

Thermal characteristics of solid–solid phase transitions in long-chain dialkyl ammonium salts

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Received 22 November 2004; received in revised form 21 April 2005; accepted 22 April 2005

Available online 3 June 2005

Abstract

A series of symmetrical dialkyl ammonium salts, DC_nX, has been prepared and characterized with respect to temperature and enthalpy of solid–solid phase transitions, temperature of melting, thermal stability as well as the reversibility of the phase transitions. The number of carbon atoms, C_n, was varied between 8 and 18 and as anions X halides, nitrate, chlorate, perchlorate and hydrogen sulphate had been chosen. In dependence on chain length and anion type transition temperatures from 20 to 100 °C were observed. Mass specific solid–solid transition enthalpies reach values of 185 J g⁻¹, which makes this class of substances attractive for heat storage applications. The influence of anion type on the transition enthalpies is explained in terms of packing requirements, hydrogen bond network formation and contributions from hindered anion rotation.

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Keywords: Dialkyl ammonium salts; Solid–solid phase transition; Heat storage materials; Rotator phases

1. Introduction

The enthalpy change accompanied with phase transitions can be used to store heat. Normally the heat of melting is considered for such applications. The exploitation of solid–solid phase transitions could be advantageous for certain applications, since the material remains in a solid state and the requirements of encapsulation will be less stringent. However, the enthalpy changes of solid–solid phase transitions are much smaller than enthalpies of melting. Pentaerythritol represents an exception, where above 459 K a plastic-crystalline phase with a high degree of orientational disorder occurs. When heating above this temperature the spherical molecules start to rotate and thus absorb 300 J g⁻¹ of heat [1]. It is assumed that hydrogen bonding contributes considerably to the high enthalpy change in this case.

Alkanes with chain lengths in the range of C₂₀ and C₃₉ also show solid–solid phase transitions due to par-

tial “chain melting”, however, with small enthalpic effects [2,6,9,12,17,18,20]. The phases are structurally characterized as rotator phases and represent the two-dimensional analoga to the plastic-crystalline phases.

In alkyl ammonium salts solid–solid transitions already occur in compounds with short carbon chains. Transition temperatures and enthalpies depend strongly on the number, length and symmetry of the alkyl groups bonded to the nitrogen atom as well as on the type of anion compensating the charge of the ammonium group [13]. Abdallah summarized the principles of structural organization of di-, tri- and tetra-alkyl ammonium and phosphonium salts in solid state and for liquid crystalline phases [13]. The structural motif of all these salts with long alkyl chains consists in ionic layers separated by the hydrophobic hydrocarbon rests of the molecules. Orientation of the alkyl chains is vertical or more or less inclined to the ionic layer. The alkyl chains can be considered as anchored at the ion plane. Thus “chain melting” can occur without destruction of the layer structure of the crystals.

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Most extensive structural and thermal investigations are available for monoalkyl ammonium salts [21]. Much less data can be found for other substitution schemes and anions [16,21]. Van Oort and White [22] found out that solid–solid transitions in dialkyl ammonium salts with $n = 8$ and 10 are accompanied by very high enthalpy changes. For example, didecyl ammonium chloride (DC_{10}Cl) has a reversible phase transition at 320 K with a specific enthalpy of 151 J g^{-1} [22]. Materials with heat effects in this order of magnitude are suitable as latent heat storage material. Obviously, the symmetrical double substituted ammonium group $[\text{R}_2\text{NH}_2]^+$ causes phase transitions at relatively low temperatures with high enthalpies.

In the present communication, results of thermal investigations of a series of symmetrical dialkyl ammonium salts with chain lengths between C_8 and C_{18} and a variety of anions (DC_nX) are reported.

