelles relative to the tendency to adsorb at the air/water interface.

$$\Gamma_{max} = -\frac{1}{2.303nRT}\left(\frac{\partial \gamma}{\partial \log C}\right)_T \qquad (3)$$

$$A_{min} = \frac{10^{16}}{N\Gamma_{max}} \qquad (4)$$

The value of *n* (the number of species whose concentration at the interface changes with *c*) is taken as 2, although for divalent geminis (having 1 surfactant ion and 2 non surfactant counterions), the values of both 2 and 3 have been proposed [22]. For gemini surfactants, it was found that one of the two counterions is frequently firmly wedged in between the two charged headgroups, especially when the spacer is quite short [23]. While the use of a different *n* does not affect the general trend for surface areas, the last finding enabled us to use *n* = 2 with some confidence.

Discussion

With the aim of enriching the fundamental understanding on self-aggregation thermodynamics of gemini surfactants, we have already reported [13] the apparent and partial molar enthalpies at 298 K of the aqueous solutions of the homologous series of cationic gemini surfactants 1,1′-didodecyl-2,2′-alkylenebispyridinium dimethanesulfonates (further indicated as 1,1′-didodecyl-2,2′-alkylenebispyridinium MS), differing for the spacer length. They show a very peculiar behaviour as a function of the spacer length, not allowing for the determination of a –CH_2– group contribution when this group is added to the spacer. The curve of the compound with spacer formed by four carbon atoms lies between those of the compound with spacer of two and three carbon atoms, not below the latter, as expected. We have suggested a conformation change of the molecule caused by stacking interactions between the two pyridinium rings, mediated by the counterion and appearing at an optimum length of the spacer. The hypothesis was also supported by the data obtained from the surface tension *vs.* log *c* curves, showing that A_{min}, the minimum area taken on the surface by the molecule, is significantly lower for 12-Py(2)-4-(2)Py-12 MS than that of the other compounds of the same homologous series, and that the same compound has a greater tendency to form micelles instead of adsorbing at the air/water interface. To confirm our hypothesis and to understand the role played by the counterion, we decided to prepare the same class of gemini compounds, but changing the methanesulfonate counterion into chloride.

In general for ionic surfactants, the curves of the apparent and partial molar enthalpies *vs. m*, after increasing in the premicellar region, tend to level off at concentrations above the CMC, where they are almost parallel. The lowering of the curves in the micellar region, proportional, for the same counterion, to the number of carbon atoms in the alkyl chain and, in general, to the global hydrophobicity of the molecule, is attributed to the electrostatic interactions in micellar solutions. The trends for the compounds with chlorides as counterions, having the same hydrophobic tail, but different alkyl spacer lengths, reported in figure 1 for the apparent and in figure 2 for the partial molar enthalpies, respect this general behaviour but still show the same very peculiar behaviour found in the case of methanesulfonates. In fact, the effect of the addition of a $–CH_2–$ to the spacer does not give rise to a monotonic change in the values of the enthalpies in the micellar region, not allowing for the evaluation of a group contribution for the $–CH_2–$ group for the shortest spacers.

We have outlined that it is difficult to foresee what should be the effect of the addition of a methylene group in the spacer because, from the data about monomeric surfactants, it is known that, if the $–CH_2–$ is added to the hydrophobic chain, it causes a lowering of the enthalpic curves of about $–1.5$ kJ mol^{-1} [15], but, if it is added to the polar head, as in the case of dodecyldimethylethylammonium bromide (DEDAB) compared with dodecyltrimethylammonium bromide (DTAB), the effect is exactly the opposite, being very close to that obtained by shortening the alkylic chain by one methylene group [24-25]. This effect is probably due to both a better charge delocalization and an increase in the size of the polar head, so that the charges are farther apart on the micelle surface of DEDAB than on that of DTAB. This is true for very short alkyl chain bound to the polar head. If the chain increases, the hydrophobicity effects prevail [26]. Moreover, the trends of all the curves do not show any peculiarity in the range of concentration examined: this is to say that structural phase transitions in micellar solution do not occur. The trends of the chlorides seem to corroborate our hypothesis of a conformation change of the molecule: when the spacer reaches the right size, the molecule doubles up, like a book, due to stacking interactions between the two pyridinium rings, independently on the counterion (see figure 4). This arrangement is not possible when the spacer is too short (2 or 3 carbon atoms), because of the lack of enough conformational freedom, and when the spacer is too long, because the pyridinium rings are too far apart.

Moreover, the data presented in this work are further evidence of the role played by the counterion in determining the energetics of micellar solutions also in the case of the compounds under study, as shown in figure 4. Some of us have already shown that, in the case of dodecyltrimethylammonium chloride (DTAC) and bromide (DTAB) [27], the substitution of chloride ion by bromide ion leads to a significant change in the thermodynamic properties of solutions, comparable with that obtained by increasing the surfactant chain length by about three methylene groups. The behaviour of N-alkylpyridinium halides [28, 29, 30], and of 1-methyl-4-octylpyridinium halides [31, 32] confirms the above described trend. Structural parameters of micelles, such as degree of counterion binding, β [27, 33, 34] and aggregation number, *n* [35] are also strongly dependent on the effective size of the hydrated counterion, both decreasing with the increasing radius of the bare ion [36, 37].

