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THE EFFECT OF ALKYLTRIMETHYLAMMONIUM BROMIDES ON THE THERMAL STABILITY OF DIOCTADECYLDIMETHYLAMMONIUM BROMIDE (DOAB) VESICLES IN AQUEOUS SOLUTIONS

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Abstract

The influence of alkyl chain length in alkyltrimethylammonium bromides on the gel to liquid crystal transitions in DOAB versicles is examined using differential scanning microcalorimetric data. The changes in melting temperature, patch number and standard enthalpy of melting for DOAB vesicles depend strongly on added surfactants and their concentration. The data show that vesicles are readily penetrated by surfactant molecules when the vesicles are in the liquid crystal state and the penetration is facile when the length of alkyl chains in both surfactants and vesicles are comparable. Furthermore, the vesicles are made up of domains that differ in composition.

Keywords: dioctadecyldimethylammonium bromide vesicles, dodecyltrimethylammonium bromide, octadecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide

Introduction

In aqueous solutions the amphiphile dioctadecyldimethylammonium bromide (DOAB) forms vesicles [1–3] which have a close relationship with biologically important structures formed by phospholipids. At low temperatures the di-alkyl chains pack in an ordered fashion but with increase in temperature the vesicles undergo a gel to liquid crystal transition at melting temperature T_m characteristic of the system. The dependence on temperature of the differential heat capacity δC_p shows a maximum at T_m which can be analysed to yield the size of the co-operative unit characterised by patch number, n, and the standard enthalpy of melting per mole of monomer $\Delta_m H^\circ$. For DOAB in aqueous solutions at concentration 0.002 (monomer mol) dm^{-3} the recorded scans identify two extrema at about 35.9 and 44.8°C attributed to intervesicular and intravesicular processes [3, 4], respectively. For the intravesicular gel to liquid crystal transition the patch number equals 131 and $\Delta_m H^\circ = 8.9$ kcal/(monomer mol). When a surfactant i.e. hexadecyltrimethylammonium bromide (CTAB) is added to DOAB vesicles in aqueous solutions T_m and other parameters characteristic of DOAB vesicles change [5]. T_m shifts to lower temperatures with in-

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crease in CTAB concentration indicating a decrease in the thermal stability of the gel state. Moreover, the first recorded DSC scans differ from all subsequent scans suggesting that CTAB monomers readily penetrate DOAB vesicles in the liquid crystal state. The similarity of the polar head group in CTAB, $-NMe_3^+ Br^-$ to that in DOAB namely $>NMe_2^+Br^-$ allows incorporation of the alkyl chains of CTAB into the bilayer structures of DOAB vesicles. The effects on the scans recorded by differential scanning microcalorimeter are reported when three other surfactants i.e. dodecyltrimethylammonium bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB) and octadecyltrimethylammonium bromide (OTAB) are added to DOAB vesicles. These surfactants have the same polar head group as CTAB but different alkyl chain lengths. Changes in alkyl chain length in compounds forming vesicles in aqueous solutions significantly change the properties of vesicles, mainly T_m [6]. We report that the length of alkyl chain in surfactant molecules introduced to vesicles also play important role in modification of parameters characteristic for the gel to liquid crystal transitions.

All chosen surfactants form micelles in aqueous solutions so they are present in the solutions as monomers below the critical micellar concentration (*cmc*) and as micelle when concentration exceeds *cmc*. The cmc equals 0.0154 (monomer mol) dm^{-3} for DTAB [7], 0.00379 (monomer mol) dm^{-3} for TTAB [7] and 0.001 (monomer mol) dm^{-3} for CTAB [7, 8] at 25°C. The *cmc* for OTAB is estimated to be significantly lower than *cmc* of CTAB.

Experimental

DTAB (Sigma), TTAB (Sigma) and OTAB (Sigma) all with purity 99% and DOAB (Fluka) were dried under vacuum at 50°C for at least two days. The measurements were made at DOAB concentration equal to 0.002 (monomer mol) dm^{-3} and for five different concentrations of added surfactants: 0.0005, 0.001, 0.0015, 0.002 and 0.0025 (monomer mol) dm^{-3}. The DOAB aqueous solutions were prepared using the protocol previously described [4]. The required amounts of DOAB and water were heated with stirring and held at about 50°C for 10 min. The solution was allowed to cool and stand at room temperature for one hour. The required amount of chosen surfactant was added at room temperature and shaken until all the added compound had dissolved. The solution was placed in the sample cell of the calorimeter held at 15°C. The differential scan was recorded from 15–90°C. The solution was cooled to 15°C and then rescanned from 15 to 90°C. This procedure was repeated three more times and then two more times for DTAB and TTAB and once for OTAB but the solution was held at 15°C for a further 3 h before rescanning.

