J Therm Anal Calorim (2011) 104:765–770
DOI 10.1007/s10973-010-1096-y

Calorimetric and densimetric examinations of aqueous solutions of heptylene-1,7-*bis*(dimethyloctylammonium bromide) and octylene-1,8-*bis*(dimethyloctylammonium bromide)

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Received: 13 July 2010 / Accepted: 6 October 2010 / Published online: 22 October 2010

Abstract The critical micelle concentrations of gemini surfactants having different spacer chain lengths 8-7-8 and 8-8-8 in aqueous solutions have been determined by calorimetric and densimetric methods within a wide temperature range. The isothermal volume change upon micellisation of the title surfactants has been obtained from density measurements using pseudo-phase model. Predicted values for apparent molar volume of the surfactant at the critical micellisation concentration (c.m.c.) agree very well with infinite dilution volumes calculated from additivity method. It has been shown that the inflection point in the curves of the dependence of volume expansion coefficient on molality can be used to determine the value of c.m.c. similar as the second one of the two maxima which are observed on the concentration function of apparent molar heat capacity. The experimental determined values of c.m.c. have been compared with the values presented in the literature data for 8-s-8 gemini surfactants.

Keywords Gemini surfactants · Alkylene-α,ω-*bis*(dimethylalkylammonium bromide) · Volumetric expansion coefficient · Heat capacity · Critical micellisation concentration

Introduction

The gemini surfactants are a relatively new group of amphiphiles. Their molecules contain, in sequence, a long hydrocarbon chain—m, an ionic group, a hydrophobic spacer—s, a second ionic group and another hydrocarbon tail m [1–4]. These surfactants can be represented by the abbreviation m-s-m, where m is the number of carbon atoms in their side hydrocarbon chain and s is the carbon atoms number in the spacer.

The unabated interest of many research centres in dimeric surfactants is connected with their behaviour and properties that considerably differ from those of corresponding monomeric surfactants, which creates new opportunities of their use in various industrial branches [3–6]. Moreover, the studies carried out on the use of gemini surfactants as vectors in genic therapies seem to be very promising [7–9]. Different than their conventional equivalents properties of dimeric surfactant such as, e.g. significantly lower critical micellisation concentration (c.m.c.), more pronounced visco-elastic properties, higher capacity to effectively reduce surface tension, etc. are determined by the structure of molecules and has been described in the literature, e.g. [3, 10]. The micellisation processes in the surfactant group under discussion are influenced by the length of hydrocarbon chains of their molecules. The influence of the side chain length m on the value of c.m.c. is predictable and shows analogous tendency to that observed in the case of monomeric surfactants, i.e. the increase in the alkyl chain length results in a decreased c.m.c. value whilst the influence of the linking chain length s is more complex [11, 12]. Of course, the properties of surfactant solutions under discussion depend also on temperature [13].

The systems that tend to form stable micellar aggregates show characteristic changes in the course of concentration dependencies amongst others of partial molar volume and partial molar heat capacity. These values, within some ranges of the system composition, exhibit characteristic extrema or show inflection points connected with the

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appearance of association processes. For that reason in this study a particular attention is paid above the mentioned functions.

We have examined the aqueous solutions of alkylene-α,ω-*bis*(dimethyl-alkylammonium bromides) with the general formula: 8-s-8 for s = 7, 8 by the calorimetric (C_p measurement) and densimetric methods at several temperatures.

No information on the micellisation process of aqueous solutions of 8-7-8 and 8-8-8 gemini surfactants is available in the literature. We expected that our results and appropriate literature data concerning other gemini surfactants would make it possible to examine the effect of the alkyl and alkanodiyl chains length as well as that of temperature on the micelle formation process and particularly on the c.m.c.

