Journal of Thermal Analysis, Vol. 50 (1997) 347-354

THERMAL ANALYSIS OF THE SYSTEM KCl–LiCl BY DIFFERENTIAL SCANNING CALORIMETRY

*E. Korin** *and L. Soifer*

Department of Chemical Engineering, Ben-Gurion University of the Negev, P.O. Box 653
Beer-Sheva 84105, Israel

(Received July 20, 1996; in revised form November 25, 1996)

Abstract

Thermal analysis of the binary system KCl–LiCl in the composition range 0.368–0.812 mol fraction of LiCl was studied by differential scanning calorimetry (DSC). On the basis of the DSC curves, the experimental data for the phase-diagram, the latent heat of fusion, and the average specific heat in the liquid and solid states are presented as a function of the composition of the mixture. The experimental results compared with literature data. The following empirical correlation between the heat of fusion (ΔH) and of compositions of the mixture in mol fraction of LiCl (x) was obtained:

$$\Delta H=26.95-50.20x+43.06x^2$$

with a minimum value of 11.8 kJ(g mol)$^{-1}$ at the eutectic point of 0.587 mol fraction of LiCl at 354.4°C. These results are required as basic data to develop thermal energy storage materials, based on the phase change of a molten mixture of KCl–LiCl.

Keywords: DSC, eutectic composition, LiCl–KCl system, phase diagram

Introduction

Molten salts and their mixtures are considered suitable candidates as phase-change materials (PCM) for thermal energy storage (TES) at relatively high temperatures. Possible applications are solar powered thermal systems, heat recovery from industrial waste heat, and load management in off peak periods in power generation stations. A variety of salts (nitrates, chlorides, fluorides and hydroxides) and their eutectic mixture have been investigated for application as PCM for TES [1, 2].

To the best of our knowledge, the binary molten mixture LiCl–KCl has not been studied for TES we thus investigated molten mixtures of LiCl–KCl in the

---

* Author to whom all correspondence should be addressed.

0368–4466/97/ $ 5.00

John Wiley & Sons Limited
Chichester

Table 1 Literature data on the eutectic point of the binary LiCl–KCl system

Eutectic composition LiCl/mol %	T_{fus}/°C	Method	Year of publication	Ref. no.
59.5	352	Cooling curves with automatic temperature recording	1910	3
58.6	358	Visual observation of temperature of appearance of crystals; cooling curves with visual readings	1917	4
58.0	361	Thermal analysis; optical study of thin sections	1920	5
58.3	359	Cooling and heating curves; crystallographic examination of thin sections	1925	6
58.3	352	Cooling and heating curves with automatic recording (self-designed instrument) in a sand bath	1932	7
57.0	352	Visual	1952	8
58.0	348	Visual	1954	9
59.5	355	Calculated	1989	10

temperature range 350–550°C for heat recovery from industrial waste heat. Available thermodynamic data on this system were obtained many years ago, by means of unsophiscated instrumentation: values for the eutectic point range from 0.570 to 0.595 mol fraction of LiCl, and the temperature range covers 348 to 361°C (Table 1). For same composition, the difference in the temperature of the liquid is as large as 13°C. None of the studies covered heat of fusion, with one exception related to the eutectic point, which was determined with a isothermal calorimeter [11]. In the light of this background, the aim of the first stage of our project was to perform thermal analysis of various compositions of molten salt mixtures of LiCl–KCl by differential scanning calorimetry (DSC). This paper presents the phase-transition temperatures and heat of fusion as functions of the composition, and compares our results with the literature data.

Experimental

The thermal analysis was performed with a Mettler Toledo DSC 820. The calorimeter was calibrated with indium (*m.p.* 156.5°C, ΔH_{melt}=28.5 J g^{-1}). The equipment facilitated accuracy of the measurement as follows: weight ±0.0001 g, temperature ±0.1°C, and rate of heating/cooling ±1 mW/s. The calorimeter cell was made of Al_2O_3.

Molten salt mixtures were prepared from potassium chloride GR (99.5%) and lithium chloride GR (99%) supplied by Merck. The reagents were oven dried at 250–260°C for 24 h. At the end of the DSC run, the molten salts were rinsed with a known amount of distilled water, and the chloride concentration was determined by titration with $AgNO_3$ [12]. The concentrations of lithium and potassium ions were determined by material-balance equations. The differences between the results of the analytical method for the composition of the sample after DSC and the initial composition determined by weighing of the salts were less than 0.5%, which fall within the accuracy range of the analytical method. The solid components were identified by X-ray diffraction analysis.