2. Experimental

2.1. Chemicals and preparations

Di- n -alkylamines (DC_n) from Fluka (DC_{10} , DC_{12} , DC_{18}) and from Aldrich (DC_8) with purity between 97 and 99% were used for the preparations. The di- n -alkylamines (DC_n) were dissolved in the appropriate solvent (isopropanol, n -hexane, cyclohexane, or acetone) at room temperature. The salts DC_nX (with X for the anion) were prepared by addition of the respective acid into the clear solution. The following acids were used: HNO_3 and HF (Merck KGaA), HCl (Riedel-de Haen), HClO_3 and HI (Fluka), HClO_4 and H_2SO_4 (Jenapharm Apolda). For complete conversion of the di- n -alkylamines the dilute acid was added in small portions until the solutions pH indicated slightly acid conditions. During addition of acid the dialkyl ammonium salts immediately precipitated in form of small white crystals. This precipitate was filtered off, washed with water and recrystallized from ethanol (p.A.) or isopropanol (p.A.). Larger crystals of needle or lamella form were obtained by slow evaporation (1–2 days) of the solvent in a water-bath. The equimolar ratio DC_n and X in the salts was concluded from the consumption of acid. In addition mass loss in thermogravimetric analysis supported the presence of hydrogen phosphate and sulphate, its absence below temperatures of 125°C confirmed the fluorides as simple neutral salts.

2.2. Techniques for thermal characterization

Differential thermal analysis (model DTA/TG22, Seiko), differential scanning calorimetry (DSC92, Setaram) and thermo-optical analysis (Mettler microscopic hot stage model FP82 with a polarization microscope Jenapol, Carl Zeiss Jena) were applied for thermal characterization of the salts. Conditions for the DTA/TG measurements were: temperature regime from 20 to 350°C , heating rate of 5 K/min, samples

mass 3–10 mg in an open aluminium crucible under nitrogen gas flow of 300 mL/min with aluminium oxide as reference. DSC recording were taken from 20 to 250°C at two heating rates 2 and 5 K/min in closed steel crucibles under argon gas flow of 167 or 250 ml/min against aluminium oxide as reference. Calibration was performed against temperatures and enthalpies of melting of indium, gallium, bismuth and palmitic acid. Uncertainty for temperature was less than 1 K and for melting enthalpies from 1 to 9 J g^{-1} (maximum 6%).

2.3. Vibrational spectra and X-ray diffraction

IR spectra were taken using a FT/IR-spectrometer 510, Nicolet, in a region from 4000 to 700 cm^{-1} . The powdered samples were mixed with KBr and pressed into pellets. Absence of the typical bands of secondary amines at 1130 and 3270 cm^{-1} were taken as evidence that the salts prepared did not contain occluded amines [10,11].

Raman spectra at different temperatures were measured with a FT spectrometer RSF 100 (Bruker) equipped with a temperature variable cell SPECAC. Excitation wave length of 1064 nm was applied. All spectra of the DC_nX in a region from 50 to 3400 cm^{-1} were taken under comparable conditions, laser power of 300 mW, spectral resolution of 4 cm^{-1} and a number of 200 scans.

X-ray powder diffraction patterns were recorded with a D5000 diffractometer (Siemens) using $\text{Cu K}\alpha$ radiation in transmission mode with samples placed in capillaries within a heating chamber.

3. Results and discussion

In Table 1 the DSC results are summarized. In the table the onset solid–solid phase transition temperature (T_e^{SS}), the solid–solid phase transition enthalpy (ΔH^{SS}), the fusion temperature (T_f), the fusion temperature given in literature T_f^{lit} and the difference between T_f and T_e^{SS} are listed.

With the substances investigated a range of transition temperatures between 20 and 100°C is covered. Mass specific transition enthalpies up to 185 J g^{-1} are reached. These values already approach the enthalpy of melting for long-chain paraffins. Taking into account the inorganic part of the compounds the densities will be higher than for paraffins and so the volume specific enthalpies.