The substitution of methanesulfonate by the chloride causes the lowering of the apparent and partial molar enthalpy curves in micellar region of an amount of about 6.1 kJ mol^{-1} in the plateau region, regardless of the length of the spacer, confirming the validity of the group contribution approach also for the counterion of the gemini surfactants, too.

In order to obtain the enthalpy change upon micellization, ΔH_{mic}, we have applied a pseudo-phase transition model, in which the aggregation process is considered like a phase transition, taking place at equilibrium. In this model, it is assumed that, at the CMC, the partial molar properties present a discontinuity due to the formation of the pseudo-phase. The micellization parameters, obtained by extrapolating at the cmc the trends of the partial molar properties before and after cmc [11-18], together with the cmc values from conductometric measurements are reported in Table 1.

The micellization enthalpies reflect the same trend described before, without possibility to extract a group contribution for the $-CH_2-$ in the spacer, and the same inversion between 12-Py(2)-3-(2)Py-12 Cl and 12-Py(2)-4-(2)Py-12 Cl. The values of micellization enthalpies are lowered by about 5.7 kJ mol^{-1} if the methanesulfonate counterion is replaced by the chloride one. Thermodynamic data about the comparison of the above mentioned counterion in the case of monomeric surfactants are not available in literature, so we are not able to evaluate how, if any, the group contribution of the counterion is modified by passing from monomeric to dimeric surfactants.

Moreover, the compound 12-Py(2)-4-(2)Py-12 MS behaves in a different way inside the homologous series we have examined, as far as not only enthalpic but also surface tension *vs.* log *c* curves are concerned (figure 3 and table 1). Also for gemini having chloride as counterion, the minimum area taken on the surface by the molecule, A_{min} is significantly lower for 12-Py(2)-4-(2)Py-12 MS in respect to the compounds of the same homologous series, suggesting a tendency of the molecules to fold. The data in table 1 show that the values of cmc from surface tension are lower than those from conductivity, confirming the data obtained for the same compounds but with methanesulfonate as counterion. This behaviour, already reported in literature for gemini surfactants [13, 38-40], has been explained by the formation of premicellar aggregates, not surface-active, preventing the adsorption on the surface to continue.

Conclusions

Apparent and partial molar enthalpies at 298 K of the aqueous solutions of the homologous series of cationic gemini surfactants 1,1′-didodecyl-2,2′-alkylenebispyridinium dichloride, obtained by means of direct methods, are here reported for the first time, with the goal of enriching the fundamental understanding on self-aggregation thermodynamics of gemini dipyridinium surfactants. They show a very peculiar behaviour as a function of the spacer length, when the spacer is short, not allowing for the determination of a –CH_2– group contribution when this group is added to the spacer. We suggested that this surprising behaviour we have found for the same compounds here studied, but having methanesulfonate as counterion, is an evidence of a conformation change of the molecule determined by stacking interactions between the two pyridinium rings, appearing at an optimum length of the spacer. The curves of apparent and molar enthalpies *vs.* concentration and surface tension measurements, here reported for the chloride counterion, show the same trend and suggest that this behaviour is independent on the counterion and probably due to a different arrangement of the molecule inside the micelle and on the interphase surface, when the spacer is four methylene long. On the contrary, the group contribution additivity for the counterion is respected, independently on the spacer length.

Supporting Information Available

Tables collecting Molality (*m*), enthalpies of dilution (ΔH_d), apparent (L_Φ) and partial molar (L_2) enthalpies of 1,1′-didodecyl-2,2′-trimethylenebispyridinium dichloride (12-Py(2)-3-(2)Py-12 Cl); 1,1′-didodecyl-2,2′-tetramethylenebispyridinium dichloride (12-Py(2)-4-(2)Py-12 Cl); 1,1′-

didodecyl-2,2′-octamethylenebispyridinium dichloride (12-Py(2)-8-(2)Py-12 Cl); 1,1′-didodecyl-2,2′-dodecamethylenebispyridinium dichloride (12-Py(2)-12-(2)Py-12 Cl) in water at 298 K.

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References

1. Rosen M. J.; Tracy, D. J. J. Surfactants Deterg., 1998, 1, 547-554 and references therein.

2. Menger, F. M.; Keiper, J. S., Gemini Surfactants. Angew. Chem. Int. Ed., 2000, 39, 1906-1920.

3. R. Zana, Novel Surfactants- Preparation, Applications, and Biodegradability. Dimeric (Gemini) Surfactants, in: K Holmberg (Eds.), Surfactant Science Series, Volume 74, Marcel Dekker, Inc., New York, 1998, p. 241.

4. E. Fisicaro, Cellular & Molecular Biology Letters, Gemini Surfactants: Chemico-Physical and Biological Properties, 2 (1997) 45-63 and references therein.

5. C. Lamprecht, J. T. Huzil, M. V. Ivanova, and M. Foldvari, Non-Covalent Functionalization of Carbon Nanotubes with Surfactants for Pharmaceutical Applications – A Critical Mini-Review Drug Delivery Letters, 1 (2011) 45-57

6. P.C. Bell, M. Bergsma, I.P. Dolbnya, W. Bras, M.C.A. Stuart, A.E. Rowan, M.C. Feiters, J.B.F.N. Engberts, Transfection mediated by gemini surfactants: engineered escape from the endosomal compartment, J. Am. Chem. Soc. 125 (2003) 1551-1558.

