Thermochimica Acta, 121 (1987) 193–202
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

INVESTIGATION OF LATENT HEAT-THERMAL ENERGY STORAGE MATERIALS. IV. THERMOANALYTICAL EVALUATION OF BINARY EUTECTIC MIXTURES OF NaOH WITH LiOH OR KOH *

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(Received 5 January 1987; in final form 29 January 1987)

ABSTRACT

Differential scanning calorimetry is used to measure the heat capacity and heat of fusion of binary eutectic mixtures of NaOH with LiOH or KOH, which are promising materials for latent heat-thermal energy storage materials. These binary mixtures are concluded to be useful for thermal energy storage, when residual water, which has a large influence on their thermal characteristics, is exclusively eliminated. The thermophysical data obtained are also useful in R&D of the technology as well as design of the equipment.

INTRODUCTION

In the present series [1–3], we have reported on thermoanalytical investigations of three organic materials, i.e., polyethylene, urea and pentaerythritol, for latent heat-thermal energy storage. The latent heat-thermal energy storage has advantages over the other schemes of thermal energy storage because of its heat release at constant temperature and of technical feasibility; its energy density is also higher than conventional sensible heat-thermal energy storage. These three organic materials were selected by comprehensive screening based on compilations of thermodynamic data and materials costs. The others selected were all inorganic materials [4,5].

By thermoanalytical evaluation of the organic materials, polyethylene and pentaerythritol were found to be very useful, mainly because of large latent heat, a small supercooling, good thermal stability and good compatibility with heat transfer fluids. A prototype equipment [6,7] and a lab-scale apparatus [8] for thermal energy storage have been constructed by using these materials, to develop latent heat-thermal energy storage technology.

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* Dedicated to Professor W.W. Wendlandt in honor of his contribution to thermal analysis on the occasion of his 60th birthday.

Their operating temperatures are about 410 and 460 K for polyethylene and pentaerythritol, respectively.

To develop equipment to be operated in a higher temperature range, inorganic materials should be considered. From the above-mentioned screening, binary eutectic mixtures of LiOH, NaOH and KOH were preliminarily selected in a temperature range from 430 to 500 K, and binary eutectic mixtures and compounds of NaOH with $NaNO_3$ or $NaNO_2$ were also selected in a higher temperature range up to 570 K [5].

In this screening, the heats of fusion were roughly estimated on the assumption that the entropy change of fusion of the mixture is equal to the sum of the entropy changes of fusion and transition of the components. For the selected materials, therefore, the heats of fusion of the mixtures should be measured, in addition to observing the dynamic behavior of the fusion and crystallization, such as supercooling. Thermoanalytical techniques, such as differential scanning calorimetry (DSC), differential thermal analysis and thermogravimetry were applied to this purpose. The preliminary results on the three binary eutectic mixtures of the hydroxides were reported elsewhere [9], and two eutectic mixtures of LiOH–NaOH and NaOH–KOH were concluded to be useful in the temperature ranges around 490 and 440 K, respectively. Residual water, however, has a large influence on the temperature and heat of fusion, so that it is essential to eliminate the residual water exclusively. On the other hand, the other binary eutectic mixture of LiOH and KOH was not selected because its residual water is hard to eliminate and the melting temperature of this mixture (503 K) is close to that of the less expensive mixture LiOH–NaOH.

Precise heats of fusion were obtained by changing both the sample treatment prior to the measurements and the calorimetric method [10]. Specific heat capacities have also been measured. The results are reported in this paper.

EXPERIMENTAL

Apparatus

A Perkin-Elmer DSC (type II) was used to measure latent heat and specific heat capacity and also for observations of the dynamic behavior. The DSC measurements were carried out under nitrogen flow at heating and cooling rates of 5 K min^{-1}.

A synthetic sapphire disk (27.87 mg) supplied by Perkin-Elmer was used as a standard for measurements of specific heat capacity and heat of fusion. This new method for measuring latent heat was reported elsewhere [10], and is described briefly below. The usual DSC method of heat capacity measurement was applied to the temperature range of transformation, and the measured apparent heat capacity was integrated to obtain the enthalpy increase. Latent heats were estimated from the difference at the extrapolated onset temperature between the linear enthalpy increase in the lower temperature range and that in the higher temperature range [10].