The solid–solid transition temperatures are far below the melting temperatures, mostly more than 100 K lower. The variation of transition temperatures and enthalpies in dependence on the alkyl chain length is visualized in Figs. 1 and 2. Both quantities increase with alkyl chain length. For comparison the corresponding values for paraffins are also plotted in both figures. Extrapolation of the trends to comparable chain lengths with the paraffins shows 30–60 K higher transition temperatures and 20–100 kJ/mol higher enthalpies for the dialkyl ammonium salts. Largest enthalpies have been found for DC_nX nitrates and perchlorates. At a given carbon num-

Table 1
Thermal characteristics of dialkyl ammonium salts

Compound	T_e^{ss} (°C)	ΔH^{ss} (J g ⁻¹)	ΔH^{ss} (kJ mol ⁻¹)	T_f (°C)	$T_f - T_e^{ss}$	T_f^{lit} (°C)
DC ₈ NO ₃ ^a (5 K/min)	45	176	53.5	190	145	185 [15]
DC ₈ F	–	–	–	96	–	–
DC ₈ Cl ^a (5 K/min)	21	132	37	247	226	238 [4], 220 [15]
DC ₈ Br ^a (5 K/min)	30	078	25	263/264	233	238 (4)
DC ₈ I ^b (2 K/min)	–2–6	058	21	254	247	–
DC ₈ H ₂ PO ₄ ^b (2 K/min)	16 (1) 98 (2), 190 (3)	12 (1) 4 (2), 14 (3)	042	242	226	190 [15]
DC ₈ ClO ₃ (2 K/min)	32	122	–	171	140	–
DC ₈ ClO ₄ (2 K/min)	23	108	37	266	242	–
DC ₈ H ₂ PO ₄	50–70 (DTA)	–	–	120	50–70	–
DC ₁₀ NO ₃	60	179	64	181	124	178 [14,15]
DC ₁₀ Cl	48	119	40	228	180	208 [3];205 [15]
DC ₁₀ Br	57	100	38	243	186	–
DC ₁₀ ClO ₃	55.5	154	59	178	123	–
DC ₁₀ H ₂ PO ₄	81	153	61	DTA:114	033	–
DC ₁₂ NO ₃ ^b (2 K/min)	66	185	77	174	108	170 [15]
DC ₁₂ F	–	–	–	164	–	–
DC ₁₂ Cl ^b (2 K/min)	65	123	48	207/208	142	205 [15]
DC ₁₂ Br ^a (5 K/min)	73	113	49	227	154	217–220 [5]
DC ₁₂ I ^a (5 K/min)	65	080	38.5	233	168	226–229 [5]
DC ₁₂ H ₂ PO ₄ ^a (5 K/min)	74 (1)–100 (2)	66.5 (1+2)	30 (1+2)	250	126	180 [15]
DC ₁₂ ClO ₃ ^a (5 K/min)	61.5	159	70	165	104	–
DC ₁₂ ClO ₄ ^a (5 K/min)	62	159	72	260	198	–
DC ₁₂ H ₂ PO ₄ ^b (2 K/min)	55 (1)–90 (2)	183 (2)	83 (2)	118	030	–
DC ₁₂ Ac	–	–	–	065	–	–
DC ₁₈ NO ₃ ^a (5 K/min)	93.5	186	109	147	054	–
DC ₁₈ F	–	–	–	111/112	–	–
DC ₁₈ Cl ^b (2 K/min)	91.2	174	097	177	086	–
DC ₁₈ Br ^b (2 K/min)	98.0	135	081	188/189	090	–
DC ₁₈ I ^b (2 K/min)	93.0	116	075	194	101	–
DC ₁₈ H ₂ PO ₄ ^b (2 K/min)	70 (1)–82 (2)	176 (1+2)	109 (1+2)	187	117	–
DC ₁₈ ClO ₃ ^b (2 K/min)	84 (1)–91 (2)	154 (1+2)	94 (1+2)	156–159	072	–
DC ₁₈ ClO ₄ ^a (5 K/min)	88.1	185	0115	230	122	–

Values in parentheses indicate number of thermal effects.