7. A.J. Kirby, P. Camilleri, J.B.F.N. Engberts, M.C. Feiters, R.J.M. Nolte, O. Soderman, M. Bergsma, P.C. Bell, M.L. Fielden, C.L. Garcia Rodriguez, P. Guedat, A. Kremer, C. McGregor, C. Perrin, G. Ronsin, M.C.P. van Eijk, Gemini surfactants: New synthetic vectors for gene transfection, Angew. Chem. Int. Ed. 42 (2003) 1448-1457.

8. a) M. D. Donkuru, S. D. Wettig, R. E. Verrall, I. Badea, and M. Foldvari, Designing pH-sensitive gemini nanoparticles for non-viral gene delivery intokeratinocytes, J. Mater. Chem., 2012, 22, 6232. b) I. Badea, N. Shaterian, and M. Foldvari, Topical Gene Delivery in Mice Using Gemini Surfactant – Lipid Nanoparticles With and Without Tape Electrode Electroporation, Drug Delivery Letters, 2011, *1,* 62-66. c) P. Yang, J. Singh, S. Wettig, M. Foldvari, R. E. Verrall, I. Badea, Enhanced gene expression in epithelial cells transfected with amino acid-substituted gemini nanoparticles, European Journal of Pharmaceutics and Biopharmaceutics 75 (2010) 311–320.

9. E. Fisicaro, C. Compari, E. Duce, G. Donofrio, B. Różycka-Roszak and E. Woźniak: Biologically Active Bisquaternary Ammonium Chlorides: Physico-Chemical Properties of Long Chain Amphiphiles and Their Evaluation as Non-Viral Vectors For Gene Delivery. Biochimica et Biophysica Acta-General Subjects, 1722 (2005) 224-233.

10. P. Quagliotto, G. Viscardi, C. Barolo, E. Barni, S. Bellinvia, E. Fisicaro, C. Compari: Gemini Pyridinium Surfactants: Synthesis and Conductimetric Study of a Novel Class of Amphiphiles. Journal of Organic Chemistry, 68(20) (2003) 7651-7660.

11. E. Fisicaro, C. Compari, E. Duce, C. Contestabili, P. Quagliotto, and G. Viscardi, First evaluation of Thermodynamic Properties for Spheres to Elongated Micelles Transition of Some Propanediyl-α,ω-bis(dimethylalkylammonium bromide) Surfactants in Aqueous Solutions, J. Phys. Chem. B, 109 (2005) 1744-1749.

12. B. Różycka-Roszak, E. Fisicaro, A. Ghiozzi, Thermodynamic Study of Aqueous Micellar Solutions of Biologically Active Bisquaternary Ammonium Chlorides, J. Colloid Interface Sci. 184 (1996) 209-215.

13. E. Fisicaro, C. Compari, M. Biemmi, E. Duce, M. Peroni, N. Barbero, G. Viscardi and P.L. Quagliotto: The Unusual Behaviour of the Aqueous Solutions of Gemini Bispyridinium Surfactants: Apparent and Partial Molar Enthalpies of the Dimethanesulfonates, *J. Phys. Chem. B*, (2008), 112,12312-12317.

14. P.L. Quagliotto, C. Barolo, N. Barbero, E. Barni, C. Compari, E. Fisicaro, G. Viscardi, Gemini Pyridinium Surfactants: Synthesis and Characterization of Highly Fluorinated Gemini Pyridinium Surfactants. *Eur. J. Org. Chem.* **2009**, 19, 3167–3177.

15. E. Fisicaro, A. Ghiozzi, E. Pelizzetti, G. Viscardi, P. Quagliotto, Effect of the Counterion on Thermodynamic Properties of Aqueous Micellar Solutions of 1-(3, 3, 4, 4, 5, 5, 6, 6, 6-nonafluorohexyl) Pyridinium Halides. Part I: Apparent and Partial Molar Enthalpies and Volumes at 298 K, J. Colloid Interface Sci. 182 (1996) 549-557.

16. E. Fisicaro, C. Compari, P. Quagliotto, and G. Viscardi: Thermodynamic Properties of Aqueous Micellar Solutions of 1-Methyl-4-Octyl-Pyridinium Halides, *Thermochimica Acta,* **397** (2003) 199-208

17. Zuidema, H. H.; Waters, G. W. Ring method for the determination of interfacial tension. *Ind. Eng. Chem. Anal. Ed.* 1941, *13*, 312-313.

18. J. E. Desnoyers, G. Perron, in: Surfactant Solutions - New Methods of Investigation, Ed. R. Zana, Marcel Dekker, Inc., New York, 1987, p.1 and references therein.

19. Alami, E.; Beinert, G.; Marie, P.; Zana, R. Alkanediyl-α,ω-(dimethylalkylammonium bromide) surfactants. 3. Behaviour at the air-water interface. *Langmuir* 9 (1993) 1465-1467.

20. Pérez, L.; Pinazo, A.; Rosen, M. J.; Infante, M. R. Surface activity properties at equilibrium of novel gemini cationic amphiphilic compounds from arginine, Bis(Args). Langmuir 14 (1998) 2307-2315.