Results and discussion

Two experiments were performed as follows:

1) To examine the effects of heating and cooling cycles, two or three cycles of heating/cooling were performed. The results are given in Fig. 1 and Table 2. The differences between the DSC results of the first and the second cycles differed considerably but the differences between the second and third cycles were insignificant. Therefore, the results of the first cycle were not included in the analysis.

2) To determine the suitability of the heating and cooling rates for these studies, several runs with different heating and cooling rates were performed. Fig. 1

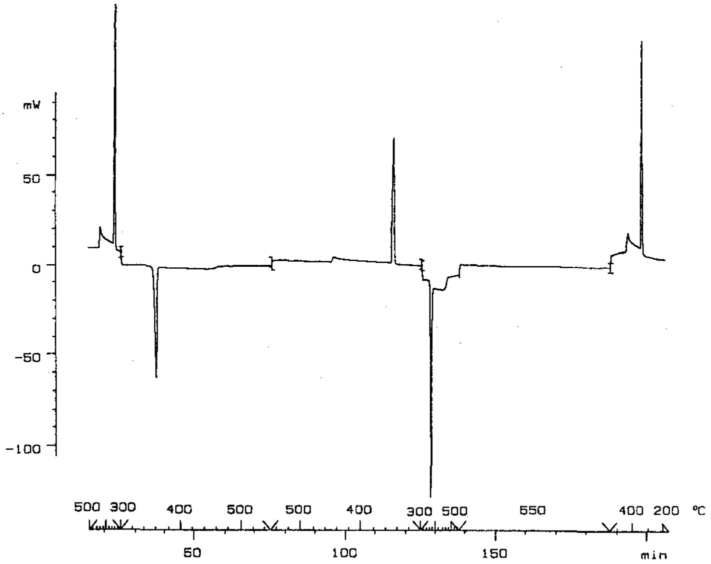

Fig. 1 DSC curves for molten of LiCl–KCl in a composition of 0.714 mol fraction of LiCl for different heating and cooling paths. Cycle 1: heating rate 40°C min^{-1}; and cooling rate 20°C min^{-1}, cycle 2: heating rate 5°C min^{-1} and cooling rate 5°C min^{-1}, cycle 3: heating rate 20°C min^{-1}, annealing at 823°C for one hour and cooling rate 20°C min^{-1}

shows the curves for a mixture with a 0.714 mol fraction of LiCl obtained at different heating and cooling rates. The results summarized in Table 2 show that the onset temperature of the liquidus in the heating step is 353.1°C compared to 353.6°C and the onset temperature of the solidus in the cooling step is 450.1°C compared to 450.3°C. The latent heats in the two cases are in the range of 13.6±0.6 J(g mol)$^{-1}$ (Table 2). It is thus evident from this experiment that in our system the effect of heating and cooling rates in the range 5–20°C min^{-1} may be neglected. In subsequent experiments, we therefore used heating and cooling rates of 5–20°C min^{-1}.

The results of the DSC for the various molten compositions are presented in Fig. 2. The data related to onset temperatures obtained during heating compared

Table 2 Effect of heating and cooling rates on DSC curves for molten LiCl–KCl in a composition containing 0.714 mol fraction of LiCl

Rate/ °C min^{-1}	Temperature/°C				Heat/ kJ (g mol)$^{-1}$	
	eutectic		liquidus			
	heating	cooling	heating	cooling	fusion	crystallization
20.0	–	350.0	–	447.1	–	13.97
5.0	353.1	351.1	461.0	450.3	13.64	13.03

with those for the cooling steps are summarized in Table 3. It can be seen that the onset temperatures for heating are systematically higher than those for cooling – a difference of 3–5°C in the solidus and 16–29°C in the liquidus. This phenome-

