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PHASE DIAGRAMS OF BINARY SYSTEMS OF ALKYLAMMONIUM TETRACHLOROMETALLATES(II)

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Abstract

The phase diagrams of four binary systems $(C_{10}H_{21}NH_3)_2CoCl_4$–$(C_{16}H_{33}NH_3)_2CoCl_4$, $(C_{12}H_{25}NH_3)_2CoCl_4$–$(C_{16}H_{33}NH_3)_2CoCl_4$, $(C_{10}H_{21}NH_3)_2ZnCl_4$–$(C_{16}H_{33}NH_3)_2ZnCl_4$ and $(C_{12}H_{25}NH_3)_2ZnCl_4$–$(C_{16}H_{33}NH_3)_2ZnCl_4$ were investigated by means of DSC. These six compounds and their binary mixtures can retain energies between 74 and 115 J/g during solid-state transformations at temperatures between 70 and 105°C, and they are therefore being considered for potential use in solar energy systems.

Keywords: alkylammonium tetrachlorometallates(II), DSC method, IR spectra, phase diagram, solid–solid phase transition

Introduction

The bis(*n*-alkylammonium) tetrahalometallates(II) (C_nM) are organometallic compounds of general formula $(n\text{-}C_nH_{2n+1}NH_3)_2MX_4$,where *M* is a divalent metal atom, *X* is a halogen and *n* varies between 8 and 18. These compounds are typical 'sandwich' systems, with structures resulting in a regular alternation of thin inorganic and thick hydrocarbon regions, so that each inorganic layer is sandwiched between two hydrocarbon layers and vice versa. They are characterized by high-enthalpy, reversible solid–solid phase transitions between two polymorphic forms in the temperature range 0–120°C [1, 2].

We are measuring the relevant thermal properties (temperature and enthalpy of the solid–solid transformation) of selected C_nM in order to evaluate their usefulness in thermal energy storage systems.

Experimental

Compounds of the type $((n\text{-}C_nH_{2n+1}NH_3)_2MCl_4$ were obtained as platelets by mixing hot ethanolic solutions of $CoCl_2$ (or $ZnCl_2$), HCl and alkylamine in a 1:2:2 molar ratio. The resulting solutions were concentrated by boiling, then allowed to cool to room temperature and filtered. The products were recrystal-

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lized twice from absolute ethanol. The results of elementary analysis of C_nM with a Perkin-Elmer 2400 Elemental Analyzer are given in Table 1.

Table 1 Elementary analyses (theoretical percentages in parentheses)

	C%		H%		N%	
$C_{10}Co$	(46.45)	45.43	(9.29)	9.76	(5.42)	5.34
$C_{12}Co$	(50.29)	49.99	(9.78)	10.14	(4.89)	4.31
$C_{16}Co$	(56.08)	55.88	(10.51)	11.12	(4.09)	3.87
$C_{10}Zn$	(45.87)	45.67	(9.18)	9.64	(5.35)	5.24
$C_{12}Zn$	(49.72)	48.27	(9.67)	9.68	(4.83)	4.48
$C_{16}Zn$	(55.56)	55.25	(10.42)	10.36	(4.05)	4.13

Mixed materials of composition $(C_{10})_x(C_{16})_{2-x}CoCl_4$ were prepared by starting from finely-powdered pure alkylammonium salts, thoroughly mixed in the appropriate composition and heated to a temperature beyond the transition point of the mixed salt.

Infrared spectra were registered with a Nicolet Magna IR 750 FT-IR spectrometer equipped with a variable-temperature sample cell. The powdered samples were mixed with KBr and pressed into pellets. DSC curves were registered between 0 and 200°C in a flow of nitrogen on a Perkin-Elmer DSC-7 differential scanning calorimeter at a scanning rate of 5 deg·min^{-1}. The temperature scale was calibrated by means of measurements on pure reference compounds. Transition enthalpies were obtained by using a sample of pure indium as reference standard [ΔH_m=28.4 J/g] [3, 4].

Results

IR Spectra

Figures 1a and 2a depict the low-frequency region of the IR spectra of $C_{10}Zn$ and $C_{12}Zn$ at room temperature [5, 6]. This is characterized by the 725 cm^{-1} band (methylene rocking mode), which is a doublet, because there are two chains in each crystallographic unit cell, and by the methylene twisting absorption, which is split into several peaks in the region 1200–1300 cm^{-1}, due to the regular interaction of the CH_2 groups of the same chain.

Figures 1b and 2b show the IR spectra of the high-temperature solid polymorphs of $C_{10}Zn$ and $C_{12}Zn$. The 725 cm^{-1} band in the case is broad, with no obvious splitting observed. The methylene twisting absorption is very broad and unsplit, because of the lack of regular interactions between the CH_2 groups in the same chain.