^a Heating rate: 2 K/min.

^b Heating rate: 5 K/min.

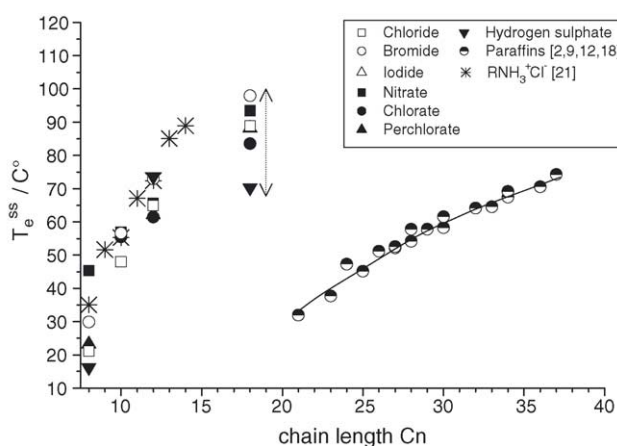


Fig. 1. Solid–solid phase transition temperatures in dependence on the number of carbon atoms per formula unit of dialkyl ammonium salts [21], monoalkyl ammonium chlorides and paraffins [2,9,12,18].

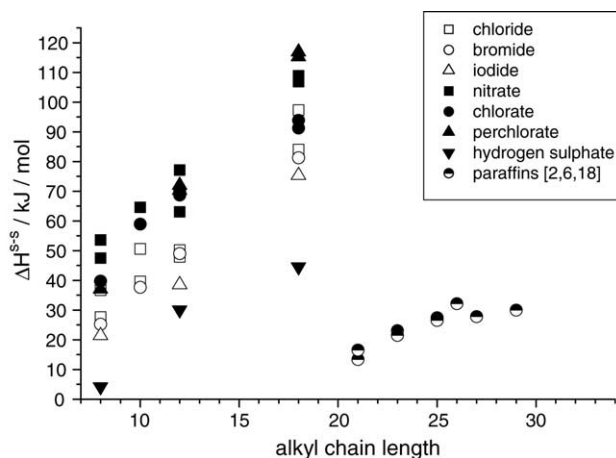


Fig. 2. Solid–solid phase transition enthalpies of dialkyl ammonium salts in dependence on the alkyl chain length of dialkyl ammonium salts and paraffins [2,6,18] (data from Tables 1 and 2).

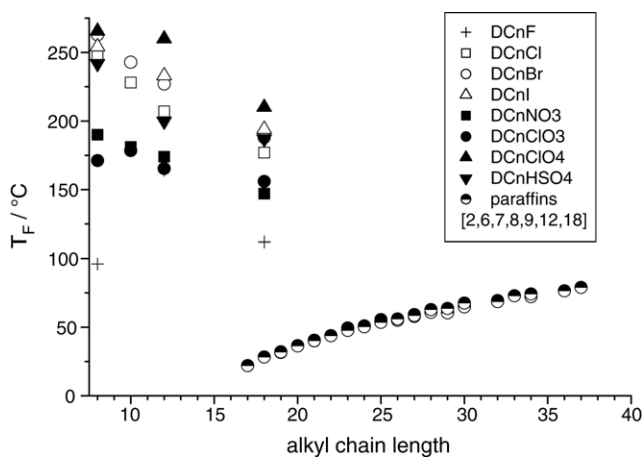


Fig. 3. Fusion temperatures of dialkyl ammonium salts compared with paraffins [2,6–9,12,18] in dependence on alkyl chain length.

ber the enthalpy of DC_nX compounds varies with the anion by about 35–50 kJ/mol (Fig. 2).

In Fig. 1 the transition temperatures of monoalkyl ammonium chlorides are included. Interestingly, the transition temperatures of the corresponding dialkyl ammonium chlorides are lower by 10–15 K.