Experimental section

Materials

The synthesis of heptylene-1,7-*bis*(dimethyloctylammonium bromide) (8-7-8) was carried out according to the procedure given by Zana [2, 11]. A solution of 1,7-dibromoheptane (0.05 mol, Aldrich) and *N*,*N*-dimehyloctylamine (0.11 mol, Aldrich) in methanol (100 cm^3) was heated for 48 h under reflux. Methanol and unreacted compounds were removed by evaporation under vacuum, and the obtained crude product was purified by crystallisation from ethyl acetate/acetone (6/4) mixtures (m.p. 172–175 °C, yield 56%).

^{1}HNMR (200 MHz, D_2O) 3.40–3.15 (8H, m, N-oct-1-CH_2 and N-hep-1.7-CH_2), 3.04 (12H, s, N-CH_3), 1.84–1.58 (8H, m, N-oct-2-CH_2 and N-hex-2.5-CH_2), 1.50–1.14 (26H, m, N-oct-3,4,5,6,7-CH_2 and N-hep-3,4,5-CH_2), 0.96–0.75 (6H, m, N-oct-8-CH_3).

^{1}HNMR (200 MHz, D_2O with addition of DMSO-d$_6$ as a reference) 3.0–3.02 (8H, m, N-oct-1-CH_2 and N-hep-1,7-CH_2), 3.86 (12H, s, N-CH_3), 1.70–1.55 (8H, m, N-oct-2 CH_2 and N-hex-2,6-CH_2), 1.46–1.14 (26H, m, N-oct-3,4,5,6,7-CH_2 and N-hep-3,4,5-CH_2), 0.92–0.75 (6H, m, N-oct-8-CH_3).

^{13}C NMR (50 MHz, D_2O with an addition of DMSO-d$_6$ as a reference) 65.6, 65.4, 32.8, 30.0, 29.9, 29.5, 27.2, 27.0, 23.8, 23.5, 15.3.

Octylene-1,8-*bis*(dimethyloctylammonium bromide) (8-8-8) was prepared as surfactant 8-7-8. The obtained crude product was purified by crystallisation from ethyl acetate/acetone (8/3) mixtures (m.p. 179–183 °C, yield 53%).

^{1}HNMR (200 MHz, D_2O with addition of DMSO-d$_6$ as a reference) 3.35–3.15 (8H, m, N-oct-1-CH_2 and N-oct-1,8-CH_2), 3.01 (12H, s, N-CH_3), 1.80–1.50 (8H, m, N-oct-2 CH_2 and N-oct-2,7-CH_2), 1.46–1.10 (28H, m, N-oct-3,4,5,6,7-CH_2 and N,N-3,4,5,6-CH_2), 0.95–0.80 (6H, m, N-oct-8-CH_3).

^{13}C NMR (50 MHz, D_2O with addition of DMSO-d6 as a reference) 63.1, 50.2, 31.3, 28.6, 28.5, 25.9, 22.2, 21.6, 14.1.

Prior to measurements the synthesised 8-7-8 and 8-8-8 surfactants were dried under vacuum at a temperature of 323.15 K. The solutions were prepared by weight with the use of three times distilled and degassed water.

Methods

Density measurements

The densities of the solutions investigated were measured within the temperature range 283.15–328.15 K using an Anton Paar 5000 densimeter.

Prior to each measurement series the densimeter was calibrated by measuring the density of three times distilled water ($d_{298.15} = 0.997043$ g cm^{-3}) and dry air ($d_{298.15} = 0.001169$ g cm^{-3}, $p = 1$ bar). The accuracy of measurements was $\pm 5 \times 10^{-6}$ g cm^{-3}.

Heat capacity measurements

Isobaric heat capacities were measured by means of a differential scanning calorimeter microDSC III Setaram (France). Measurements were carried out within the temperature range 292.15–333.15 K (depending on the surfactant), using the “continuous with reference” mode at a scanning rate of 0.35 K min^{-1}.