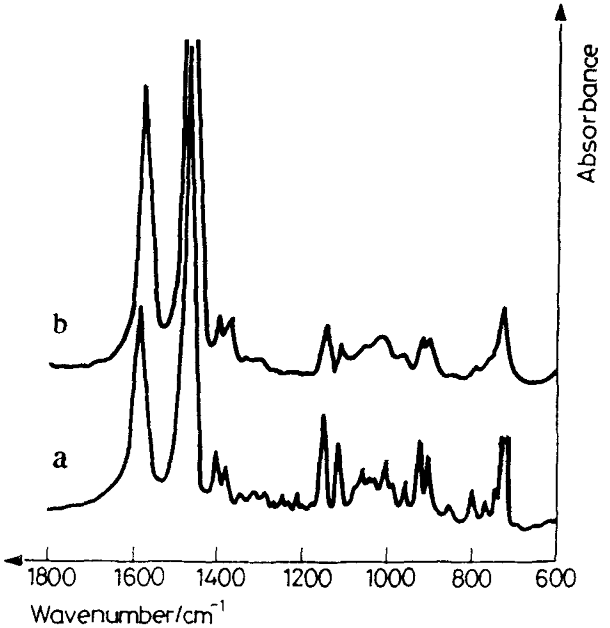

Fig. 1 1800–600 cm^{-1} region of the IR spectrum of $C_{10}Zn$. a. Room-temperature ordered phase; b. high-temperature disordered solid phase (t=90°C)

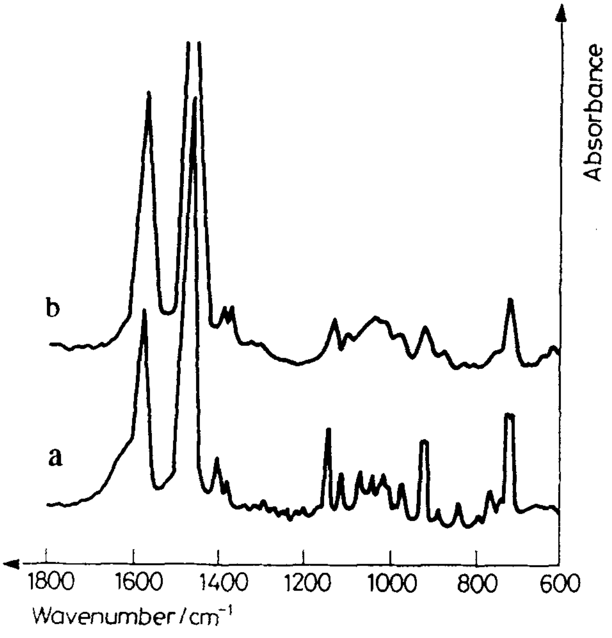

Fig. 2 1800–600 cm^{-1} region of the IR spectrum of $C_{12}Zn$. a. Room-temperature ordered phase; b. high-temperature disordered solid phase (t=100°C)

The IR spectra of the mixed materials were subjected to similar characterizations.

DSC

Figure 3 displays some typical heating curves.

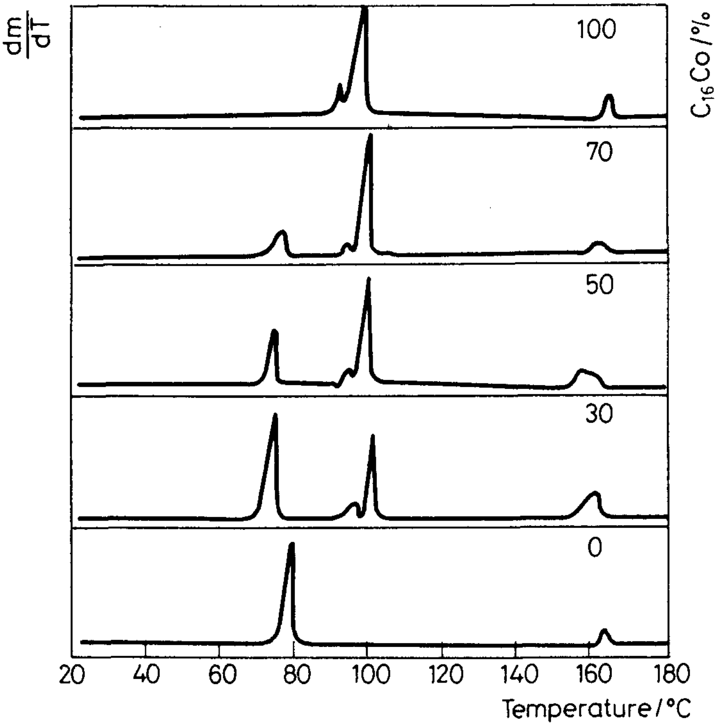

Fig. 3 Heating curves of the some mixed materials of type $C_{10}Co$–$C_{16}Co$ and of their pure component salts

Transition temperatures and enthalpies measured from the DSC curves for the mixed materials and their pure components are given in Table 2. Temperatures refer to peak onset; for a peak with two or more unresolved maxima, the temperature are reported as T_1, T_2. Heating enthalpies always refer to the overall endotherm.

