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CALORIMETRIC STUDY OF THE REACTION BETWEEN FORMIC ACID AND N,N,N',N'-TETRAMETHYLETHYLENEDIAMINE FROM THE ASPECT OF THERMAL ENERGY STORAGE

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The attack by formic acid on the nitrogen electron pairs of N,N,N',N'-tetramethylethylenediamine leads to the stoichiometric salt or to many other complexes with different molar fractions. Physical and thermodynamic parameters of two adducts, obtained by calorimetric study, are discussed in terms of their use as potential phase change materials in thermal energy storage because of their large heat of fusion between 288 and 333 K.

Introduction

In our investigations concerning reversible reactions between carboxylic acids and Lewis bases, giving hydrogen-bonded complexes for applications in thermochemical energy storage at low temperature and atmospheric pressure, we first studied the reversible reaction between acetic acid and triethylamine, which gives a liquid complex at room temperature with the liberation of much heat [1–4]. The acetic acid self-association leads in this case to a non-stoichiometric complex with acid/amine = 1.6/1; this complex can be decomposed by heat absorption. First investigated by conventional thermal analysis, and then by dynamic analysis [5], this reaction can be used for energy storage from ambient temperature up to 423 K.

We continued our investigations of carboxylic acid-tertiary amine reactions by studying the reactions between other pairs [6]. Here, we present in-

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teresting results obtained by means of calorimetry in the reaction between formic acid HCOOH (AH) and the bifunctional N,N,N',N'–tetramethylethylenediamine $C_6H_{16}N_2$ (TMEDA) at different molar fractions. The heat of fusion was high for many mixtures, with melting points between 288 and 333 K.

Experimental

The formic acid (HCOOH) and N,N,N',N'–tetramethylethylenediamine (TMEDA) used, obtained from Aldrich Chemical Company, had purities of 98% and 99%, respectively.

The apparatus and experimental techniques were described previously [3]. The different HCOOH–TMEDA mixtures were conveniently prepared in a Calvet calorimeter [7, 8] by injecting TMEDA into the acid in the working cell, thereby allowing determination of the heat of the mixture and testing of the reproducibility of the reaction. A Setaram DSC 111 differential scanning calorimeter [9] was used to determine many thermophysical parameters of the different acid-amine mixtures, such as heat of fusion and melting point. The specific heats were determined for the liquid and solid states by means of stepwise programming. The values of these parameters were obtained at different heating rates between 0.25 and 2 $\deg\cdot\min^{-1}$.

For the solid state, the thermal conductivity was deduced from the diffusivity of heat obtained by the flash method [10, 11]. The density was determined for the liquid and solid states with a picnometer. The elementary compositions of the acid-amine mixtures were measured by the Microanalysis Center of Lyon (CNRS), France.

Results

In order to study the reaction between AH and TMEDA, a series of differential scanning calorimetry experiments was conducted on different binary AH/TMEDA mixtures, where the molar fraction X of formic acid was decreased from 1 to 0.5. Many mixtures for the same molar fraction have been used here, and we have ascertained the perfect reproducibility.

At molar fractions X from 1 to 0.85, the mixtures display no crystallinity; this is probably due to the presence of a eutectic point below 153 K, the limit temperature of the D. S. C. 111.

For values of X between 0.83 to 0.79, we obtained mixtures with melting points near room temperature and we here present the study of the mixtures with $X = 0.83$, 0.80 and 0.79.

For values of X between 0.78 and 0.69, the thermal analysis showed two peaks, cleanly separated, corresponding to two phases, 1 and 2. The melting point of phase 1 underwent a slight variation between 286 and 289 K, while the regular increase of the melting point of phase 2 from 313 to 323 K was observed. The ratio of the two observed melting enthalpies varied markedly with the molar fraction (see Figure). The melting enthalpies of the phases varied in the opposite direction, with a significant decrease in that of phase 1 as X decreased. After the filtration of these different mixtures, we identified (by thermal and elemental analyses) phase 2 as the stoichiometric salt A_2B (either AH/TMEDA = 2/1 or $X = 0.66$).