The differential isobaric heat capacities were recorded using a differential scanning microcalorimeter MC2 (Microcal Ltd., USA). The scan rate was 60 deg·h^{-1} from low to high temperatures. The volumes of the sample and ref-

erence cells were approximately 1.2 cm^3. The reference, in all cases, was water. The data were stored on floppy disc and analysed using the ORIGIN software (MicroCal Ltd.). In all cases a water–water reference scan was recorded and subtracted from the recorded scans [9] to obtain the dependence on temperature of the differential heat capacity δC_p. In event that an extremum is observed in the dependence of δC_p on temperature the simplest model attributes the 'bell-shaped' plot to a two state chemical equilibrium where the substance X undergoes to substance Y [10]. The dependence on temperature of the molar relaxational heat capacity [3–5, 10] is given by Eq. (1):

$$C_{pm} = \Delta_m H^\circ(\text{cal})\ \Delta_m H^\circ(vH)\ K/RT^2\ (1 + K)^2 \qquad (1)$$

where K is the temperature dependent equilibrium constant and the area under the 'bell' is a direct measure of the standard enthalpy of melting $\Delta_m H^\circ$(cal). The maximum in C_{pm} at T_m where $K=1$ yields an estimate of the van't Hoff standard enthalpy of melting $\Delta_m H^\circ(vH)$. In the case considered here symbols X and Y refer to two states of vesicles i.e. gel state and liquid crystal state, respectively. Although the monomer concentration is known, the number of monomers which form domains involved in the transitions – the patch number, n, is unknown. Hence in fitting the dependence of δC_p on temperature to Eq. (1) three parameters are used in the least square analysis i.e. patch number n, $\Delta_m H^\circ(vH)$ and T_m. Agreement between calculated and recorded scans yields estimates of the enthalpy change $\Delta_m H^\circ(\text{cal}) = \Delta_m H^\circ(vH)$, patch number n and melting temperature T_m. The ratio of the standard enthalpy of melting to the patch number yields to standard enthalpy of melting per (monomer mol).

Results and discussion

DSC scans for all investigated surfactants at a concentration 0.0015 (monomer mol) dm^{-3} in DOAB solutions are shown in Fig. 1. The patterns observed for different concentrations of given surfactant are similar and characteristic of the system. The scans obtained for the systems containing DTAB and TTAB are similar. The latter scans differ from those for systems containing CTAB and OTAB. In all cases the first recorded scan (Fig. 1) and often the second scan (Fig. 1a,b,d) differ from subsequent ones, indicating that surfactants readily penetrate DOAB vesicles when the latter are in the liquid crystal state. For systems containing DTAB and TTAB the scans recorded immediately after cool-heat-cool-heat... cycles (scans 3–5 in Fig. 1a and b) differ from the scans recorded when the solution was held at 15°C for 3 h. For CTAB and OTAB all subsequent scans are the same and independent of the time when the samples were held in the calorimeter cell before rescanning. Hence penetration of

