Thermochimica Acta, 134 (1988) 49–54
Elsevier Science Publishers B.V., Amsterdam

THERMAL BEHAVIOR OF SOME LONG-CHAIN DI-n-DODECYL QUATERNARY AMMONIUM SALTS

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ABSTRACT

In the present work the thermal behavior of some liquid crystalline quaternaries of the formula $(C_{12}H_{25})_2N^+CH_3RBr^-$, where R is $-CH_3$, $-CH_2CH=CH_2$, $-CH_2COOH$, $-CH_2CH_2COOH$, is reported. Their thermal behavior was investigated by DSC studies immediately after the first heating-cooling run and after various periods of time. From this data the peculiar characteristics of each compound are indicated and also a general conclusion can be obtained: the recrystallization rate of these quaternaries depends crucially on the nature of the R-group. Specifically, quaternaries in which R is $-CH_2COOH$, $-CH_2CH_2COOH$, recrystallize very fast, due probably to their ability to form hydrogen bonds, while such a behavior cannot be justified for the derivatives where R is $-CH_3$, $-CH_2CH=CH_2$.

INTRODUCTION

It is known that surfactants (or amphiphilic compounds) such as long chain carboxylates, n-alkylammonium halides, or quaternaries, in addition to their well known property to aggregate in water and to form micelles, bilayers, vesicles, or lyotropic liquid crystals [1-8], can also exhibit thermotropic liquid crystalline character [1,7-11].

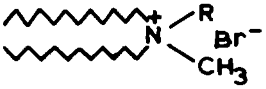
The mesomorphic structure or rather the mesomorphic-like character of these surfactants has been systematically studied only recently. Their mesomorphic-like character was established by optical microscopy, thermal analysis (DTA, DSC) and x-ray diffraction [4-5, 7-18]. The last technique, i.e. x-ray diffraction has shown that they consist of alternating bidimensional polar and non-polar layers [4,9].

The observed low temperature transitions of thermotropic liquid crystalline compounds are attributed to conformational melting of the long alkyl chains, while the polar layers retain their rigid structure (as in the solid phase). High temperature transitions correspond to mesomorphic-like isotropic phase transformations [11,14,17]. In this connection it has to be mentioned that the

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

thermal behavior of the surfactants may be affected by their thermal history. Thus, samples originating from the same batch behave differently if their thermal history is different [13,14,18].

The purpose of this study was to investigate by DSC the thermal behavior of certain quaternaries shown in the scheme, taking into consideration the thermal history of the samples.



Compound I R=-CH_3

" II R=-$CH_2CH{=}CH_2$

Compound III R=-CH_2COOH

" IV R=-CH_2CH_2COOH

Scheme

EXPERIMENTAL

Di-n-dodecyl quaternary ammonium salts were prepared by the interaction of di-n-dodecylmethyl amine with the appropriate bromide, i.e. $BrCH_2CH{=}CH_2$, $BrCH_2COOH$, $BrCH_2CH_2COOH$ in ethyl acetate at room temperature. The precipitated salts were recrystallized from ethyl acetate and dried in vacuum over phosphorus pentoxide. Elemental analysis results agreed with the calculated values. Thermotropic character of these compounds was established by DSC and the mesomorphic-like behavior by optical microscopy [8].

Differential scanning calorimetric measurements were carried out with a Du Pont 910 DSC system equipped with a R90 Programmer (Thermal analyzer). The heating rate was 10 ^{o}C/min. Four heating runs were performed for each compound. As standard for the calculation of the cell calibration coefficient was used a sample of indium.

RESULTS AND DISCUSSION

The quaternaries of this study may be characterized as functionalized derivatives of didodecyldimethyl ammonium bromide which was the first, totally synthetic molecule that formed vesicles in solution [6] and exhibited mesomorphic-like properties in the bulk [8].