The acquisition and processing of data and the control of the DSC apparatus were carried out with a personal computer (HP-9816S) and a data acquisition/control unit (HP-3497A).

Because of corrosion and wettability of the hydroxides, sample containers made of aluminum, platinum and quartz can not be used; the hydroxides corrode the containers and they also creep up the inner wall of the container. A new sample container was made of polytetrafluoroethylene. It is an open pan, of diameter 7 mm and depth 2.5 mm.

The new sample containers made of polytetrafluoroethylene were shown to be applicable to measurements of latent heats and specific heat capacities, and the inaccuracy was found to be less than 2% [10]. Because of crystalline transitions and the fusion of polytetrafluoroethylene (about 290, 300 and 600 K), the thermoanalytical measurements were limited to between 323 and 573 K.

Materials

The hydroxides used are $LiOH \cdot H_2O$ (guaranteed grade, Kanto Chemicals Co. Ltd.), NaOH and KOH (both guaranteed grade, Showa Chemicals Co. Ltd.). The hydroxide and carbonate contents of these reagents were analyzed by acid–base titration, using a potentiometric titration apparatus (Metrohm E 336) with a glass electrode and 0.1 mol l^{-1} HCl solution. The results are shown in Table 1. The reagents were used as received. The mixtures were made by weighing the components in an ambient atmosphere and heating them at ~ 573 K for ~ 5 h in nitrogen, and they were kept in a vacuum desiccator. Each sample was weighed into the DSC sample container in an ambient atmosphere and set into the DSC immediately. Prior to DSC measurements, the specimen was heated to 573 K at 5 K min^{-1} in the DSC, kept at that temperature for ~ 2 h and cooled at 5 K min^{-1} to ambient temperature under a flow of dry nitrogen.

TABLE 1

Analytical results of hydroxides

Substance	Hydroxides (wt%)	Carbonates (wt%)
LiOH	96.8	1.2
NaOH	95.6	2.5
KOH	84.4	2.7

RESULTS AND DISCUSSION

As mentioned above, residual water greatly influences the thermophysical characteristics of the mixture; its presence remarkably decreases the heat of fusion, and it can be detected by additional peaks around 350 K in the DSC curve. Thus the presence of residual water is checked by observing the additional peaks.

After confirming elimination of the residual water, heat capacity measurement was begun. The measurement was made at intervals of 50 K, each interval overlapping the next by 10 K. Thus, continuity of the data was confirmed. In the temperature range of the transformation, the measurement was continued to steady state after the transformation, as described elsewhere [10]. The specific heat capacity was determined at 1 K intervals for NaOH. For the mixtures, 0.25 K intervals were used for the transformation regions and 0.5 K intervals for the other regions.

The measured heat capacity of NaOH at 5 K intervals is given in Table 2, where C_{pr}, C_{ps} and C_{pl} are raw data from the DSC measurements, the heat capacity calculated by the following regression equation based on the raw data and the heat capacity reported in the literature [11], respectively. The regression equation obtained from the raw data at 1 K intervals is:

$$C_p(\mathrm{J\,g^{-1}\,K^{-1}}) = 1.0279 + 0.001443T \text{ for } 330\text{–}505 \text{ K} \qquad (1)$$

The raw data obtained at every 1 K are plotted in Fig. 1, where the previously reported values [11] are also shown. The cause of the small peak at ~ 520 K is not known at the present, but may be due to impurities. As is

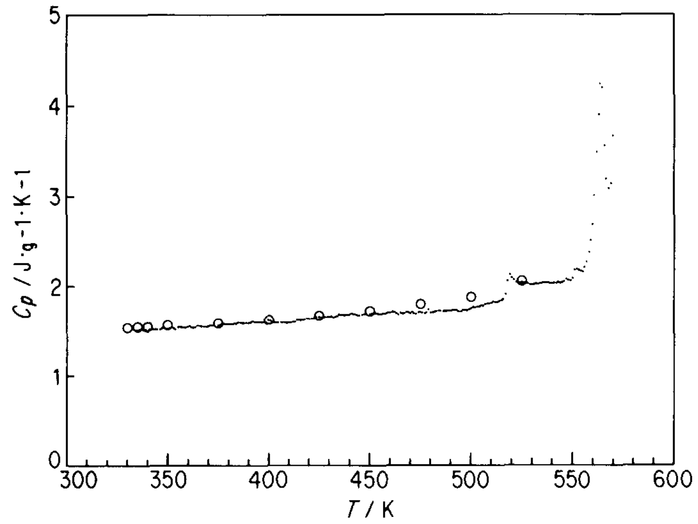

Fig. 1. Specific heat capacity of NaOH. (○) Data reported in ref. 11.