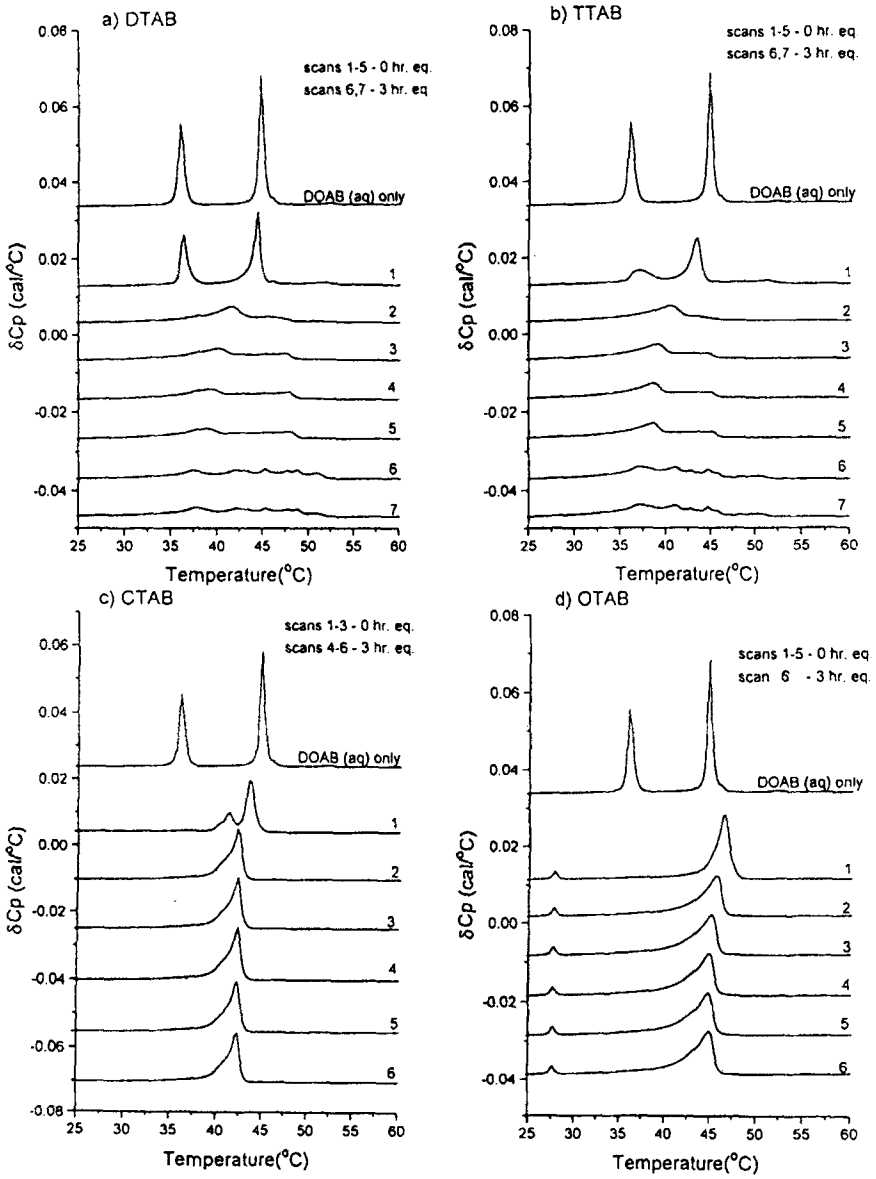

Fig. 1 Dependencies on temperature of the differential heat capacities δC_p for DOAB vesicle aqueous solutions [0.002 (monomer mol) dm^{-3}] containing surfactants [0.0015 mol·dm^{-3}]; a) DTAB, b) TTAB, c) CTAB from Ref. [4], d) OTAB. Scans are recorded after the preparation of the solution and cooling it to 15°C–scan 1; following heating to 90°C and cooling to 15°C–scans 2–5 for DTAB, TTAB and OTAB and 2 and 3 for CTAB; following standing for 3 h at 15°C in the cell before rescanning-scans 6, 7 for DTAB and TTAB, 4–6 for CTAB and 6 for OTAB. For clarity the scans have been displaced on the heat capacity axis