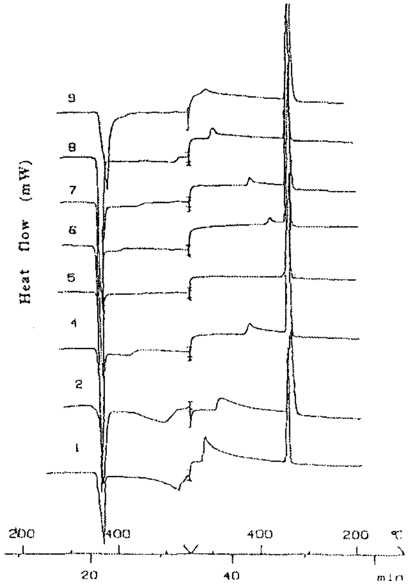

Fig. 2 DSC curves for different compositions of molten LiCl–KCl (in mol fraction of LiCl) : 1) 0.812; 2) 0.775; 4) 0.694 5) 0.587; 6) 0.551; 7) 0.507; 8) 0.442; 9) 0.388 Heating and cooling rates 15°C min^{-1}

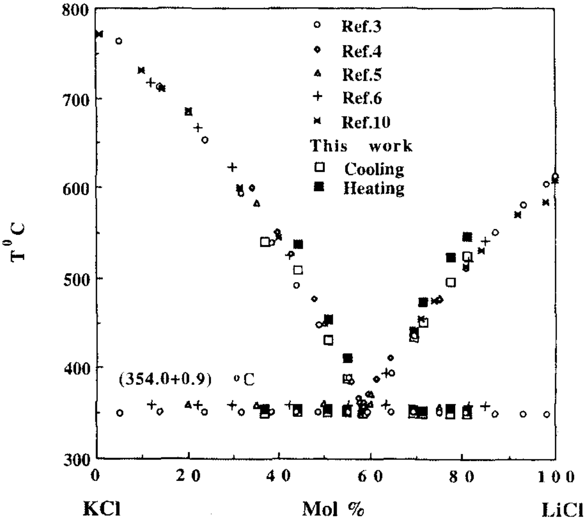

Fig. 3 Phase diagram for the LiCl–KCl system

Table 3 Experimental data for the binary LiCl–KCl system based on the DSC curves shown in Fig. 3

Mol% LiCl in alloy	Temperature/°C				Heat/ kJ (g mol)$^{-1}$	
	eutectic		liquidus			
	heating	cooling	heating	cooling	fusion	crystallization
81.2	353.8	349.9	547.6	525.2	–	14.82
77.5	357.0	350.0	523.6	496.6	14.41	14.35
71.4	353.6	349.6	474.0	450.1	14.14	13.68
69.4	354.7	349.7	440.0	434.6	–	12.48
58.7*	354.4	349.9	354.4	349.9	12.12	11.79
55.1	353.6	351.1	411.8	388.9	13.20	12.60
50.7	354.9	351.3	454.3	432.2	12.59	12.14
44.2	355.4	351.4	538.4	508.7	12.98	12.84
36.8	355.0	350.7	–	541.4	–	15.00

*Eutectic alloy

non is due to the nonequilibrium conditions in the cell, i.e., over-heating and supercooling effects in the heating and cooling processes respectively. Figure 2 shows that for a 0.587 mol fraction of LiCl (curve 5) there is a single sharp peak for both the cooling process, and the heating process, which indicates that this mixture is the eutectic composition. For all other compositions, the onset temperatures of the solidus are in the range 354.4±0.9°C on heating and 350±0.7°C on cooling. The onset for the liquidus curves depends on the compositions.

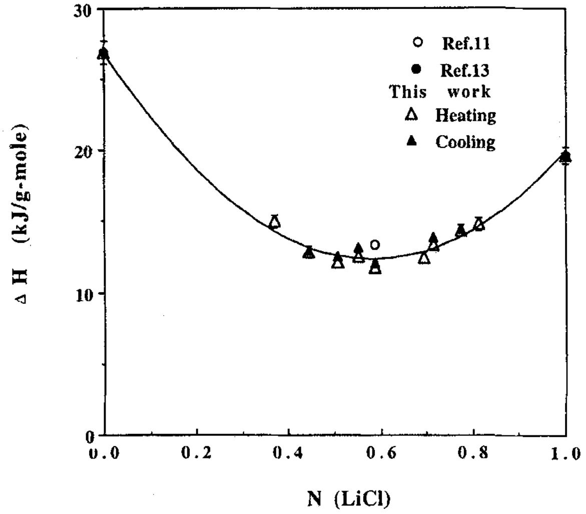

Fig. 4 Heat of crystallization/fusion as a function of composition in the LiCl–KCl system

Qualitative X-ray diffractometry of the solid phase indicated that there are only crystals of KCl and LiCl; there is no solid solution or double salt compounds.