Figure 4 presents an approximate phase diagram derived from the data in Table 2. Figures 5–7 depict phase diagrams of $C_{10}Zn$–$C_{16}Zn$, $C_{12}Co$– $C_{16}Co$ and $C_{12}Zn$–$C_{16}Zn$ [1].

In our discussion, we shall use the phase diagram of the $C_{10}Co$–$C_{16}Co$ system as an example. For $C_{16}Co$=57%, the product is the mixed compound $(n\text{-}C_{10}H_{21}NH_3)_2CoCl_4$–$(n\text{-}C_{16}H_{33}NH_3)_2CoCl_4$. The crystallization products

Table 2 Solid–solid transition temperatures, enthalpies of the $(C_{10})_x(C_{16})_{1-x}Co$ system

$C_{16}Co$ /wt%	T /°C		ΔH/J·g^{-1}
0	82.00	165.00*	74.38
11.41	76.50, 89.50		
30.00	77.55, 98.78	157.81*	78.17
40.00	80.32, 99.68	160.07*	86.62
50.00	77.34, 99.02	156.71*	76.34
56.95	79.52, 99.87	159.76*	82.35
62.95	81.80, 91.50		
74.05	80.02, 99.41	156.57*	73.67
82.00	86.00, 99.80		
90.00	88.95, 95.00		
100	99.70	164.11*	114.98

*Melting temperatures

Table 3 Solid–solid transition temperatures of the $(C_{10})_x(C_{16})_{1-x}Zn$ system

$C_{16}Zn$ /wt%	T /°C
0	80.14
10.45	78.00, 80.25
21.77	76.20, 80.60
25.00	81.19, 98.82
40.00	75.80, 90.00
62.50	88.40, 94.50
90.00	89.40, 96.00
100	91.13

obtained with $C_{16}Co<57\%$ are crystal mixtures of this mixed salt and the pure α-phase decylammonium salt, while the products obtained with $C_{16}Co>57\%$ are mixtures of the mixed salt and the pure α-phase hexadecylammonium salt. At temperatures lower than the eutectic points, the system contains the pure decylammonium salt and the mixed salt in the α-phase. At temperatures intermediate between the eutectic point and the transition point of the mixed salt, the system contains a β-phase. At temperatures high than the transition point of the mixed salt, the system contains two β-phases of different composition in the stable β-phase region. At temperatures higher than the melting point of the mixed salt, the system is in a liquid state.