In Fig. 3 the temperatures of melting for DC_nX compounds and paraffins are plotted against the alkyl chain length. Whereas for paraffins the melting temperatures increase with chain length the opposite can be stated for the DC_nX compounds. For very long alkyl chains the melting temperatures of salts will approach those of the paraffins. Highest temperatures of melting are observed for dialkyl ammonium perchlorates followed by the chlorides and bromides.

For all substances DSC heating-cooling cycles have been recorded between room temperature and 30 K above the transition temperatures avoiding melting of the samples.

As an example the DSC records of three thermal cycles for $DC_{12}NO_3$ are shown in Fig. 4. Temperatures and enthalpies of transition are identical in the second and third cycle. The transition enthalpy remains constant at $145 \pm 6 \text{ J g}^{-1}$ in all cycles and both directions of the transition. Hysteresis of the solid–solid transition on cooling is about 13 K. The only significant variation represents the transition temperature at the first heating, which is 3 K higher than in the subsequent cycles. X-ray studies revealed that the initial phase is not reformed on cooling as can be seen easily by comparing the diffraction patterns RT, RT¹, RT² in Fig. 5. Also the spectral features of the Raman spectrum changed in the region of low wave numbers (Fig. 6). Similar effects have been observed for $DC_{12}I$ and $DC_{12}ClO_3$. All other cycling experiments indicated no changes in dependence on cycle number. All characteristic data on cycling are listed in Table 2. The hysteresis ($T_H - T_C$) between heating and cooling varies from 4 to 17 K for the various salts.

The optical appearance of the salts on heating and cooling was watched and film sequences had been saved for later

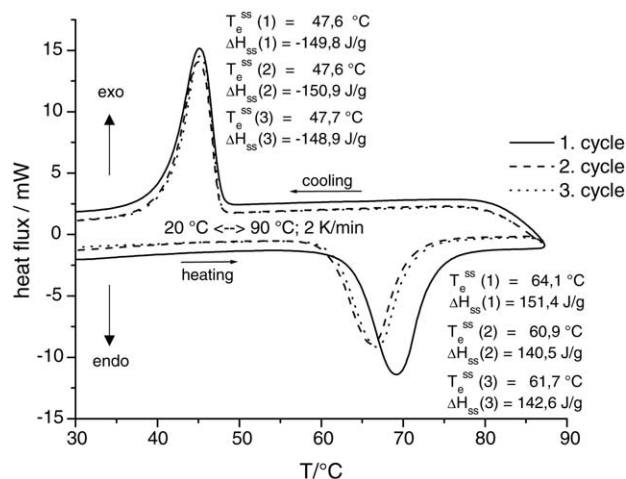


Fig. 4. DSC cycles. (1–3) Cycles of $DC_{12}NO_3$ with the T_e^{ss} (°C) and ΔH^{ss} (J g^{-1}).

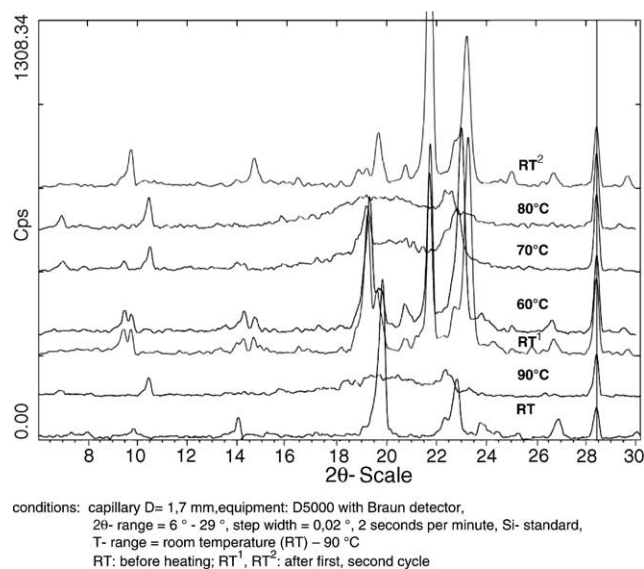


Fig. 5. Cycles of powder X-ray diffraction pattern of $DC_{12}NO_3$ $T_e^{ss} = 64$ °C.