TABLE 2

Specific heat capacity of NaOH and eutectic mixtures (J g^{-1} K^{-1})

T (K)	NaOH			NaOH–KOH		LiOH–NaOH	
	C_{pr}	C_{ps}	C_{pl}	C_{pr}	C_{ps}	C_{pr}	C_{ps}
330	–	1.504	1.539	–	1.267	–	1.699
335	1.51	1.511	1.547	1.28	1.281	1.73	1.713
340	1.52	1.519	1.553	1.30	1.287	1.74	1.728
345	1.52	1.526	–	1.30	1.292	1.75	1.742
350	1.53	1.533	1.564	1.29	1.298	1.75	1.756
355	1.54	1.540	–	1.31	1.304	1.78	1.770
360	1.55	1.547	–	1.36	1.309	1.78	1.784
365	1.56	1.555	–	1.33	1.329	1.80	1.798
370	1.56	1.562	–	1.35	1.342	1.82	1.812
375	1.57	1.569	1.593	1.36	1.354	1.82	1.826
380	1.58	1.576	–	1.37	1.366	1.83	1.840
385	1.59	1.583	–	1.38	1.378	1.84	1.854
390	1.60	1.591	–	1.40	1.391	1.86	1.868
395	1.60	1.598	–	1.38	1.403	1.88	1.882
400	1.62	1.605	1.625	1.41	1.415	1.89	1.896
405	1.59	1.612	–	1.42	1.427	1.90	1.910
410	1.59	1.620	–	1.43	1.440	1.91	1.924
415	1.63	1.627	–	1.45	1.452	1.93	1.938
420	1.63	1.634	–	1.47	1.464	1.94	1.952
425	1.66	1.641	1.668	1.49	1.476	1.95	1.966
430	1.66	1.648	–	1.51	1.489	1.95	1.980
435	1.68	1.656	–	melting region		2.02	1.994
440	1.69	1.663	–			2.02	2.008
445	1.68	1.670	–			2.03	2.023
450	1.69	1.677	1.725			2.05	2.037
455	1.69	1.684	–			crystalline	
460	1.71	1.692	–			transition and	
465	1.70	1.699	–			melting region	
470	1.70	1.706	–	1.83	1.811		
475	1.71	1.713	1.798	1.81	1.811		
480	1.70	1.721	–	1.83	1.812		
485	1.72	1.728	–	1.80	1.812		
490	1.73	1.735	–	1.81	1.812		
495	1.72	1.742	–	1.79	1.812		
500	1.75	1.749	1.880	1.80	1.812		
505	1.78	1.757	–	1.83	1.812		
510	crystalline		–	1.82	1.812	2.83	2.806
515	transition and		–	1.79	1.812	2.81	2.813
520	melting region		–	1.77	1.812	2.82	2.821
525			2.063	1.81	1.813	2.84	2.829
530				1.81	1.813	2.83	2.837
535				1.79	1.813	2.81	2.844
540				1.83	1.813	2.87	2.852
545				1.82	1.813	2.85	2.860
550				1.84	1.813	2.87	2.867
555				1.84	1.813	2.90	2.875
560				1.84	1.813	2.89	2.883
565				1.82	1.813	2.87	2.890
570				1.79	1.814	2.89	2.898
575				–	1.814	–	2.906

clearly seen, the agreements are very good, and the accuracy of the present measurements is confirmed.

The eutectic mixture of NaOH and KOH

For the equimolar mixture of NaOH and KOH, the additional slight peak due to residual water was still observed in the heating DSC curve, because it is very difficult to remove all the water from KOH due to its very hygroscopic nature, and the measurement was made for this sample.