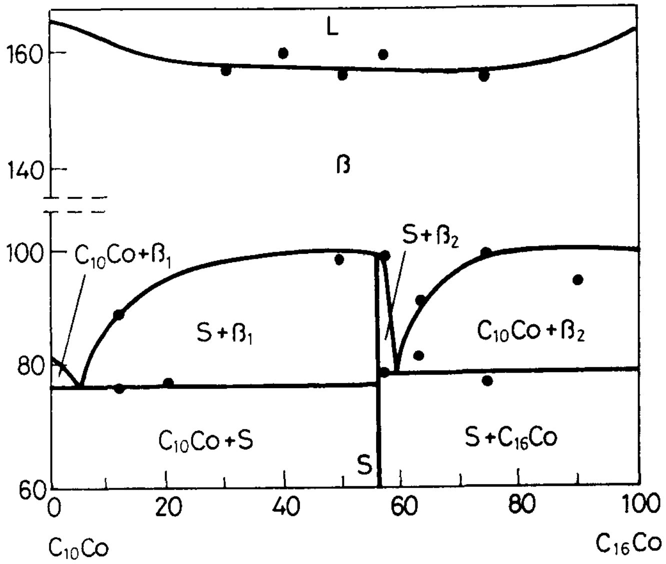

Fig. 4 Phase diagram of the system $C_{10}Co$–$C_{16}Co$

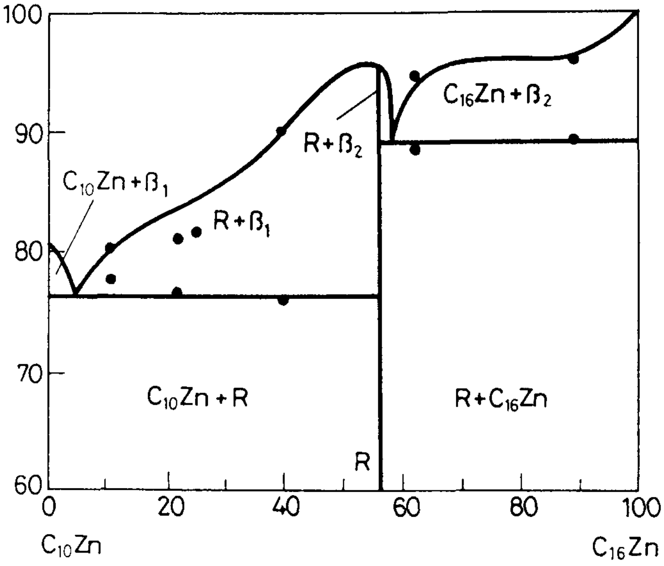

Fig. 5 Phase diagram of the system $C_{10}Zn$–$C_{16}Zn$

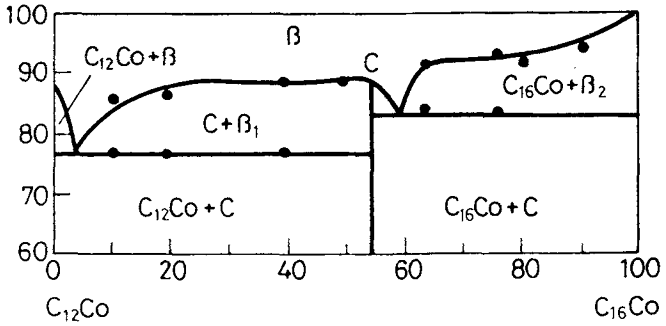

Fig. 6 Phase diagram of the system $C_{12}Co$–$C_{16}Co$

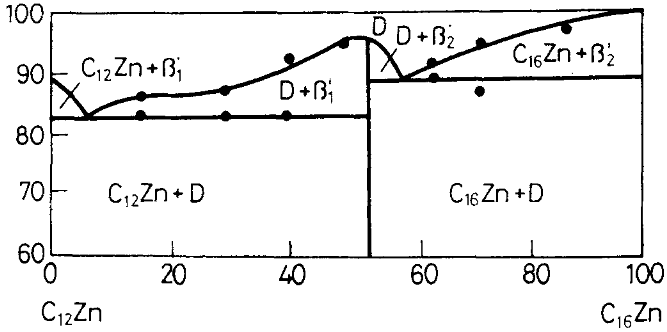

Fig. 7 Phase diagram of the system $C_{12}Zn$–$C_{16}Zn$

Conclusions

By means of cooling curves and DSC methods, the phase diagram of the solid–solid transition systems $C_{10}Co$–$C_{16}Co$, $C_{12}Co$–$C_{16}Co$, $C_{10}Zn$–$C_{16}Zn$ and $C_{12}Zn$–$C_{16}Zn$ have been determined. Their phase diagrams are very similar, belonging to the eutectic type. Compounds C_nM and their binary mixtures have solid–solid transition temperatures between 70 and 105°C, and the transition enthalpies are in the region 74 to 115 J/g, and they are therefore potential thermal energy storage materials.

References

1 V. Salerno, A. Greco and M. Vacatello, J. Phys. J. Phys. Chem., 80 (1976) 2444.
2 V. Busico, C. Carfagna, V. Salerno and M. Vacatello, Solar Energy, 24 (1980) 575.
3 C. Paraggio, V. Salerno, V. Busico and M. Vacatello, Thermochim. Acta, 42 (1980) 185.
4 V. Busico, T. Tartaglione and M. Vacatello, Thermochim. Acta, 62 (1983) 77.
5 C. Carfagna, M. Vacatello and P. Corradini, Gazzetta Chimica Italiana, 107 (1977) 131.
6 Xu Ruiyun, Kong Dejun, Cia Xian-E and Zhu Jing, Thermochim. Acta, 164 (1990) 307.

Zusammenfassung — Mittels DSC wurden die Phasendiagramme der vier binären Systeme $(C_{10}H_{21}NH_3)_2CoCl_4$–$(C_{16}H_{33}NH_3)_2CoCl_4$, $(C_{12}H_{25}NH_3)_2CoCl_4$–$(C_{16}H_{33}NH_3)_2CoCl_4$, $(C_{10}H_{21}NH_3)_2ZnCl_4$–$(C_{16}H_{33}NH_3)_2ZnCl_4$ und $(C_{12}H_{25}NH_3)_2ZnCl_4$–$(C_{16}H_{33}NH_3)_2ZnCl_4$ untersucht. Diese sechs Verbindungen und ihre binären Gemische können bei Feststoffumwandlungen zwischen 70 und 105°C Energien zwischen 74 und 115 J/g zurückhalten und werden deshalb für einen potentiellen Einsatz als Sonnenenergiesysteme in Betracht gezogen.