A comparison of the results of the present study with the literature data is presented in Fig. 3. In the composition range of this study, 0.368–0.812 mol fraction of LiCl, the latent heat for the solid/liquid phase-change lies in the range 11.8–15.0 kJ mol^{-1} (Table 3 and Fig. 4). We found that the heat of fusion is about 3–4% higher than the heat of crystallization. This difference is due to heat losses to the surroundings during the crystallization process, which are not taken into account by the calorimeter. The relationship between the heat of fusion (ΔH) and the composition in the mol fraction of LiCl (x) followed the correlation given below:

$$\Delta H = 26.95 - 50.20x + 43.06x^2 \tag{1}$$

The average specific heats in the solid and liquid states are presented in Fig. 5. The experimental results for the liquid state show a positive deviation from ideal solution (the experimental values are higher than the calculated values assuming an ideal solution). The results for the solid state are in agreement with the predicted results based on data for the pure components.

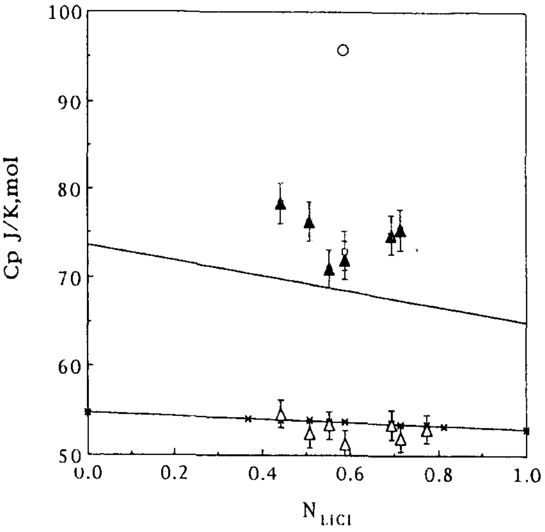

Fig. 5 Average specific heat as a function of composition in the LiCl–KCl system: Δ – solid state (300–350)°C, ▲ – liquid state (500–540)°C; calculated values assuming an ideal solution (specific heat for pure components from Ref. [13]; - - solid state (300–350)°C; — liquid state (500–540)°C; O – Ref. [11]. (354–384)°C, o – Ref. [14] (354–800)°C

The study thus provides the basic thermal data for KCl–LiCl molten mixtures that will enable us to investigate the possibility using them as PCM for TES media in the 300–550°C temperature range.

References

1 G. A. Lane, Solar Heat Storage: Latent Heat Materials, Vol. 1, Background and Scientific Principles, CRC Press, Inc. 1983.
2 Y. Abe, M. Kamimoto, Y. Takashahi, R. Sakamoto, K. Kanari and T. Ozawa, Proc. 19th IECEC, 1114 (1984).
3 S. Zemczyzny and F. Rambach, Z. Anorg. Chem., 65 (1910) 403.
4 Th. W. Richards and W.B. Meldrum, J. Am. Chem. Soc., 39 (1917) 1816.
5 W. Schaefer, Neues Jahrb. Mineral., Geol., Paleontol., Beil, 43 (1920) 132.
6 H. Keitel, Neues Jahrb. Mineral., Geol., Paleontol., Beil, 52 (1925) Sect. A-38.
7 E. Elchagardus and P. Laffite, Bull. Soc. Chim. de France, 51 (1932) 1572.
8 G. M. Unzakov, DAN SSSR., 87 (1952) 791.
9 E. K. Akopov and A.G. Bergman, Izv. SFKhA, 25 (1954) 255.
10 E. L. W. Cook, Phase Diagram for Ceramists, Vol. 7., The Am. Soc. Inc., Westerville, Ohio, 1989.
11 C. Solomons, J. Goodkin, H. J. Gardner and G. J. Janz, J. Phys. Chem., 62 (1958) 249.
12 N. M. Furman, Standard Methods of Chemical Analysis, 6th edn. Van Nostrand Comp. Princeton, New Jersey, 1968.
13 JANAF Thermochemical Tables, Third Edn. Part 1, Al-Co. Amer. Chem. Soc., New York, 1986.
14 C. J. Raseman, H. Susskind, G. Farber, W. E. McNulty and F. J. Salzano, Declass. Rep. U.S. Atom Energ. Commn., BNL 627 (1960).