Results and discussion

Thermal expansion coefficient and apparent molar volumes

Thermal expansion coefficient, α_t, and apparent molar volumes, V_ϕ of 8-7-8 and 8-8-8 surfactants in aqueous solutions at various temperatures, were calculated from Eqs. 1, 2:

$$\alpha_T = -\frac{1}{d_T} \cdot \frac{\partial d}{\partial T} \tag{1}$$

$$V_\phi = \frac{M_2}{d} + \frac{1000(d_0 - d)}{m_2 d d_0} \tag{2}$$

where d is the density of solution, d_0 is the density of solvent (water), M_2 (g mol^{-1}) is the amphiphile molecular mass and m (mol kg^{-1}) is the solution molality.

The calculated α_T and V_ϕ values of 8-7-8 and 8-8-8 surfactant solutions in water as a function of solution molalities at a temperature of 298.15 K are presented in Figs. 1, 2, 3 and 4. The dependences of volumetric expansion coefficient on molality for the aqueous solutions of 8-7-8 and 8-8-8 surfactants have similar shapes with a characteristic break point corresponding to the solution concentrations of 0.090 mol kg^{-1} for 8-7-8 and 0.073 mol kg^{-1} for 8-8-8 at a temperature of 298.15 K. This break point shifts towards lower concentrations with the increase in temperature (Table 1).

The apparent molar volume functions for aqueous solutions of 8-7-8 and 8-8-8 surfactants (Figs. 3, 4) have similar shapes within the whole temperature range investigated with the inflection point followed by rapid growth of the V_ϕ values. The position of this inflection point depends on temperature and moves to the lower values of concentration with the temperature increase. The course of the function $V_\phi = f(m)$ observed here is characteristic of most micellar systems examined so far [14].

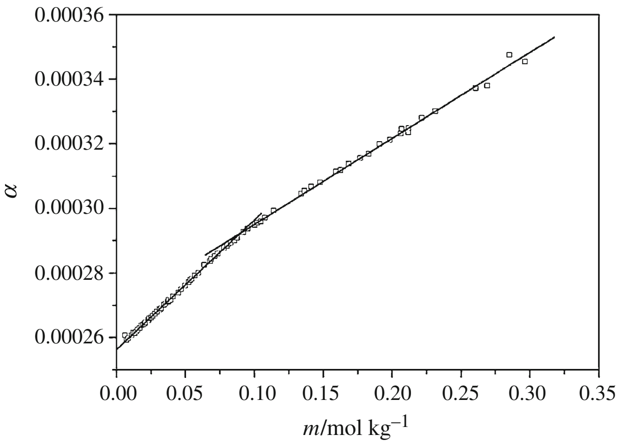

Fig. 1 Dependence of volumetric expansion coefficient on the concentration of 8-7-8 surfactant at a temperature of 298.15 K

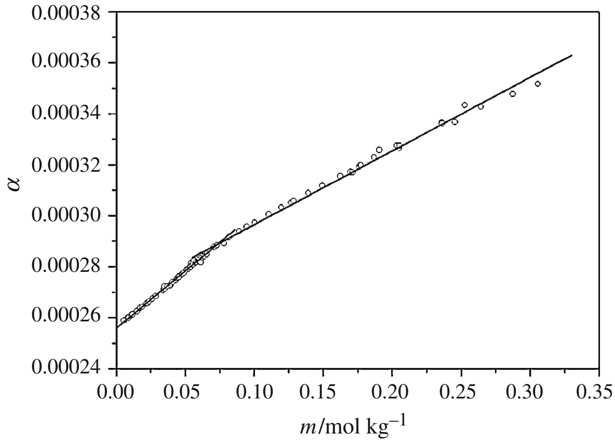

Fig. 2 Dependence of volumetric expansion coefficient on the concentration of 8-8-8 surfactant at a temperature of 298.15 K

As it is known, the increase in apparent molar volumes is caused by the changes in the water structure in the neighbourhood of the surfactant molecule non-polar groups (hydrophobic hydration) [14, 15, and the reference therein] and by the changes in the electrostriction effect connected with the polar groups of surfactant molecule. The strongest changes in the solute–solvent interactions in these systems take place in the c.m.c. region where the micelles formation process starts [16, 17]. Therefore, it is generally accepted that the position of the inflection point corresponds to the critical micelles concentration c.m.c. Such an approach makes it possible to determine the c.m.c. values from the course of the $V_\phi = f(m)$ function. In this article the c.m.c. values have been evaluated by the interception point between the linear trends obtained interpolating the experimental data at the pre-micellar region and the data