21. Rosen, M. J. *Surfactants and Interfacial Phenomena;* second ed.; John Wiley & Sons: New York, 1989.

22. Tsubone, K.; Arakawa, Y.; Rosen, M. J. Structural Effects on Surface and Micellar Properties of Alkanediyl-α,ω–bis(sodium N-acyl-β-alaninate) Gemini Surfactants. *J. Colloid Interface Sci.* 262 (2003) 516-524.

23. Li, Z. X.; Dong, C. C.; Thomas, R. K. Neutron reflectivity studies of the surface excess of gemini surfactants at the air water interface. *Langmuir* 15 (1999) 4392-4396.

24. E. Fisicaro, M. Biemmi, C. Compari, E. Duce, M. Peroni: Thermodynamics of Aqueous Solutions of Dodecyldimethylethylammonium Bromide, *Journal of Colloid and Interface Science*,305 (2007) 301–307.

25. R. De Lisi, E. Fisicaro, S. Milioto: Thermodynamic Properties and Conductivities of some Dodecylsurfactants in Water. J. Solution Chem.,17 (1988) 1015-1041.

26. B. Róøycka-Roszak and E. Fisicaro. Thermochemical Study of Aqueous Micellar Solutions of Some Amphiphilic Quaternary Ammonium Chlorides at 313°K, Thermochim. Acta, 205 (1992) 19-31.

27. R. De Lisi, E. Fisicaro, and S. Milioto, Thermodynamic properties and conductivities of some dodecylsurfactants in water J. Solution Chem., 17 (1988) 1015-41.

28. E. Fisicaro, E. Pelizzetti, M. Barbieri, P. Savarino and G. Viscardi, Aqueous micellar solutions of some N-alkylnicotinamide and N-alkylpyridinium halide surfactants: apparent and partial molar enthalpiesThermochimica Acta 168 (1990) 143-59.

29. E. Fisicaro, A. Ghiozzi, E. Pelizzetti, G. Viscardi, and P. L. Quagliotto, Effect of the counterion on thermodynamic properties of aqueous micellar solutions of 1-(3,3,4,4,5,5,6,6,6-nonafluorohexyl) pyridinium halides. I. Apparent and partial molar enthalpies and volumes at 298 K. J. Colloid Interface Sci., 182(1996) 549-557.

30. E. Fisicaro, A. Ghiozzi, E. Pelizzetti, G. Viscardi, and P. L. Quagliotto, Effect of the counterion on thermodynamic properties of aqueous micellar solutions of 1-(3,3,4,4,5,5,6,6,6-nonafluorohexyl) pyridinium halides J. Colloid Interface Sci., 184 (1996) 147-154.

31. K. Bijma, J.B.F.N. Engberts, G. Haandrikman, N. van Os, M.J. Blandamer, M. D. Butt, and P. M. Cullis, Thermodynamics of Micelle Formation by 1-Methyl-4-alkylpyridinium Halides Langmuir 10 (1994) 2578-82

32. E. Fisicaro, C. Compari, P. Quagliotto, and G. Viscardi: Thermodynamic Properties of Aqueous Micellar Solutions of 1-Methyl-4-Octyl-Pyridinium Halides, *Thermochimica Acta,* **397** (2003) 199-208.

33. W. P. J. Ford, R. H. Ottewill, H. C. and Parreira, Light-scattering studies on dodecylpyridinium halides J. Colloid Interface Sci., 21 (1966) 522-533.

34. A. L. Underwood, and E. W. Anacker, Organic counterions as probes of the micellar surface, J. Colloid Interface Sci., (1987), 117(1), 296-8

35. A. L. Underwood, and E. W. Anacker, Counterion lyotropy and micelle formation J. Colloid Interface Sci., 117 (1987) 242-250.

36. J. N. Israelachvili, *Intermolecular & Surface Forces*, Academic Press, London, 2nd Edition (1991).

37. Y. Marcus, *Ion Solvation*, Wiley, New York (1985).

38. Pinazo, A.; Wen, X.; Perez, L.; Infante, M. R.; Franses, E. I. Aggregation Behaviour in Water of Monomeric and Gemini Cationic Surfactants Derived from Arginine. *Langmuir* 15 (1999) 3134-3142.

39. Yoshimura, T.; Yoshida, H.; Ohno, A.; Esumi, K. Physicochemical Properties of Quaternary Ammonium Bromide-type Trimeric Surfactants. *J. Colloid Interface Sci.* 267 (2003) 167-172.

40. Tsubone, K.; Arakawa, Y.; Rosen, M. J. Structural Effects on Surface and Micellar Properties of Alkanediyl-α,ω–bis(sodium N-acyl-β-alaninate) Gemini Surfactants. *J. Colloid Interface Sci.* 262 (2003) 516-524.