The four heating DSC curves of the quaternaries investigated in this study are shown in Fig. 1. The second heating run for each compound was performed immediately after the first heating-cooling run, while the third heating run

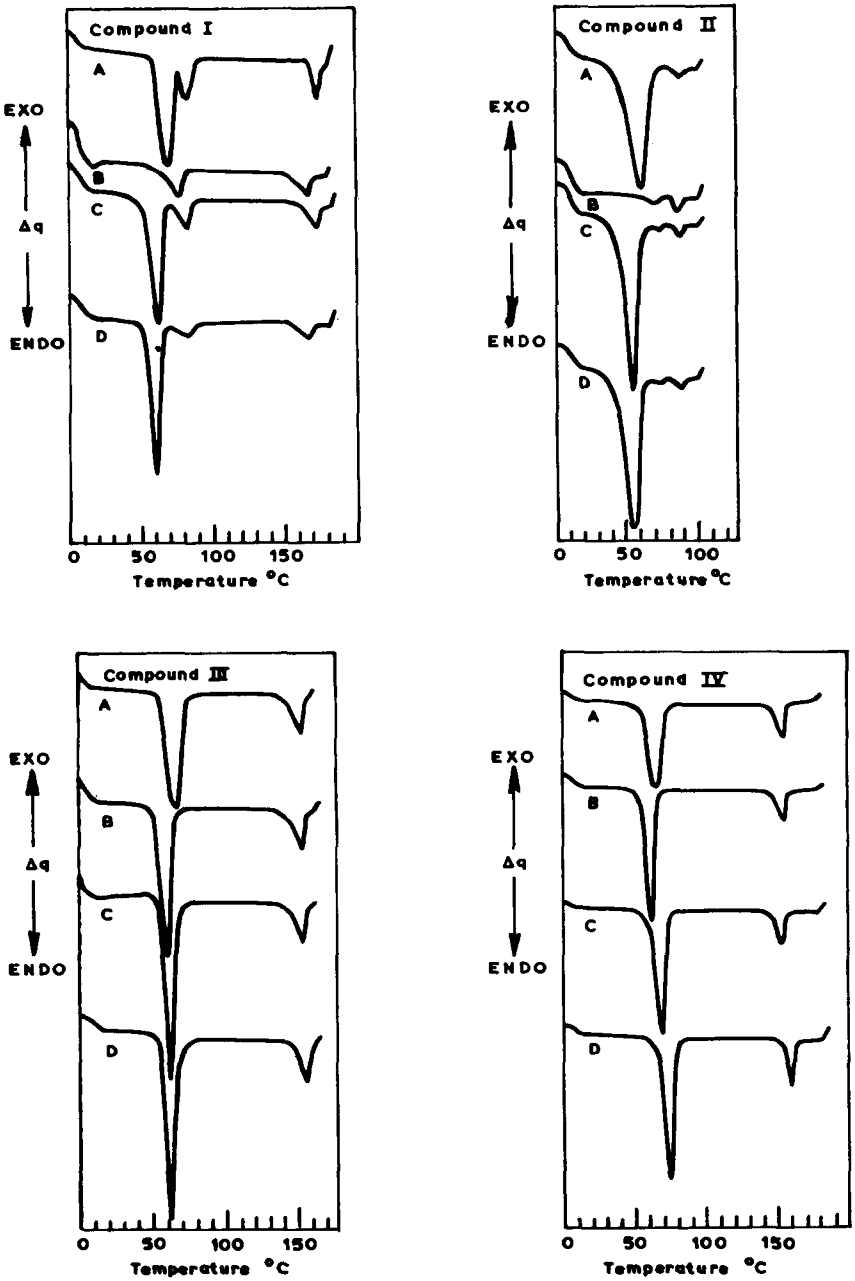


Fig. 1. DCS heating curves of compounds I-IV.

A: first heating run, B: second heating run immediately after the first heating-cooling run, C: third heating run after three months at room temperature, D: fourth heating run after eleven months following the third.

TABLE I

Transition temperatures, enthalpies and entropies obtained by DSC of $(C_{12}H_{25})_2\ N^+CH_3RBr^-$* from the compounds I to IV.