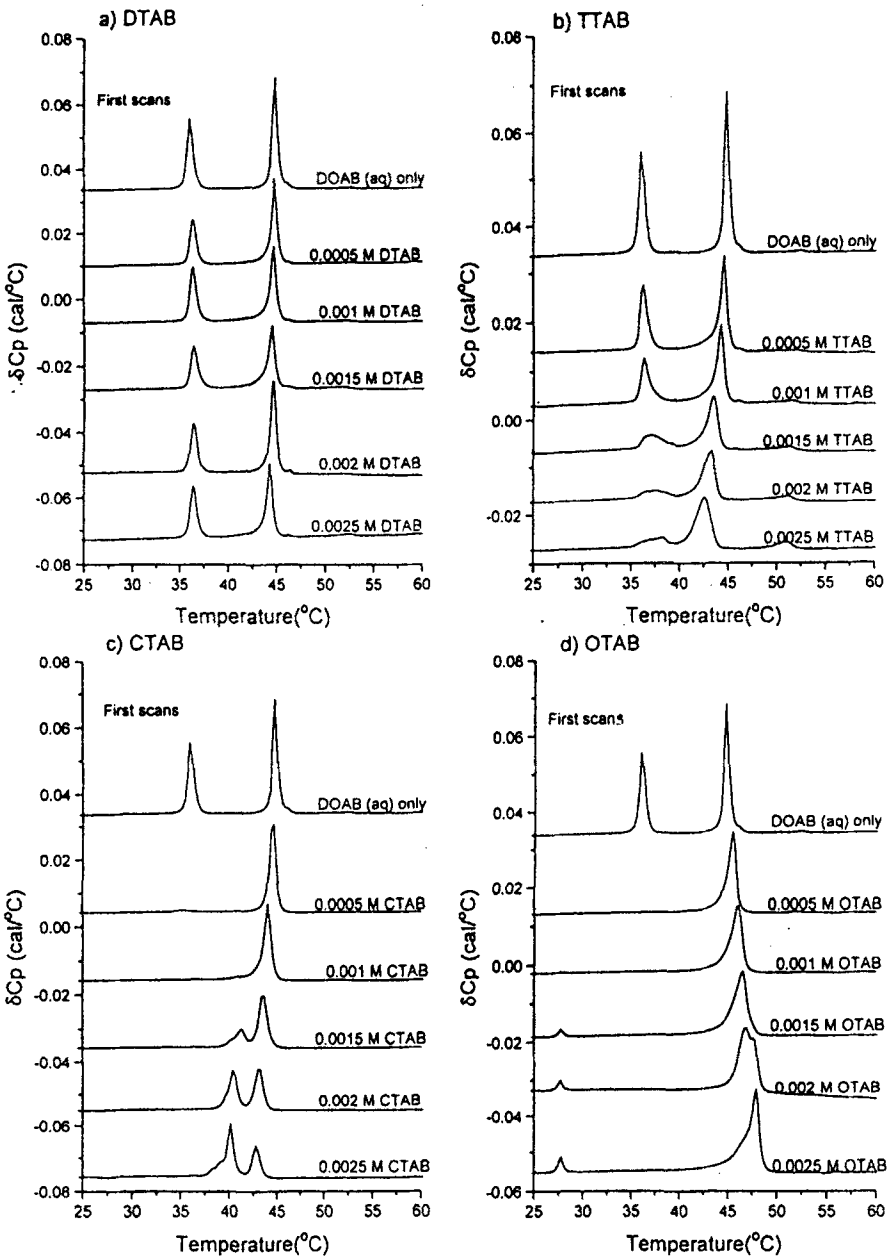

Fig. 2 Dependencies on temperature of differential heat capacities δC_p for DOAB aqueous solutions [0.002 (monomer mol) dm^{-3}] in presence of various concentrations of added surfactants: a) DTAB, b) TTAB, c) CTAB from Ref. [4], d) OTAB. Scans are recorded following the preparation of the solution at room temperature and cooling them to 15°C in the calorimeter cell. For clarity the scans have been displaced on the heat capacity axis