TABLE 1[a]

Compound	s	cmc [b] (conduc.) [mmol/L]	β [b]	ΔH_{mic} [kJ/mol]	cmc (surf. tens.) [mmol/L]	γ_{cmc} [dyne/cm]	$\Gamma \cdot 10^{10}$ [mol/cm^2]	A_{min} [nm^2]	pC_{20}	cmc/C_{20}
12-Py(2)-3-(2)Py-12 Cl	3	1.45	68	-11.2	1.11	42.5	1.44	11.5	3.58	4.24
12-Py(2)-4-(2)Py-12 Cl	4	1.07	69	-10.1	0.28	42.1	2.36	7.0	3.94	2.44
12Py(2)-8-(2)Py-12 Cl	8	1.06	44	-16.5	0.12	43.6	1.02	16.3	4.71	6.23
12-Py(2)-12-(2)Py-12 Cl	12	0.21	70	-23.5	0.023	42.4	0.95	17.4	5.56	8.35

[a] Cmc, from conductivity and from surface tension; β, degree of counterion association; ΔH_{mic}, change in enthalpy upon micellization; Γ, the maximum surface excess concentration; A_{min}, the area per molecule at the interface; C_{20}, the surfactant concentration required to reduce the surface tension of the solvent by 20 mN/m; γ_{cmc}, the surface tension at the cmc; the cmc/C_{20} ratio, as a function of the number of carbon atoms in the spacer, s for the surfactants under investigation.

[b] Ref. 10

Captions

Figure 1. Apparent molar relative enthalpies of 1,1′-didodecyl-2,2′-trimethylenebispyridinium dichloride (12-Py(2)-3-(2)Py-12 Cl, empty squares); 1,1′-didodecyl-2,2′-tetramethylenebispyridinium dichloride (12-Py(2)-4-(2)Py-12 Cl, empty tringles); 1,1′-didodecyl-2,2′-octamethylenebispyridinium dichloride (12-Py(2)-8-(2)Py-12 Cl, empty circles); 1,1′-didodecyl-2,2′-dodecamethylenebispyridinium dichloride (12-Py(2)-12-(2)Py-12 Cl, diamonds) as a function of surfactant molality, *m*.

Figure 2. Partial molar relative enthalpies of 1,1′-didodecyl-2,2′-trimethylenebispyridinium dichloride (12-Py(2)-3-(2)Py-12 Cl, full squares); 1,1′-didodecyl-2,2′-tetramethylenebispyridinium dichloride (12-Py(2)-4-(2)Py-12 Cl, full tringles); 1,1′-didodecyl-2,2′-octamethylenebispyridinium dichloride (12-Py(2)-8-(2)Py-12 Cl, full circles); 1,1′-didodecyl-2,2′-dodecamethylenebispyridinium dichloride (12-Py(2)-12-(2)Py-12 Cl, diamonds) as a function of surfactant molality, *m*.

Figure 3. Surface tension as a function of the logarithm of surfactant molarity, *c* of 1,1′-didodecyl-2,2′-trimethylenebispyridinium dichloride (12-Py(2)-3-(2)Py-12 Cl, full squares); 1,1′-didodecyl-2,2′-tetramethylenebispyridinium dichloride (12-Py(2)-4-(2)Py-12 Cl, full triangles); 1,1′-didodecyl-2,2′-octamethylenebispyridinium dichloride (12-Py(2)-8-(2)Py-12 Cl, full circles); 1,1′-didodecyl-2,2′-dodecamethylenebispyridinium dichloride (12-Py(2)-12-(2)Py-12 Cl, full diamonds).

Figure 4. Comparison between compounds having chloride (empty symbols) and methanesulfonate (full symbols) as counterion for the compounds with spacer constituted by 3 (squares), 4 (tringles), 8 (circles) and 12(diamonds) carbon atoms. Stars indicate 12-Py(2)-2-(2)Py-12 MS.