	First heating run			Second heating run			Third heating run			Fourth heating run		
Compound	T_{tr} K	ΔH kJ/mol	ΔS J/Kmol	T_{tr} K	ΔH kJ/mol	ΔS J/Kmol	T_{tr} K	ΔH kJ/mol	ΔS J/Kmol	T_{tr} K	ΔH kJ/mol	ΔS J/Kmol
I	334	40.1	120.0				326	32.9	100.9	324	34.9	107.7
	350	10.1	28.8	340	10.3	30.3	344	8.0	23.2	337	6.0	17.9
	439	5.1	11.6	427	4.8	11.2	435	5.2	11.9	425	4.7	11.1
II	318	44.2	138.8				317	44.2	139.2	316	43.9	138.9
				332	1.9	5.7	334	1.0	3.1	335	1.2	3.6
	355	1.4	4.0	356	1.4	3.9	355	1.4	3.9	355	1.4	3.9
III	333	47.8	143.4	328	41.8	127.5	331	42.8	129.2	330	47.4	143.5
	419	10.9	25.9	420	10.8	25.7	420	11.2	26.7	421	12.1	28.8
IV	333	53.5	160.7	331	50.1	151.4	335	56.4	168.3	338	67.7	200.9
	421	13.9	33.0	420	13.9	33.1	422	14.3	33.8	428	15.2	35.5

*I (R=-CH_3), II (R=-$CH_2CH{=}CH_2$), III (R=-CH_2COOH), IV (R=-CH_2CH_2COOH).

was done after three months. Finally, the fourth heating run was performed eleven months after the third one. Their thermodynamic parameters are listed in Table I.

As already discussed the first transition was attributed to the conformational melting of the long aliphatic chains and the last transition to mesomorphic-like isotropic transformation of the quaternaries. Due to functionalization of the polar head the quaternaries exhibit significant differentiation as far as their thermodynamic parameters are concerned. Specifically the introduction of the functional groups of the surfactants modifies the ionic bonding between the polar head and counter-ion which consequently affects the van der Waals forces of the molecules.

In the first heating curves, Fig. 1, all samples show the characteristic melting and clearing transitions. Compound I which had been used for the formation, of the first totally synthetic bilayer membrane [6] shows a post-melting transition. For compounds III ($R=-CH_2COOH$) and IV ($R=-CH_2CH_2COOH$) it has been determined that the heat content during the clearing transition is higher compared to compounds I ($R=-CH_3$) and II ($R=-CH_2CH=CH_2$). So, it is concluded that the compounds with the carboxyl functional groups retain a higher degree of order than the other investigated groups.

In the second, third and fourth heating curves, Fig. 1, compound II ($R=-CH_2CH=CH_2$) exhibited an additional pre-clearing transition. Probably, after the first heating, the allyl group affects the electrostatic forces of the head in such a way that a two-step clearing transitions are observed.

In the second heating curves as shown, Fig. 1, and according to the data of Table I, compounds I ($R=-CH_3$) and II ($R=-CH_2CH=CH_2$) are completely differentiated from their first heating runs. The mesomorphic-like textures appear in the third heating curves after the samples were kept at room temperature for very long periods of time. On the contrary, compounds III ($R=-CH_2COOH$) and IV ($R=-CH_2CH_2COOH$) show almost the same behavior as exhibited during the first heating. Thus, these quaternaries recrystallize very fast to their original crystalline structures. The carboxyl groups, able to form hydrogen bonds probably contribute to this facile recrystallization of these compounds. Apparently, such a behavior cannot be justified for the derivatives where R is $-CH_3$ and $-CH_2CH=CH_2$.

In the third and fourth heating curves (Table I), a tendency is observed for a continuous increase in temperature and heat content, particularly for compound IV ($R=-CH_2CH_2COOH$), in both melting and clearing transitions. This is probably attributed to a morphological variation, due to a puckering of the layer structures with a slight increase in interlayer spacing.

Acknowledgements

I wish to thank Dr. C.M. Paleos of the N.R.C. "Demokritos" for providing the samples and for valuable discussion and helpful remarks.

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