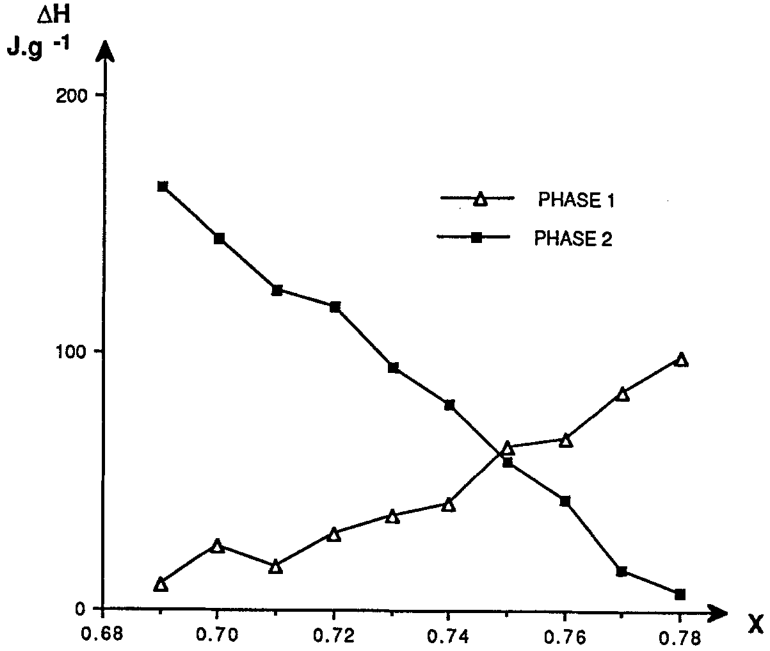

Fig. 1 Variation of melting enthalpies of phases 1 and 2 with molar fraction X of formic acid between 0.78 and 0.69.

As X was varied from 0.68 to 0.66, thermal analysis showed only one phase. Besides formation of the salt A_2B, we retained samples with $X = 0.68$.

For values of X lower than 0.65, the melting enthalpy of the single peak steadily decreased as the proportion of TMEDA in the mixture was increased; this decrease was a result of the lack of reaction between **A_2B** and the added TMEDA and of the insolubility of **A_2B** in TMEDA.

In Table 1, we report the remaining results for $X = 0.83$–0.66.

Table 1 Melting enthalpy ΔH_m and temperatures of crystallization T_c and melting T_m for different molar fractions X of HCOOH.

X	T_m, K	T_c, K	ΔH_m, $J \cdot g^{-1}$
0.83	282.3	276.5	72
0.80	291.3	285.7	132
0.79	287.4	285.7	93
0.68	327.1	321.5	185
0.66	333.1	327.3	193

From the results in Table 1, the following points deserve special attention:

The systematic study in the range $X = 0.83$–079 has contributed to the observation of a rupture at $X = 0.80$ in the values of the melting enthalpies and the melting points (see Table 1). Special mention must be made of the exceptional enhancements of the enthalpy and melting point for the molar fraction $X = 0.80$. This rupture can be rationalized by assuming the formation of a complex **A_4B** (AH/TMEDA = 4/1), dimeric formic acid binding to each electron pair of the two nitrogens of TMEDA.

The melting point at room temperature and the high melting enthalpy obtained for **A_4B** are of interest as concerns the potential use of **A_4B** as a phase change material (PCM), and a more complete thermal analysis was performed (see Table 2).

For $X = 0.66$, the reaction between AH and TMEDA fits the general patterns of carboxylic acid-amine reactions, which proceed stoichiometrically to give a solid adduct **A_2B** (AH/TMEDA = 2/1). Indeed, the elemental analysis of the isolated adduct (46.03% of C, 13.19% of N, 9.7% of H) agreed well with the values calculated for the salt **A_2B** with a molecular mass of 208.27 g.

These first results indicate that **A_2B** and **A_4B** are potential PCMs; studies were undertaken to support this. For **A_2B**, the heat balance of the reaction between AH and TMEDA at 298 K includes the reaction enthalpy and the enthalpy of crystallization; this latter being obtained by differential scanning calorimetry, we deduced that the reaction enthalpy is -54.27 $kJ \cdot mol^{-1}$ or 261 $J \cdot g^{-1}$.