DSC curves of the equimolar eutectic mixture are reproduced in Fig. 2. The onset temperature on cooling is a little lower than the eutectic temperature at 444 K and a sharp peak was observed, indicating a slight tendency towards supercooling.

The heat of fusion and specific heat capacity were also measured. They are shown in Tables 2 and 3, and the raw data obtained at every 0.5 K are plotted in Fig. 3, where the small additional peak is clearly shown by the magnification. The regression equations for the specific heat capacity were obtained from the raw data at every 0.5 K:

$$C_p(\mathrm{J\,g^{-1}\,K^{-1}}) = 0.9047 + 0.001124T \text{ for } 330\text{–}360 \text{ K} \tag{2}$$

$$C_p(\mathrm{J\,g^{-1}\,K^{-1}}) = 0.4347 + 0.002451T \text{ for } 365\text{–}430 \text{ K} \tag{3}$$

$$C_p(\mathrm{J\,g^{-1}\,K^{-1}}) = 1.8005 + 0.000023T \text{ for } 470\text{–}575 \text{ K} \tag{4}$$

The interruption between 360 and 365 K is due to the above-mentioned additional peak. The coefficients in eqns. (2) and (3) are quite different from each other, but there is no discontinuity, as is seen in Table 2 and Fig. 3.

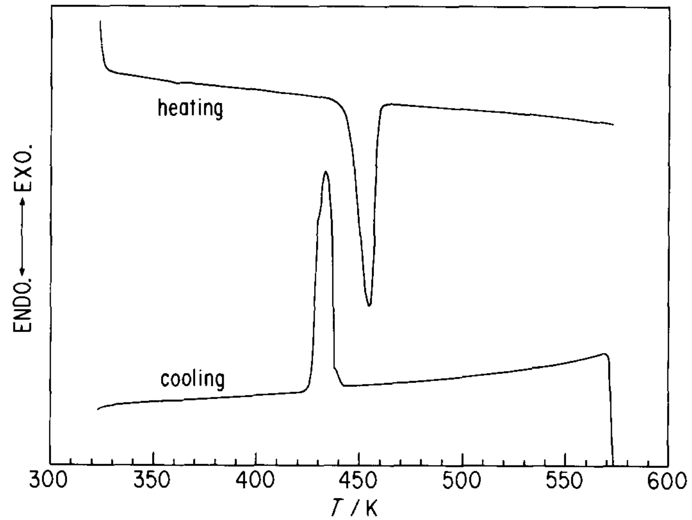

Fig. 2. DSC curves of a eutectic mixture consisting of NaOH (50 mol%) and KOH (50 mol%).

TABLE 3

Latent heat of eutectic mixtures

Mixture	Composition (mol%)	T_h (K)	T_c (K)	ΔH_h (J g^{-1})	ΔH_c (J g^{-1})	Note
NaOH-KOH	50-50	444	442	213	202	
LiOH-NaOH	30-70	458	446	58	54	transition
		488	489	290	278	fusion
				348	332	total sum

The heat of fusion is estimated to be 213 J g^{-1} on heating and 202 J g^{-1} from the peak area in the cooling DSC curve. They are, respectively, 93 and 88% of the heat estimated on the assumption of the additivity of the entropy changes of the fusion and transition of the components [5,12].

From these results, the eutectic mixture of NaOH and KOH is thought to be a promising material for latent heat-thermal energy storage in the temperature range around 440 K, provided that it is dry enough.

The eutectic mixture of LiOH and NaOH

The DSC curves obtained for the mixture of LiOH (30 mol%) and NaOH (70 mol%) are reproduced in Fig. 4. Two endothermic peaks beginning at 458 and 488 K are observed on heating, and an exothermic peak beginning at 489 K and a sharp exothermic peak beginning at 446 K are observed on