Figure 1

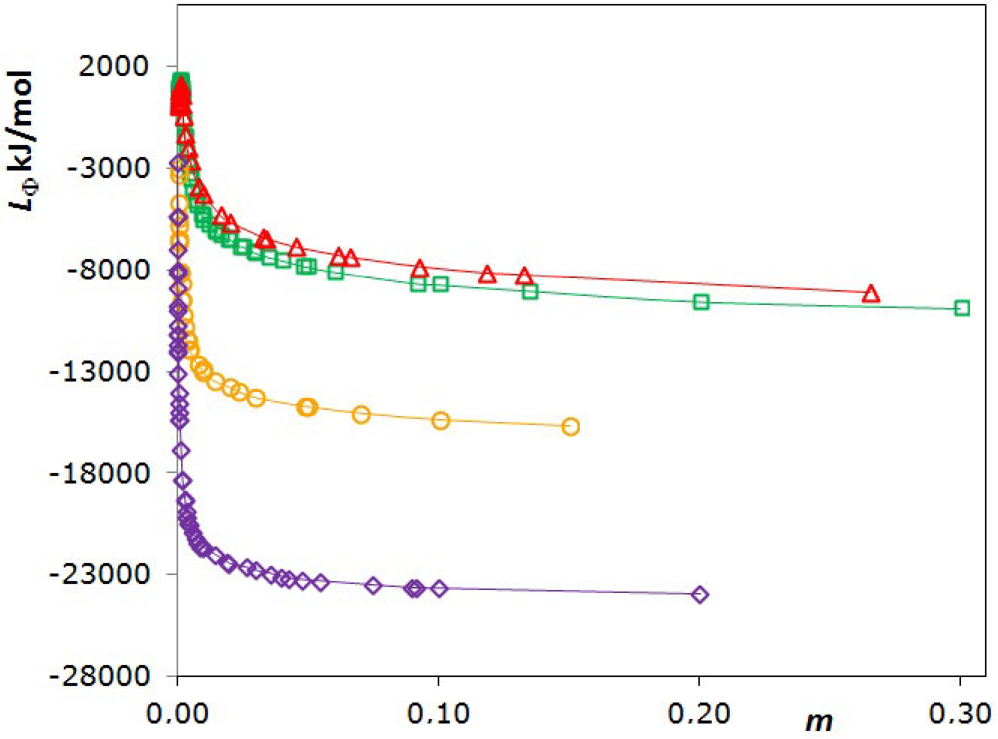

L_Φ kJ/mol
2000
-3000
-8000
-13000
-18000
-23000
-28000
0.00
0.10
0.20
0.30
m

Figure 2

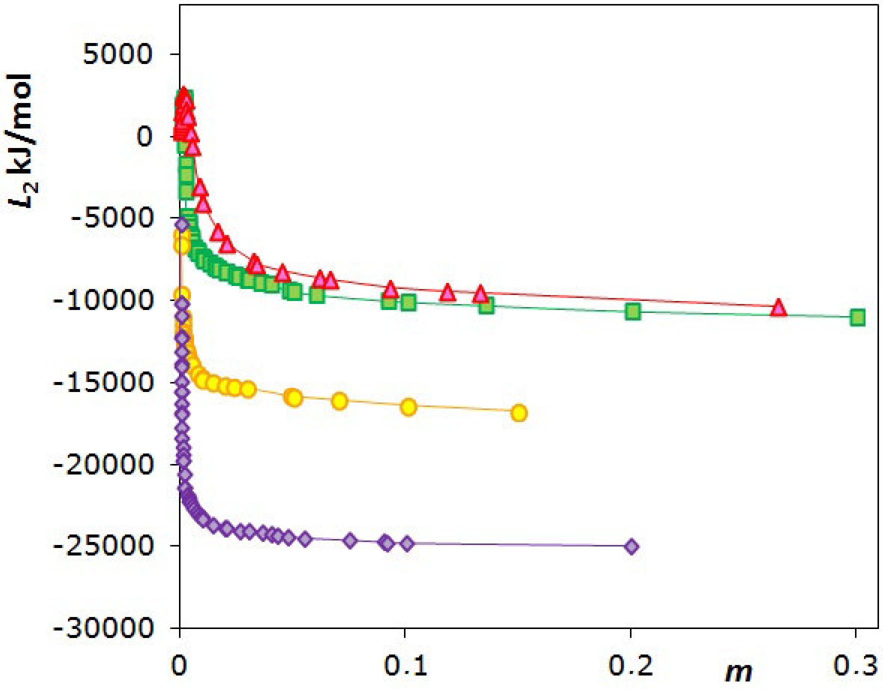


Figure 3

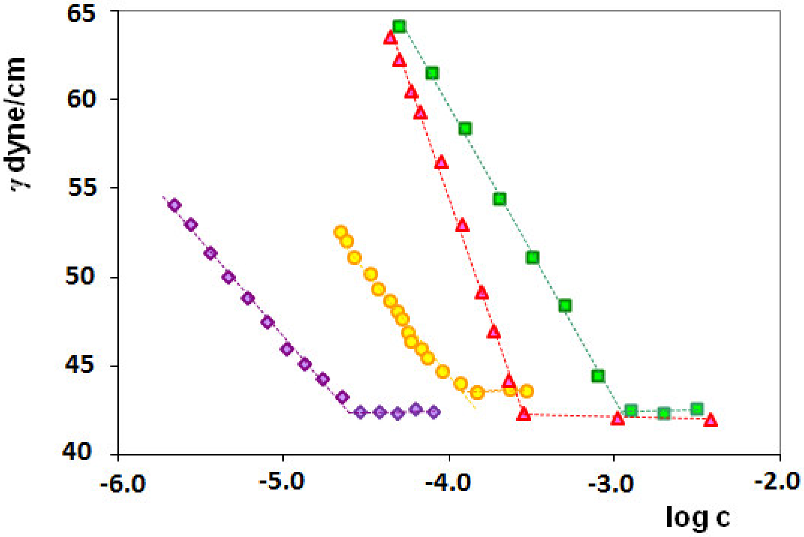
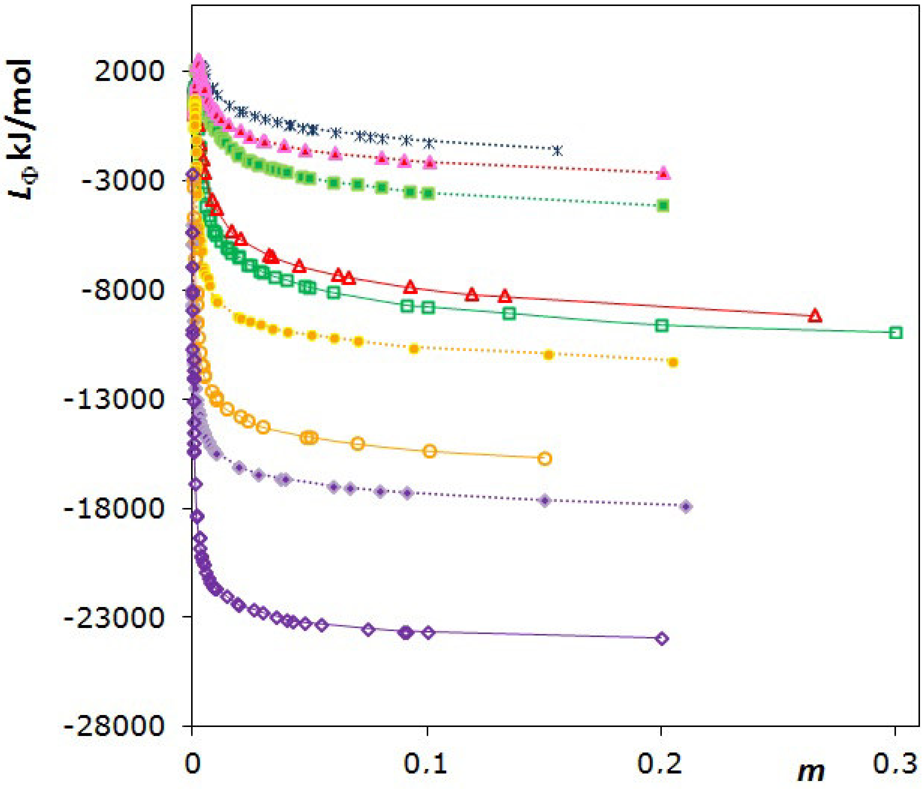