Table 2 Thermophysical data on A_2B and A_4B

	T_f, K	T_c, K	ΔH_f, $J \cdot g^{-1}$	$C_{p(s)}$, $J \cdot g^{-1} \cdot K^{-1}$	$C_{p(l)}$, $J \cdot g^{-1} \cdot K^{-1}$	$\lambda_{(s)}$, $W \cdot m^{-1} \cdot K^{-1}$	$\rho_{(s)}$, $kg \cdot m^{-3}$	$\rho_{(l)}$, $kg \cdot m^{-3}$	S. D., $kWh \cdot m^{-3}$
A_2B	333.1	327.3	193	1.65	2.7	0.306	1130	980	60.0
A_4B	291.3	285.7	132	2.05	2.12	0.20	1194	1071	43.8

Abbreviations: T_f: melting point, T_c: crystallization point, ΔH_f: melting enthalpy, C_p: specific heat, λ: thermal conductivity, ρ: density, S. D.: storage density, with s for solid and l for liquid.

Some physical constants of the salt A_2B and the complex A_4B are given in Table 2, which lists the thermodynamic parameters. The lowest supercoolings were obtained for a scan rate of 0.25 $deg \cdot min^{-1}$.

We observed a volume variation of about 15.3% for the liquid-solid change of A_2B a good diffusibility of $0.164 \cdot 10^{-6}$ $m^2 \cdot s^{-1}$, and therefore a good thermal conductivity, and a significant storage density as compared with other compounds such as salt hydrates, paraffins and especially organic compounds [12–13]. Thus A_2B appears to be a PCM of potential in thermal energy storage, but its use is contingent on its thermal stability.

Since we observed a fall in the melting heat and in the diffusibility ($0.082 \cdot 10^{-6}$ $m^2 \cdot s^{-1}$) for A_4B, we obtained here a new potential PCM at room temperature with reasonable conductivity and storage density.

A series of experiments was undertaken to test the stabilities of A_2B and A_4B, and in all cases we observed perfect stability of the melting temperature and of the melting enthalpy after 450 cycles of melting-crystallization.

Conclusions

Via the use of differential scanning calorimetry, with variation of the molar fraction of HCOOH in the mixtures in 1% steps, the thermal analysis of formic acid-N,N,N',N'–tetramethylethylenediamine binary mixtures revealed the formation of two adducts. The first stoichiometric salt, has thermophysical parameters, and especially the melting enthalpy, which favor its potential use as a PCM. In view of melting temperature, the second adduct is a new potential PCM at room temperature. Although the goal of these investigations was to provide applications of acid-amine couples in thermal energy storage, this study should make a contribution to a subsequent study of the binary phase diagram.

References

1 L. Elegant, M. Salman and Y. Schwob, Actes des XV J. C. A. T. Naples, (1984) 43.
2 L. Elegant, M. Salman and Y. Schwob, Actes des XVII J. C. A. T. Ferrara, (1986) 309.
3 M. Salman, Thesis, Nice, France, 1988.
4 L. Elegant, M. Salman and Y. Schwob, Thermochim. Acta, 130 (1988) 149.
5 N. Balbi, J. Chim. Phys., 86 (1989) 955.
6 N. Balbi, J. H. Balbi, L. Elegant and Y. Girault, J. Thermal Anal., in press.
7 E. Calvet, H. Prat, Microcalorimétrie: applications physico-chimiques et biologiques, Masson et Cie, Paris, 1956.
8 H. Brown, Biochemical Microcalorimetry, Academic Press, New York, 1969.
9 L. Elegant, Techniques de l'ingénieur, 7(1986) R 3010.
10 A. Degiovanni, Thesis, Lyon, France, 1975.
11 A. Degiovanni, Rev. Gén. Therm., 185, May 1977.
12 G. A. Lane, Solar Heat Storage: Latent Heat Materials, vol. 1, C. R. C. Press, 1983.
13 H. P. Grag, S. C. Mullik and D. K. Bhargava, Solar Heat Storage: Latent Heat Materials, Solar Thermal Energy Storage", D. Reidel Publishing Company, 1987.

Zusammenfassung — Bei der Einwirkung von Ameisensäure auf die Elektronenpaare von N,N,N',N'-Tetramethylethylendiamin entsteht ein stöchiometrisches Salz oder mehrere andere Komplexe mit unterschiedlichem Molenbruch. Es werden physikalische und thermodynamische Parameter zweier bei der kalorimetrischen Untersuchung erhaltenen Addukte hinsichtlich ihrer Verwendung als potentielle Phasenwechselsubstanzen bei der thermischen Energiespeicherung diskutiert, da sie im Bereich 288-333 K eine große Schmelz-wärme besitzen.