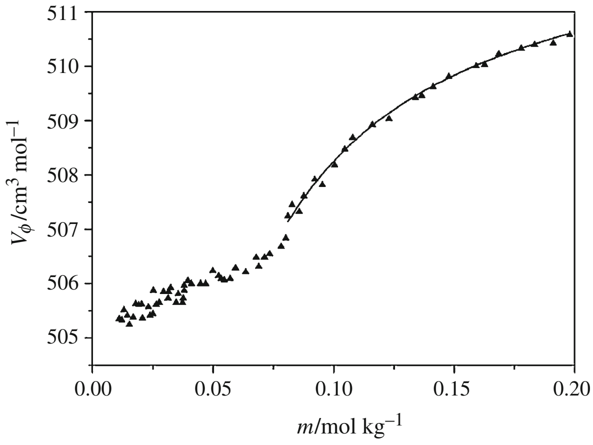

Fig. 3 Apparent molar volume of 8-7-8 gemini surfactant as a function of surfactant molality at 298.15 K. The *solid line* results from the fitting of the experimental data by Eq. 3

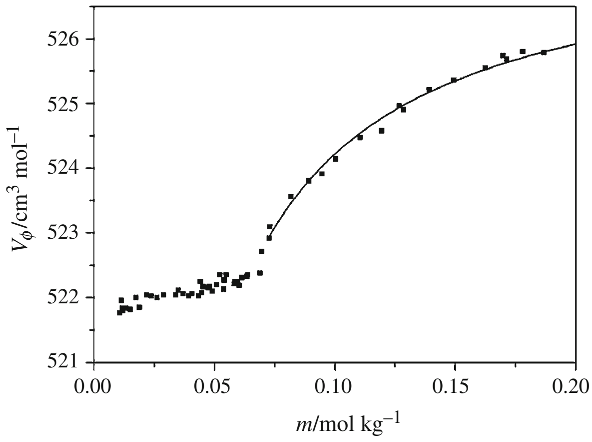

Fig. 4 Apparent molar volume of 8-8-8 gemini surfactant as a function of surfactant molality at 298.15 K. The *solid line* results from the fitting of the experimental data by Eq. 3

concerning the region just above the beginning of the micellisation process. The c.m.c values determined on this basis are listed in Table 1.

The volumetric properties of micellar systems within the concentration range above the c.m.c. can be described using the so-called pseudo-phase model [18]. According to this model the concentration dependence of the apparent molar volume of the surfactant can be expressed in the form:

$$V_\phi = V_{\phi,\mathrm{M}} - \frac{\mathrm{c.m.c.}}{m}\Delta V_{\phi,\mathrm{M}} \tag{3}$$

where $V_{\phi,\mathrm{M}}$ and $\Delta V_{\phi,\mathrm{M}}$ are the adjustable parameters. $V_{\phi,\mathrm{M}}$ represents the value of the apparent molar volume of the surfactant in the micellar phase and $\Delta V_{\phi,\mathrm{M}}$ denotes the volume change in the micelle formation [17]. The results of the fitting procedure for aqueous solutions of 8-7-8 and 8-8-8 gemini surfactants within the examined temperature range are collected in Table 2.