Figure 4



SUPPORTING INFORMATION

TABLE 1

Molality (m), enthalpies of dilution (ΔH_d), apparent (L_Φ) and partial molar (L_2) enthalpies of the 1,1′-didodecyl-2,2′-trymethylenebispyridinium dichloride (12-Py(2)-3-(2)Py-12 Cl), in water at 298 K (subscript i stands for initial and f for final state).

m_i (mol kg^{-1})	m_f (mol kg^{-1})	ΔH_d (J mol^{-1})	$\Phi_{\mathrm{L}i}$ (J mol^{-1})	$\Phi_{\mathrm{L}f}$ (J mol^{-1})	L_{2i} (J mol^{-1})	L_{2f} (J mol^{-1})
0.00060	0.00029	-361	800	410	1440	810
0.00070	0.00034	-410	900	500	1610	920
0.00082	0.00039	-449	1010	550	1790	1030
0.00090	0.00043	-501	1090	620	1910	1120
0.00100	0.00050	-520	1201	700	2040	1250
0.00120	0.00059	-568	1340	760	2270	1410
0.00160	0.00080	0	990	990	-540	1760
0.00180	0.00087	322	750	1060	-1700	1870
0.00200	0.00096	650	500	1150	-3400	1990
0.00251	0.00122	1952	-600	1360	-4900	2280
0.00301	0.00141	2679	-1440	1260	-5300	220
0.00401	0.00193	3300	-2700	600	-6010	-2390
0.00601	0.00297	2647	-4158	-1510	-6850	-5260
0.00701	0.00340	2315	-4565	-2250	-7075	-5600
0.00902	0.00442	2046	-5236	-3250	-7440	-6240
0.01002	0.00489	1930	-5501	-3570	-7570	-6500
0.01503	0.00736	1323	-6099	-4776	-8000	-7130
0.02004	0.00979	1132	-6460	-5328	-8310	-7530
0.02506	0.01232	1120	-6850	-5730	-8570	-7770
0.03006	0.01460	1111	-7160	-6050	-8790	-7970
0.03508	0.01689	1070	-7370	-6300	-8940	-8120
0.04008	0.01963	1039	-7520	-6490	-9090	-8280
0.05010	0.02394	1013	-7850	-6837	-9510	-8520
0.06013	0.02904	1002	-8100	-7100	-9710	-8750
0.10024	0.04816	940	-8740	-7800	-10135	-9450
0.20040	0.09169	890	-9570	-8680	-10700	-10065
0.30020	0.13516	870	-9910	-9040	-11020	-10345

TABLE 2

Molality (*m*), enthalpies of dilution (ΔH_d), apparent (L_Φ) and partial molar (L_2) enthalpies of the 1,1′-didodecyl-2,2′-tetramethylenebispyridinium dichloride (12-Py(2)-4-(2)Py-12 Cl), in water at 298 K (subscript *i* stands for initial and *f* for final state).

m_i (mol kg^{-1})	m_f (mol kg^{-1})	ΔH_d (J mol^{-1})	Φ_{Li} (J mol^{-1})	Φ_{Lf} (J mol^{-1})	L_{2i} (J mol^{-1})	L_{2f} (J mol^{-1})
0.0006	0.0003	-394	446	55	1465	299
0.0007	0.00035	-522	625	98	1975	437
0.0008	0.0004	-682	833	153	2559	607
0.0009	0.00045	-937	1150	213	2555	786
0.001	0.0005	-755	1037	282	2550	990
0.00201	0.00099	866	179	1045	2200	2552
0.00301	0.00149	1962	-1332	630	1200	2450
0.00501	0.00248	2223	-2623	-400	-600	1600
0.00802	0.00397	1851	-3871	-2020	-3100	200
0.02005	0.00993	1398	-5657	-4260	-6500	-4100
0.03364	0.01661	1137	-6467	-5330	-7830	-5800
0.06621	0.0325	1000	-7400	-6400	-8755	-7670
0.09268	0.0451	983	-7862	-6880	-9225	-8220
0.1328	0.06157	978	-8278	-7300	-9560	-8655
0.26546	0.11837	970	-9155	-8185	-10400	-9480