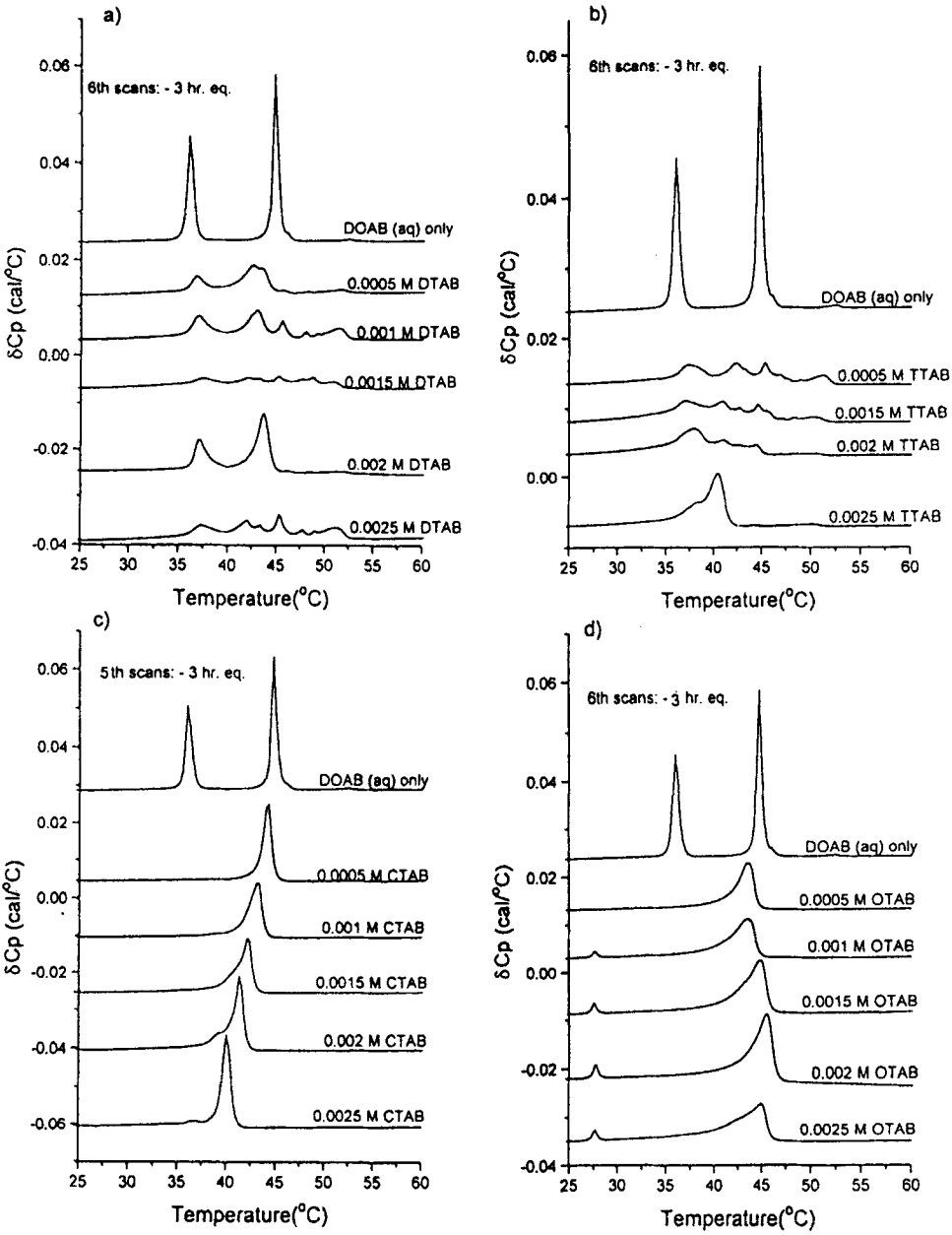

Fig. 3 Dependencies on temperature of differential heat capacities δC_p for DOAB aqueous solutions [0.002 (monomer mol) dm^{-3}] in presence of various concentrations of surfactants: a) DTAB, b) TTAB, c) CTAB from Ref. [4], d) OTAB. Scans are recorded following heating to 90°C and cooling to and storing at 15°C in the cell for 3 h before rescanning. For clarity the scans have been displaced on the heat capacity axis

DOAB vesicles by DTAB and TTAB monomers requires more time to reach equilibrium. We attribute this phenomenon is probably steric effect connected with the large differences in the length of alkyl chains in DTAB, TTAB and DOAB. The solutions containing vesicles and either OTAB or CTAB rapidly reach equilibrium when the solutions are heated above the melting temperature. The temperatures of the phase transition for all subsequent scans are constant for given concentration of added surfactant.

The two maxima in δC_p, observed for aqueous solutions of DOAB vesicles [4] at 35.9 and 44.8°C, are almost unaffected in the first scan when DTAB monomers are added to vesicle solutions (Figs 1a and 2a) independently of the latter concentration. The δC_p maximum at 44.8°C for pure DOAB vesicle solution corresponds to the gel to liquid crystal transition and is analysed in terms of one step independent reversible transition. Hence all patches inside the vesicles have identical composition. When DTAB was added, the δC_p maximum does not have a symmetrical 'bell-shape' and satisfactory agreement between experimental and calculated curves was obtained using equations describing three independent transitions. In other words the vesicles consist of three slightly different types of domains in which melting take place at three very slightly different T_m's. Adding TTAB to DOAB vesicles causes considerable changes to the recorded first scans (Figs 1b and 2b). The intensity of low temperature transition decrease rapidly and the temperature of transition shifts towards higher temperatures with increase in surfactant concentration i.e. from 36.2 to 38°C. The decrease of intensity of the low temperature transition corresponding to intervesicular interaction is caused by TTAB monomers in the solution which insulate vesicles and prevent their aggregation. Some of TTAB monomers enter the vesicles when the latter are in the gel state and the high temperature transition shifts slightly to lower temperatures i.e. from 44.6 to 42.4°C for the solution at concentration 0.0005 and 0.0025 (monomer mol) dm^{-3}, respectively. These δC_p dependencies can be analysed in terms of two or three reversible independent transitions for the solution containing 0.0005–0.0015 and 0.002–0.0025 (monomer mol) dm^{-3}, respectively, indicating that TTAB monomers penetrate DOAB vesicles to create patches which differ in the ratio of DOAB to TTAB.