Table 1 The position of inflection point of function $\alpha_\mathrm{T} = f(m)$ (*a*), and the position of the second maximum in curve $C_{\mathrm{p},\phi,2} = f(m)$ curve (*b*) for the temperature range investigated

T/K	8-7-8		8-8-8	
	a/mol kg^{-1}	*b*/mol kg^{-1}	*a*/mol kg^{-1}	*b*/mol kg^{-1}
288.15	0.101		0.084	
293.15	0.095	0.091	0.079	0.075
298.15	0.090	0.088	0.073	0.074
303.15	0.087	0.090	0.072	0.074
308.15	0.082		0.070	
313.15	0.078	0.090	0.067	0.075
318.15	0.077		0.067	
323.15	0.077	0.083	0.068	0.08

Table 2 Isothermal volume changes due to micelle formation $\Delta V_{\phi,\mathrm{M}}$ and apparent molar volume of the surfactant in the micellar phase $V_{\phi,\mathrm{M}}$ for 8-7-8 and 8-8-8 surfactants at various temperatures

T/K	8-7-8		8-8-8	
	$\Delta V_{\phi,\mathrm{M}}$/ cm^3 mol^{-1}	$V_{\phi,\mathrm{M}}$/ cm^3 mol^{-1}	$\Delta V_{\phi,\mathrm{M}}$/ cm^3 mol^{-1}	$V_{\phi,\mathrm{M}}$/ cm^3 mol^{-1}
288.15	4.9 ± 0.1	507.4	5.5 ± 0.1	522.8
293.15	5.0 ± 0.1	510.3	5.2 ± 0.1	525.4
298.15	5.2 ± 0.1	513.0	4.4 ± 0.1	527.6
303.15	4.4 ± 0.1	514.7	4.1 ± 0.1	530.0
308.15	3.8 ± 0.1	516.6	3.7 ± 0.1	532.2
313.15	3.5 ± 0.1	518.5	3.0 ± 0.1	534.3
318.15	4.0 ± 0.1	521.2	3.1 ± 0.1	536.9
323.15	3.7 ± 0.1	523.3	2.0 ± 0.1	538.8

The additivity model presented in the literature allows one to calculate the partial molal volumes of the gemini surfactants of the 8-s-8 type at the critical micelle concentration [18]. According to this model the apparent molar volume of the surfactant is a sum of the contributions made by appropriate monomers, groups and atoms. In our case we have:

$$V^{\mathrm{o}}_\phi(\text{8-s-8}) = 2\,V^{\mathrm{o}}_\phi(\mathrm{OTAB}) + (\text{s-2})V^{\mathrm{o}}_\phi(\mathrm{CH_2}) - 2\,V^{\mathrm{o}}_\phi(\mathrm{H})$$

where V^{o}_ϕ (OTAB) = 225.1 cm^3 mol^{-1}, V^{o}_ϕ (CH$_2$) = 15.8 cm^3 mol^{-1}and V^{o}_ϕ(H) = 10.7 cm^3 mol^{-1}.

Owing to the low values of the c.m.c.'s for investigated series of gemini surfactants it is widely assumed that $V_{\phi,\mathrm{c.m.c.}}$ are equal to V^{o}_ϕ. The values of V^{o}_ϕ (8-s-8) calculated in this way for 8-7-8 and 8-8-8 surfactants are listed together in Table 3 with the appropriate V_ϕ data calculated from Eq. 3 for m = c.m.c. using the data obtained in this study. For the sake of comparison the analogous data for 8-3-8 and 8-6-8 surfactants calculated on the basis of literature data are also given in Table 3. As it can be seen the values obtained are well consistent with those calculated on the basis of the pseudo-phase model, similarly as in the case of 12-s-12 surfactant [16]. The values of $\Delta V_{\phi,\mathrm{M}}$ for 8-s-8 surfactants (Table 3) decrease with the increase in the length of spacer (s). The same dependence of decreasing $\Delta V_{\phi,\mathrm{M}}$ values for gemini surfactants of the 12-s-12 series, in which the number of carbon atoms in the chain was s ≤8, has been observed by Wettig and Verrall [18]. As proposed by Zana [10, 12], this dependence can be explained in terms of conformation changes taking place in short and quite rigid spacers, s ≤8.

The changes in $\Delta V_{\phi,\mathrm{M}}$ values can also indicate changes in the structure of micelles as well as changes in the packing and arrangement of micellar forms in the surfactant solution. As can be concluded from the data presented, in the solutions of 8-3-8 and 8-6-8 surfactants, the packing of both alkyl chains and micelles themselves is more effective than that in the case of compounds with longer chains, which results in a considerably greater change in the $\Delta V_{\phi,\mathrm{M}}$ of the solutions of these surfactants.