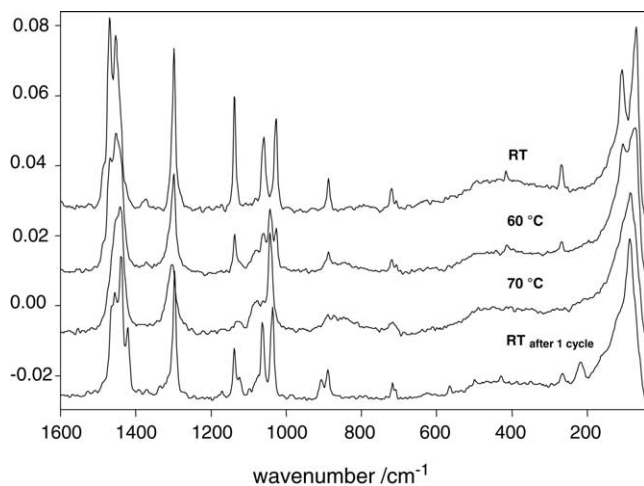


Fig. 6. Raman spectra of $DC_{12}NO_3$ at various temperatures below and above the solid–solid transition at $T_e^{ss} = 64$ °C. RT = room temperature.

Table 2
Results of DSC heating-cooling cycles

Compound	T_{e}^{ss} heating ($^{\circ}\text{C}$)	T_{e}^{ss} heating ($^{\circ}\text{C}$)	$T_{\text{H}} - T_{\text{C}}$	$\Delta H_{\text{heating}}$ (kJ mol^{-1})	$\Delta H_{\text{cooling}}$ (kJ mol^{-1})	T_{dec}
DC ₈ NO ₃	43	26.5	17.5	47.5	46	170
DC ₈ Cl	21	18; 4	3	28	18; 8	220
DC ₈ Br	29	26.5	2.5	24	26	200
DC ₈ I	-2; 7	2	5	21	17	220
DC ₈ HSO ₄	-0; 7; 17	11		0.2; 4; 5	6	190
DC ₈ ClO ₃	32	17	15	40	39	160
DC ₈ ClO ₄	23	16	8	37	38	250
DC ₁₂ NO ₃	64	48	16	63	62	170
DC ₁₂ Cl	65	60	5	50	50	200
DC ₁₂ Br	72	68	4	49	52.5	200
DC ₁₂ I	64	57	7	39	48	200
DC ₁₂ HSO ₄	59; 82	83		14; 11	14	200
DC ₁₂ ClO ₃	60	49	11	69	75	150
DC ₁₂ ClO ₄ (1)	62	54	8	70	70	220
DC ₁₂ ClO ₄ (2)	62	55	7	70	70.5	220
DC ₁₈ NO ₃ (1)	92	87.5	4.5	107	68	120
DC ₁₈ NO ₃ (2)	62; 85	54; 87		10; 60	21; 68	120
DC ₁₈ NO ₃ (3)	63; 86	55; 87		9; 62.5	22; 67	120
DC ₁₈ Cl	93	92; 84	1	84	10.5; 61.5	140
DC ₁₈ Br	97	91	6	84.5	92	140
DC ₁₈ I	93	88	5	75	92	140
DC ₁₈ HSO ₄ (1)	69	73	4	76	76	150
DC ₁₈ HSO ₄ (2)	69	73	4	71	73	150
DC ₁₈ HSO ₄ (3)	69	73	4	67	82	150
DC ₁₈ ClO ₃	84; 92	81		41; 39	89	150
DC ₁₈ ClO ₄ (1)	87	79	8	117	112	200
DC ₁₈ ClO ₄ (2)	87	79	8	110	113	200

Data in the same row = two effects at the same cycle; numbers in parentheses = (1) cycle, (2) cycle of the same compound; heating rate = 2 K/min.

analysis. All substances showed clearly visible changes of polarization colours and development of cracks or domain structures at the transition temperature. From the optical investigations formation of liquid crystalline phases or partial melting can be excluded for all temperatures, which have been assigned as solid–solid transitions.