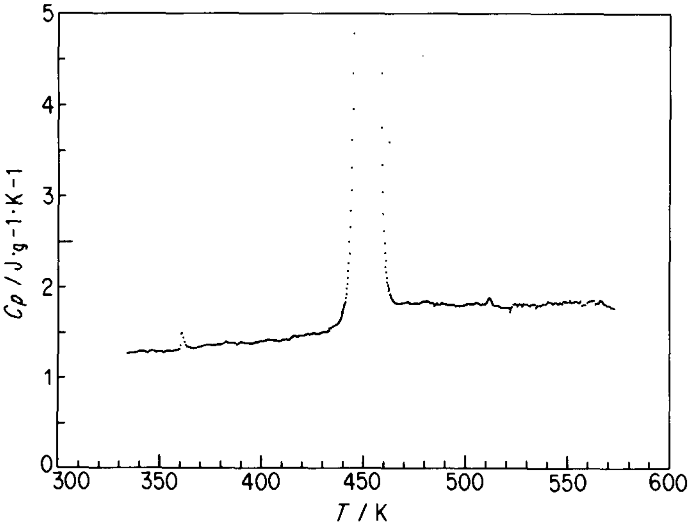

Fig. 3. Specific heat capacity of a eutectic mixture consisting of NaOH (50 mol%) and KOH (50 mol%).

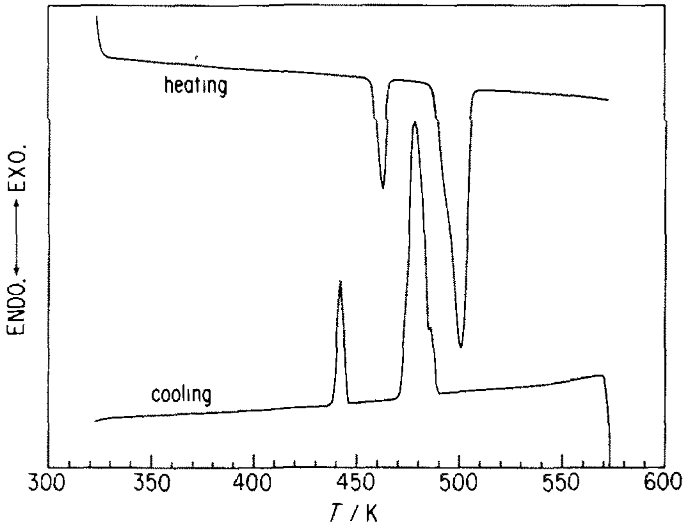

Fig. 4. DSC curves of a eutectic mixture consisting of LiOH (30 mol%) and NaOH (70 mol%).

cooling. These two peaks correspond well with the transition and the fusion previously reported in a phase diagram [13]. The extrapolated onset temperature in the cooling curve is somewhat higher than that in the heating curve. From this fact, the composition of the sample seems to be slightly different from that of the eutectic mixture. However, the melting temperature of the eutectic mixture measured from the extrapolated onset temperature in the heating curve is assumed to be correct, although the reported melting temperature is a little lower than the observed temperature. On the other hand, the extrapolated onset temperature of the transition in the cooling curve is 13 K lower than that in the heating curve, due to supercooling, whereas a supercooling tendency is not observed in the crystallization.

The heat capacity and heat of fusion of the mixture are given in Tables 2 and 3, and the raw data obtained from the DSC curve at every 0.5 K are shown in Fig. 5. The regression equations for the specific heat were calculated with the raw data obtained at every 0.5 K:

$$C_p(\mathrm{J\ g^{-1}\ K^{-1}}) = 0.7721 + 0.00281T \text{ for } 330\text{–}450 \text{ K} \tag{5}$$

$$C_p(\mathrm{J\ g^{-1}\ K^{-1}}) = 2.0198 + 0.00154T \text{ for } 510\text{–}575 \text{ K} \tag{6}$$

The heats of fusion and transition are estimated to be 290 and 58 J g^{-1}, respectively, while those in the cooling curve are measured from the peak areas to be 278 and 54 J g^{-1}, respectively. The sum of the heats in the heating curve is 348 J g^{-1} which is almost the same but slightly higher than the predicted value of 339 J g^{-1} calculated assuming additivity of the entropy changes for fusion and transition of the components [5,12]. Thus,