TABLE 3

Molality (m), enthalpies of dilution (ΔH_d), apparent (L_Φ) and partial molar (L_2) enthalpies of the 1,1′-didodecyl-2,2′-octamethylenebispyridinium dichloride (12-Py(2)-8-(2)Py-12 Cl), in water at 298 K (subscript i stands for initial and f for final state).

m_i (mol kg^{-1})	m_f (mol kg^{-1})	ΔH_d (J mol^{-1})	$\Phi_{\mathrm{L}i}$ (J mol^{-1})	$\Phi_{\mathrm{L}f}$ (J mol^{-1})	L_{2i} (J mol^{-1})	L_{2f} (J mol^{-1})
0.00007	0.00003	-731	805	77	2518	407
0.00008	0.00004	-850	1063	207	3238	804
0.00010	0.00005	-1285	1657	374	4870	1295
0.00020	0.00010	-400	2057	1657	1880	4870
0.00030	0.00015	215	1735	1950	45	2975
0.00040	0.00019	875	1170	2045	-1615	2050
0.00050	0.00024	1470	525	1995	-3730	1035
0.00060	0.00029	1906	-115	1790	-5040	225
0.00070	0.00034	2540	-1040	1500	-6300	-610
0.00080	0.00039	3086	-1856	1230	-7025	-1450
0.00090	0.00044	3448	-2528	920	-8125	-2430
0.00110	0.00053	3917	-3582	335	-8935	-4175
0.00150	0.00072	3455	-4675	-1220	-9265	-6460
0.00171	0.00085	3200	-5410	-2210	-9400	-7620
0.00200	0.00099	2935	-6310	-3375	-9595	-8650
0.00401	0.00199	2023	-8303	-6280	-10485	-9580
0.00501	0.00243	1758	-8708	-6950	-10780	-9865
0.00802	0.00385	1450	-9665	-8215	-11405	-10440
0.01003	0.00485	1306	-9945	-8645	-11635	-10735
0.02006	0.00974	1203	-11130	-9930	-12225	-11640
0.03009	0.01425	1064	-11614	-10550	-12630	-11915
0.05014	0.02350	803	-12108	-11305	-13165	-12380
0.10083	0.04871	781	-12845	-12065	-13990	-13135
0.15049	0.07037	730	-13250	-12520	-14700	-13570

TABLE 4

Molality (*m*), enthalpies of dilution (ΔH_d), apparent (L_Φ) and partial molar (L_2) enthalpies of the 1,1′-didodecyl-2,2′-dodecamethylenebispyridinium dichloride (12-Py(2)-12-(2)Py-12 Cl), in water at 298 K (subscript *i* stands for initial and *f* for final state).

m_i (mol kg^{-1})	m_f (mol kg^{-1})	ΔH_d (J mol^{-1})	Φ_{Li} (J mol^{-1})	Φ_{Lf} (J mol^{-1})	L_{2i} (J mol^{-1})	L_{2f} (J mol^{-1})
0.00010	0.00005	2674	-5339	-2665	-10170	-5339
0.00020	0.00010	2810	-8149	-5339	-12300	-10170
0.00030	0.00013	3071	-10015	-6944	-13975	-10915
0.00040	0.00019	3156	-11201	-8045	-15575	-12195
0.00050	0.00024	3200	-12100	-8900	-16940	-13060
0.00060	0.00029	3280	-13080	-9800	-17790	-13810
0.00070	0.00035	3332	-14047	-10715	-18435	-14965
0.00080	0.00040	3360	-14561	-11201	-18960	-15575
0.00090	0.00045	3380	-15045	-11665	-19450	-16320
0.00100	0.00049	3391	-15401	-12010	-19815	-16820
0.00200	0.00099	2998	-18363	-15365	-21430	-19780
0.00300	0.00148	2451	-19333	-16882	-21865	-20570
0.00402	0.00199	1880	-20210	-18330	-22230	-21425
0.00600	0.00296	1590	-20910	-19320	-22710	-21855
0.00701	0.00351	1340	-21190	-19850	-22890	-22060
0.00801	0.00395	1220	-21412	-20192	-23050	-22210
0.00901	0.00445	1180	-21625	-20445	-23190	-22350
0.01002	0.00490	1090	-21651	-20561	-23320	-22470
0.02004	0.00988	805	-22453	-21648	-23895	-23210
0.03007	0.01467	757	-22786	-22029	-24105	-23670
0.04007	0.01939	714	-23104	-22390	-24285	-23850
0.05513	0.02653	670	-23310	-22640	-24505	-24025
0.07515	0.03608	560	-23510	-22950	-24640	-24195
0.09017	0.04288	474	-23645	-23171	-24740	-24315
0.10036	0.04788	428	-23670	-23242	-24820	-24415
0.20043	0.09145	305	-23955	-23650	-24980	-24755