The low temperature transitions at about 36°C are not observed on the first scans recorded for the systems containing CTAB and OTAB (Figs 1c, d and 2c,d) at all concentrations of the solutions. The CTAB and OTAB micelles in the solution insulate DOAB vesicles preventing their aggregation. For the system containing OTAB a very weak transition at 27.7°C appears for the solution with concentrations higher than 0.001 (monomer mol) dm^{-3}. The intensity of this transition increases very slightly with increase in OTAB concentration and is attributed to the presence of OTAB micelles in the solutions. The shift in T_m

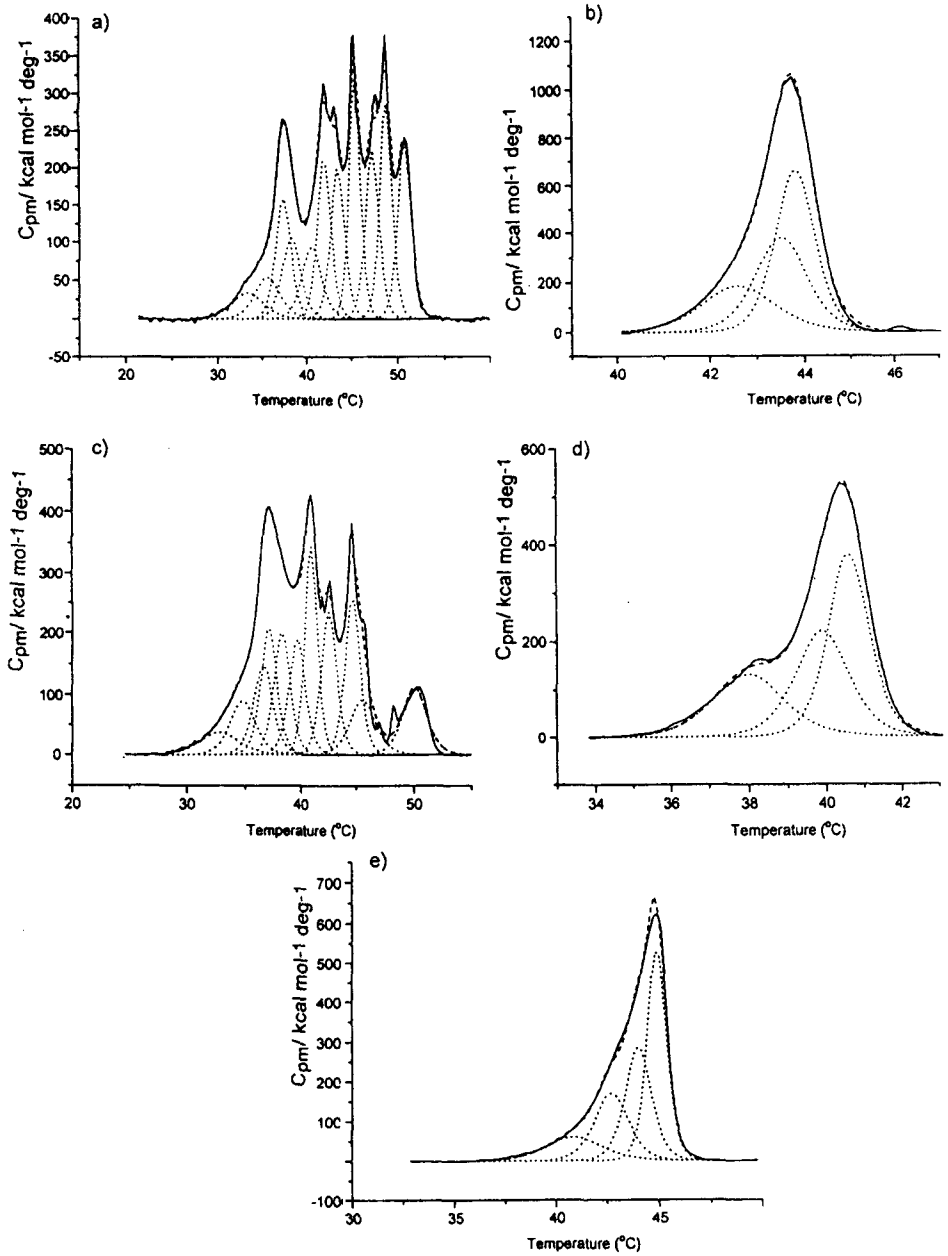

Fig. 4 Dependencies on temperature of molar heat capacities C_p for DOAB aqueous solutions [0.002 (monomer mol) dm^{-3}] in presence of added surfactants: a) DTAB [0.0015 mol·dm^{-3}]; b) DTAB [0.002 mol·dm^{-3}]; c) TTAB [0.0015 mol·dm^{-3}]; d) TTAB [0.0025 mol·dm^{-3}]; e) for OTAB [0.0015 mol·dm^{-3}]; recorded dependence (—) and calculated dependence (---)