Table 3 Additivity and experimental volume data and isothermal volume changes due to micelle formation for the 8-s-8 gemini surfactants at 298.15 K

Surfactant	V^{o}_ϕ/cm^3 mol^{-1}	$V_{\phi,\mathrm{c.m.c.}}$/cm^3 mol^{-1}	$\Delta V_{\phi,\mathrm{M}}$/cm^3 mol^{-1}
8-3-8	444.6$^{\mathrm{a}}$	437.0$^{\mathrm{b}}$	11 ± 2$^{\mathrm{b}}$
8-6-8	492.0$^{\mathrm{a}}$	492.0$^{\mathrm{b}}$	11 ± 2$^{\mathrm{b}}$
8-7-8	507.8$^{\mathrm{a}}$	507.8$^{\mathrm{c}}$	5.2$^{\mathrm{c}}$ ± 0.1
8-8-8	523.6$^{\mathrm{a}}$	523.2$^{\mathrm{c}}$	4.4$^{\mathrm{c}}$ ± 0.1

[a] From additivity method

[b] From reference [13]

[c] Obtained from the pseudo-phase model

Apparent molar heat capacities

On the basis of experimentally determined specific heat capacity data, we have calculated the apparent molar heat capacities ($C_{p,\phi,2}$) of the examined surfactants in aqueous solutions, using the well-known formula (4):

$$C_{p,\varphi,2} = M_2 c_p + \frac{1000\left(c_p - c^*_{p,1}\right)}{m_2} \tag{4}$$

where M_2 (g mol^{-1}) is the amphiphile molecular mass; m (mol kg^{-1}) is the solution molality; c_p and $c^*_{p,1}$ (J g^{-1} K^{-1}) are the specific heat capacities of solution and pure water, respectively.

The dependences of $C_{p,\phi,2}$ on the concentration of solution (molality) for the compounds under investigation are shown in Figs. 5 and 6. As it can be seen from the figures each of the curves exhibits two maxima. At the temperature $T = 293.15$ K the first one corresponds to the concentration about 0.02 mol kg^{-1} for both surfactants and the second one about 0.087 mol kg^{-1} for 8-7-8 and near 0.075 mol kg^{-1} for 8-8-8. As in the case of apparent molar volumes, the curves become flatter with the increase in temperature what makes more difficult to determine the position of characteristic points. The position of the second maximum in curves $C_{p,\phi,2} = f(m)$ corresponds to position of the inflection point of $\alpha = f(m)$ as well as to concentration from which the value of V_ϕ starts to increase rapidly. Thus, it may be assumed that the maximum of $C_{p,\phi,2}$ reflects the structural changes connected with the formation of micelles in solution and its position corresponds to c.m.c. (Table 1). In this article, the determined c.m.c. values obtained by different methods are listed in Table 4. Table 4 also included values of c.m.c. for 8-3-8 and 8-6-8, which were found in the literature. These results suggest that the spacer group in 8-s-8 series strongly influences on c.m.c. and structural changes in the micellar aggregates formed.

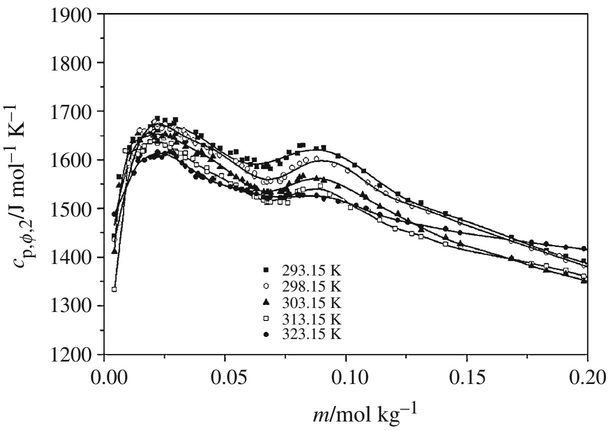

Fig. 5 Dependence of apparent molar heat capacity of 8-7-8 surfactant within the temperature range 293.15–323.15 K