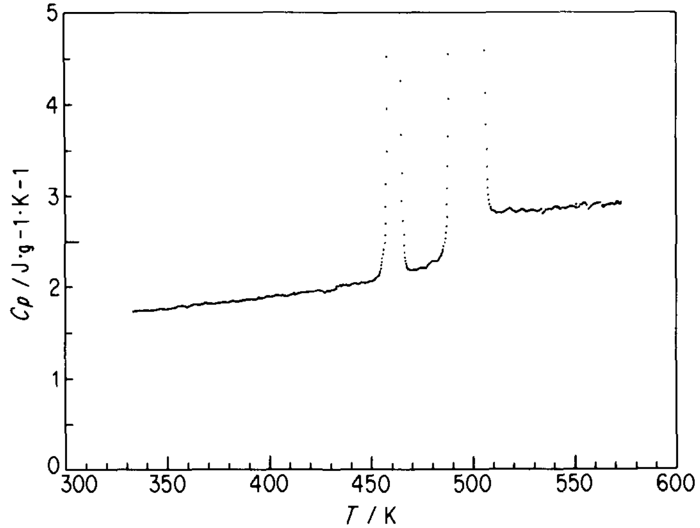

Fig. 5. Specific heat capacity of eutectic mixture consisting of LiOH (30 mol%) and NaOH (70 mol%).

the prediction based on assuming additivity of the entropy change of fusion is confirmed to be useful.

From the above observation, it can be concluded that the eutectic mixture is a promising material in the temperature range around 490 K.

CONCLUSION

The eutectic mixture of NaOH with LiOH or KOH can be used in latent heat-thermal energy storage equipment, which will be operated in the temperature range around 490 or 440 K, because of a high latent heat and low cost. It has recently been shown that these eutectic mixtures are so corrosive that even stainless steel does not withstand their melts. Explorative work is now in progress in our laboratory to modify this corrosive nature with additives such as nitrates.

It is also clearly seen in this report that the assumption of additivity of entropy changes of fusion and transition of the components is valid and effective for predicting the heat of fusion of a mixture for explorative screening of the materials.

REFERENCES

1 Y. Takahashi, R. Sakamoto, M. Kamimoto, K. Kanari and T. Ozawa, Thermochim. Acta, 50 (1981) 31.

2 M. Kamimoto, R. Sakamoto, Y. Takahashi, K. Kanari and T. Ozawa, Thermochim. Acta, 74 (1984) 281.
3 R. Sakamoto, M. Kamimoto, Y. Takahashi, Y. Abe, K. Kanari and T. Ozawa, Thermochim. Acta, 77 (1984) 241.
4 T. Ozawa, M. Kamimoto, R. Sakamoto, Y. Takahashi and K. Kanari, Denshi Gijutsu Sogo Kenkyujo Iho, 43 (1979) 289.
5 T. Ozawa, M. Kamimoto, R. Sakamoto, Y. Takahashi and K. Kanari, Denshi Gijutsu Sogo Kenkyujo Iho, 44 (1980) 707.
6 M. Kamimoto, Y. Abe, S. Sawata, T. Tani and T. Ozawa, Trans. ASME, J. Solar Energy Eng., 108 (1986) 282.
7 M. Kamimoto, Y. Abe, S. Sawata, T. Tani and T. Ozawa, Trans. ASME, J. Solar Energy Eng., 108 (1986) 290.
8 M. Kamimoto, Y. Abe, K. Kanari, S. Sawata, T. Tani and T. Ozawa, Proc. 21st Intersoc. Energy Conv. Eng. Conf., San Diego, CA, Am. Chem. Soc., 1986, p. 730.
9 Y. Takahashi, M. Kamimoto, R. Sakamoto, K. Kanari and T. Ozawa, Nippon Kagaku Kaishi, (1982) 1049.
10 Y. Takahashi, Thermochim. Acta, 88 (1985) 199.
11 L.E. Murch and W.F. Giauque, J. Phys. Chem., 66 (1962) 2052.
12 For example, D.D. Wagman, J.L. Tobe, E.S. Domalski and R.H. Schumm, American Institute of Physics Handbook, McGraw-Hill, New York, 3rd edn., 1972, pp. 4–222.
13 E.M. Levin, C.R. Robbins, H.F. McMurdie and M.K. Reser, Phase Diagrams for Ceramists, American Ceramic Society, Columbus, OH, 3rd edn., 1974; E.M. Levin, H.F. McMurdie and M.K. Reser, Phase Diagram for Ceramists 1975 Supplement, American Ceramic Society, Columbus, OH, 3rd edn., 1975.