For most of the salts DTA/TG records show no mass losses below the melting point. Temperatures of decomposition (T_{dec} , Table 2) are well above the solid–solid transition and decomposition often starts just before melting. The temperature difference between solid–solid transition and melting decreases with increasing chain length from DC₈X to DC₁₈X. For dioctyl ammonium salts the solid–solid phase transition occurs 140–250 K below the melting point and for dioctadecyl ammonium salts this difference reduces to 50–120 K.

The solid chlorides, bromides and iodides are stable at least 140 $^{\circ}\text{C}$ for DC₁₈X. The salts with shorter alkyl chains have more extended stability ranges, in case of DC₈X until 220 $^{\circ}\text{C}$. Fluorides possess low melting points (see Table 1) and thus a smaller stability range. The perchlorates exhibit a remarkable thermal stability up to 200 $^{\circ}\text{C}$ for DC₁₂ClO₄ and DC₁₈ClO₄ and up to 250 $^{\circ}\text{C}$ for DC₈ClO₄.¹

¹ Despite the observed thermal stability it should be taken into account that organic salts of chlorates, perchlorates and nitrates on heating represent potential explosives.

The nitrates and chlorates started to decompose at a temperature of about 170 $^{\circ}\text{C}$. In case of DC₁₈NO₃ and DC₁₈ClO₃ decomposition was detected already at about 120 $^{\circ}\text{C}$. The chlorates show exothermic effects caused by the oxidation of the organic part of the compounds.

4. Conclusions

Temperature and enthalpy of solid–solid transitions have been determined for a series of dialkyl ammonium salts DC_{*n*}X with chain lengths up to $n=18$. The thermal characteristics corresponds with the expectations for transitions to rotator phases. The magnitude of the enthalpy correlates with the chain length and packing density of the alkyl chains. The latter is controlled by the anion size in the salt. For dioctadecyl ammonium bromide data from a crystal structure analysis are available [3]. According to these data ammonium nitrogen atoms and bromide ions are arranged exactly in one plane. Distances between nitrogen atoms correspond to the distances of the alkyl chains and amount to 537 and 539 pm, which is close to the estimated rotational diameter of approximately 400–500 pm. The ionic radii of chloride, bromide and iodide ions ($r_{\text{Cl}^-} = 181$ pm, $r_{\text{Br}^-} = 196$ pm, $r_{\text{I}^-} = 220$ pm [19]) are compatible with this packing requirement. With $r_{\text{F}^-} = 133$ pm the fluoride ion obviously does not fulfil these geometric criteria. Thus,

the fluorides on heating are melting without solid–solid transition.

Significant higher transition enthalpies occur with structured anions as NO_3^- , ClO_3^- and ClO_4^- . The reason can be seen in additional enthalpic contributions from hindered rotations of the anions within a hydrogen bond network $[\text{XO}_n]^-[\text{H}_2\text{NR}_2]^+$, in the ionic layer. It seems that two hydrogen atoms per ammonium nitrogen provide optimal conditions for the formation of hydrogen bonds as in the neutral dialkyl ammonium salts. In acidic salts as in the investigated hydrogen sulphates, $[\text{HSO}_4]^-[\text{H}_2\text{NR}_2]^+$, or the monoalkyl ammonium salts, $\text{X}^-[\text{H}_3\text{NR}]^+$, transition enthalpies are considerably lower.

Acknowledgement

The work was supported by “Bundesministerium für Wirtschaft und Technologie” (BMW) within the framework of the program “Innovative PCM Technologies” and Merck KGaA, Darmstadt.

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