from 44.8°C corresponding to melting for pure DOAB solution, observed in presence of CTAB and OTAB shows that some penetration of the DOAB vesicles occurs in the gel state but it is incomplete. Penetration becomes complete after heating the systems above the temperature of transition. The patterns observed for rescans of these systems are similar (Fig. 1c and 1d). All scans recorded after heating the systems above the melting temperature are the same and repeatable. Second scans are a little different for systems containing OTAB. A detailed discussion of the influence of CTAB on DOAB vesicles melting processes is given in Ref. 5. For solutions containing CTAB the phase transition shifts towards lower temperatures with increase of CTAB concentration (Fig. 2c). Two extrema are recorded for the solutions with concentrations ≥0.0015. For systems containing OTAB (Fig. 2d) the transition shifts to higher temperatures i.e. from 45.5 to 47.8°C for the solution at OTAB concentration 0.0005 and 0.0025, respectively. This pattern reflects an increase in the stability of the gel state of vesicles containing OTAB molecules. The plots are significantly broader on the low temperature side and can be satisfactorily fitted to two contributing 'bell-shaped' dependencies for the lower concentration of OTAB and to three dependencies for the other cases.

Figure 3 shows the scans recorded after leaving the solution at 15°C in the calorimeter cell for three hours before rescanning. The patterns emerging from the scans are much more complicated when the number of $>CH_2$ groups in the length of alkyl chains in DOAB and added surfactant differs by more than two. The most complicated scans, showing several extrema, were recorded when either DTAB and TTAB were added to aqueous solutions of DOAB vesicles. Many transitions occur over a wide range of temperatures for almost all these solutions. When DTAB is added to DOAB the intensity of transition at 35.9°C is lower than observed for pure DOAB solutions indicating a weaker intervesicular interaction. Analysis shows that the maxima corresponding to intervesicular and intravesicular interaction overlap and they are impossible to separate. Table 1 summarises the number of independent phase transitions, the range of temperature, average enthalpies of melting and patch numbers. The changes of T_m, patch number and $\Delta_m H^\circ$ corresponding to the gel to liquid crystal transition of DOAB vesicles depend strongly on added surfactant and concentration. When DOAB vesicles are penetrated by DTAB molecules the number of independent transitions and patch number increase with increase in DTAB concentration up to 0.0015 (monomer mol) dm^{-3} indicating that different kinds of domains exist inside the vesicles which melt co-operatively at slightly different temperatures and have different sizes. Analysis of the experimental data obtained for DTAB solution at concentration 0.0015 (monomer mol) dm^{-3} shows this complexity (Fig. 4a). The complexities in the scans we attribute to the problem of packing chains of different lengths in the vesicles. For the equimolar

solution of DOAB and DTAB the transitions corresponding to intervesicular and intravesicular process are distinctly separated. Good agreement between experimental and calculated data for the gel to liquid crystal transition is obtained using three independent transitions (Fig. 4b). Hence the distribution of DTAB molecules inside vesicles is the most homogeneous. Moreover, the patch size is the smallest for this solution but much higher than observed for pure DOAB. With further increase in DTAB concentration there is a rapid increase in the types of patches.

A similar complicated patterns emerge when TTAB is added into DOAB vesicles (Fig. 3b and Table 1). A small amount of TTAB (0.0005 *M*) increases the number of independent transition to 10 and then to 11 when the TTAB concentration increase to 0.0015 (monomer mol) dm^{-3}. The range of temperature of transitions is very wide (see an example in Fig. 4c) and probably the δC_p plots corresponding to intervesicular and intravesicular interactions overlap. Hence the distribution of TTAB in DOAB vesicles is irregular and the patches differ in size and in the ratios of TTAB and DOAB molecules. Average patch numbers are much higher than for pure DOAB solution and increase slightly with TTAB concentration. The most homogeneous packing of TTAB molecules inside vesicles is observed at concentration 0.0025 (monomer mol) dm^{-3}. The best fit of experimental data is obtained using three independent transitions (Fig. 4d) with melting temperatures equal 38.1, 40.0 and 40.6°C, respectively. The patch number of the vesicles decreases rapidly to 186 but it is still higher than for pure DOAB vesicles. The standard enthalpies of melting are higher than for pure DOAB solution and decrease with increase of TTAB concentration.