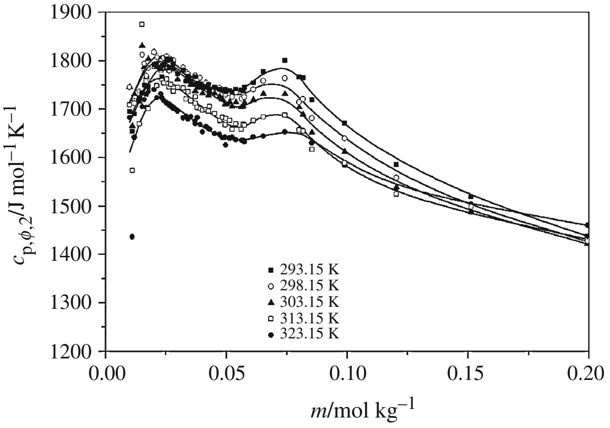

Fig. 6 Dependence of apparent molar heat capacity of 8-8-8 surfactant on molality within the temperature range 293.15–323.15 K

There is a lack of experimental data in the literature allowing one to verify the determined values of c.m.c. of 8-7-8 and 8-8-8. Though Zana et al. [4] give the c.m.c. value for 8-8-8 amounting to 0.050 M but it has been determined by extrapolation of the c.m.c. value for 8-3-8 and 8-6-8 surfactants and therefore it seems to be insufficiently reliable.

The presence of $C_{p,\phi,2}$ maximum in the range of lower concentration is not clear. Within the concentration range where that maximum appears, one cannot observe any significant changes in other functions (α_T V_ϕ) examined here. However, it is worth mentioning that Frindi and Michels [13], examining the electric conductance of aqueous 8-3-8 and 8-6-8 solutions, observed two inflection points in the curve of the dependence of solution conductivity on concentration. One of them, corresponding to higher solution concentrations, is ascribed by the authors to the critical concentration of micellisation, whilst the second one, corresponding to lower concentrations (about 0.02 M), is ascribed to the formation of ionic pairs or small molecular aggregates. According to our knowledge, no $C_{p,\phi,2}$ maximum caused by the formation of ionic pairs has been observed yet. Therefore, we are inclined to ascribe the

Table 4 The c.m.c. at 298.5 K for the 8-s-8 surfactants

Surfactant	c.m.c./mol kg^{-1}
8-3-8	0.056[a]
8-6-8	0.073[a]
8-7-8	0.088[b], 0.090[c]
8-8-8	0.074[b], 0.073[c]

[a] From reference [13, 14]

[b] Obtained from the calorimetric method

[c] Obtained from the densimetric method

maximum observed within the concentration range of about 0.02 M to the formation of small aggregates in solution.

Conclusions

It has been shown that the inflection point in the curves of the dependence of volume expansion coefficient on molality corresponds to the position of c.m.c., and so it can be used to determine the value of c.m.c.

The concentration dependence of the apparent molar volume of the gemini surfactant solutions investigated has been successfully described by means of the pseudo-phase model. The changes observed in $\Delta V_{\phi,\mathrm{M}}$ suggest that the change in spacer length influences not only the effectiveness of micelle formation but probably also their shape, packing and size. In the case of compounds with longer spacers, one can expect the formation of greater micelles, but with a lesser extent of packing.

The concentration functions of apparent molar heat capacity exhibit two extremes. The solution concentration, at which the second maximum is observed, can be interpreted as critical concentrations of micellisation. The values of c.m.c. determined in this way are consistent with those of the concentrations, at which the apparent molar volume started to grow rapidly (Figs. 3, 4), and which have been earlier interpreted in the literature as c.m.c. points. The appearance of the first maximum in $C_{\mathrm{p},\phi,2}$ curves has been assumed as a change connected with the formation of other structures—small aggregates [4, 14].

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