At first sight the scans produced when CTAB and OTAB are added to DOAB vesicles are much simpler. Only one maximum is found but the plot is distinctly asymmetric (Fig. 3c and d). With increase of CTAB concentration the position of the main T_m shifts to lower temperatures (from 44.8 to 40.1°C observed for 0.0005 and 0.0025 (monomer mol) dm^{-3}, respectively [5]) consistent with a decrease in thermal stability of the gel state. The data were fitted using 1, 2 or 3 independent transitions depending on CTAB concentration. Adding small amount of OTAB to DOAB vesicles shifts the main transition (Table 1) to lower temperatures but with increase of OTAB concentration T_m moves to the temperature slightly higher than observed for pure DOAB. For the equimolar solution of DOAB and OTAB T_m is the highest i.e. 45.7°C, consistent with an increase of the thermal stability of vesicles. Agreement between the experimental and calculated curves is obtained using 3, 4 and 5 independent transitions depending on OTAB concentration (Table 1 and Fig. 4e). In other words, there are 3, 4 or 5 different kind of patches inside vesicles with different distribution of OTAB molecules, undergoing the gel to liquid crystal transitions at slightly different T_m's. The temperature range for the transitions become wider with in-

crease in OTAB concentration. The patch numbers decrease from 191 observed for the lowest OTAB concentration to 137 for the solution with OTAB concentration equals 0.002 *M* and higher. So, the size of the patches for the latter solutions are comparable with that found for pure DOAB solutions. The standard enthalpies of melting per (monomer mol) increase with the OTAB concentration. Taking into account the main temperatures of transitions, the average enthalpy of melting and the size of patches of the DOAB vesicles containing OTAB for the latter concentration higher than 0.001 *M* we conclude that incorporation of OTAB molecules inside of DOAB vesicles is facile and increases their thermal stability.

In conclusion the length of alkyl chains in surfactants plays an important role in the packing inside DOAB vesicles. Penetration of vesicles by surfactant molecules, produced by strong surfactant-vesicles interaction, is facile when the

Table 1 Characteristic parameters of melting processes taking place in DOAB vesicles [0.002 (monomer mol) dm^{-3}] containing DTAB, TTAB or OTAB at concentration *c* [(monomer mol) dm^{-3}]; number of independent transition (No X ↔ Y); range of melting temperatures (T_m's) in °C; the average standard enthalpies of melting $\Delta_m H^\circ$ [kcal/(monomer mol)]; average patch numbers (*n*) and for the system containing OTAB for which the only one maximum is observed – main T_m

c	No X ↔ Y	Range of T_m's	$\Delta_m H^\circ$	*n*	Main T_m
		DTAB			
0.0005	4	36.8–43.6	7.4	277±15	
0.001	9	36.8–51.4	11.4	370±18	
0.0015	11	33.7–50.8	9.1	461±74	
0.002	3[a]	37.0–40.2		444±0	37.0
	3[b]	42.6–43.9	11.5[c]	229±9	43.5
0.0025	10	35.3–51.3	13.7	328±16	
		TTAB			
0.0005	10	34.4–51.0	9.4	389±16	
0.0015	11	32.8–50.1	9.5	409±12	
0.002	10	33.0–44.3	8.1	580±12	
0.0025	3	38.1–40.6	6.7	186±1	
		OTAB			
0.0005	3	41.8–44.0	7.8	191±6	43.8
0.001	4	40.1–44.1	8.9	193±5	43.8
0.0015	4	41.2–45.1	11.4	154±5	45.0
0.002	4	42.7–45.8	13.1	137±3	45.7
0.0025	5	37.2–45.1	12.4	139±4	45.1

[a]First maximum; [b]second maximum corresponding to the gel to liquid crystal transition; [c]the overall enthalpy of melting for both extrema

length of alkyl chains of molecules forming vesicle and surfactant molecules introduced to vesicles are comparable. Increase in the difference between length of alkyl chains more than two methylene groups produces an increase in complexity of recorded scans and their change with time, points to the importance of satisfactory packing of the alkyl chains in controlling the phase transition pro-cesses. Similar patterns were reported for vesicles prepared using equimolar mixtures of two symmetric di-*n*-alkylphosphates where the alkyl groups differ in chain length [11].

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Zusammenfassung — Mittels DS-Mikrokalorimetrieangaben wurde der Einfluß der Alkylkettenlänge in Alkyltrimethylammoniumbromiden auf den Gel/Flüssigkeitskristall-Übergang in DOAB-Bläschen untersucht. Die Änderung der Schmelztemperatur und der Standard-Schmelzenthalpie hängt bei DOAB-Bläschen stark von den oberflächenaktiven Substanzen und deren Konzentration ab. Die Angaben zeigen, daß die Bläschen von den Molekülen der oberflächenaktiven Substanzen leicht durchdrungen werden, wenn sich die Bläschen im Flüssigkeitskristallzustand befinden und daß das Durchdringen leicht ist, wenn die Länge der Alkylketten sowohl in den oberflächenaktiven Substanzen als auch in den Bläschen vergleichbar ist. Weiterhin setzen sich die Bläschen aus Bereichen verschiedener Zusammensetzung zusammen.