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CALORIMETRIC STUDY OF SOME CARBOXYLIC ACIDS LEWIS-BASES COMPLEXES IN VIEW OF THERMAL ENERGY STORAGE *

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ABSTRACT

This paper studies the equilibrium reaction between acetic acid and triethylamine induced by the formation of an H-bonded complex. These compounds were used as bulk reagents to form a complex in the liquid state. This type of reaction can be used in thermochemical energy storage at low temperature (from ambient temperature up to 423 K) and atmospheric pressure. Only one storage tank is required: the formation of the H-bond is an exothermic process, and this bond can be broken by heat absorption. Physical and thermodynamic parameters were determined by means of a Calvet calorimeter and a DSC 111 differential scanning calorimeter.

INTRODUCTION

Hydrogen bonding is an interaction between covalently bonded H-atom (A–H) and a region of high electron density around an electronegative atom or group of atoms (B), which can accept the proton [1]. Therefore, a carboxylic acid A–H (proton donor) reacts with tertiary amine B (proton acceptor), generally by a reversible process [2,3].

In such systems for thermal energy storage the formation of the H-bond is an exothermic process (discharge phase), whilst the dissociation of the H-bond is an endothermic process (storage phase) where the complex's bond is broken by heat absorption

$$\mathrm{A{-}H} + \mathrm{B} \underset{\text{storage}}{\overset{\text{discharge}}{\rightleftharpoons}} \mathrm{A{-}H} \cdots \mathrm{B}$$

Such reactions have already been studied by a number of authors [4–8] whose methods and applications were different from those described here.

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This work deals with an alternative method for storing thermochemical energy. Since our major interest is the thermal energy produced by this system, it was necessary to find the most profitable and readily producible pair of carboxylic acids and tertiary amines or diamines. It should be emphasized that throughout this investigation no solvent was used to increase storage density (by decreasing volume).

EXPERIMENTAL

Materials and instruments

In this study a Calvet calorimeter was used to determine the heat produced by the reaction. The reference cell was empty and similar to the working cell where the reaction took place; a syringe was used to inject the base upon the acid placed in this cell.

A Setaram differential scanning calorimeter DSC 111 was used to measure heat capacity and to study the thermal analysis of the complex.

The acetic acid (AH) and triethylamine (B) used were $\geqslant 99.5\%$ pure.

Calorimetric measurements

Maximum heat with respect to minimum mass was sought in the reaction between acetic acid (AH) and triethylamine (B). The experimental result was found to be at 298 K

$$n\mathrm{AH} + \mathrm{B} \underset{\text{endo}}{\overset{\text{exo}}{\rightleftharpoons}} (\mathrm{AH})_n\mathrm{B}$$

where $n = 1.6$ instead of 1. This value of 1.6 confirmed by numerous experiments shows that though there is acetic acid in excess, it is not free because no heat can be detected by the calorimeter upon the addition of more triethylamine.

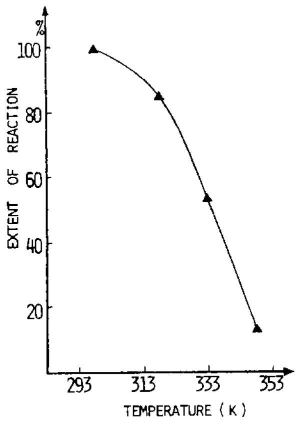
For $n = 1.6$ the mean molecular weight of the liquid complex was found to be 196.27 g mol^{-1} (Table 1).

The enthalpy of the reaction ΔH can be obtained from

$$n_c(T) = \frac{Q(T)}{\Delta H} \tag{1}$$

where $Q(T)$ is the heat released and detected by the calorimeter at different temperatures, and $n_c(T)$ is the number of moles produced at different temperatures. Thus $\Delta H = -32.7$ kJ mol^{-1}.

The reaction was studied at different temperatures in order to determine the extent of the reaction $\alpha(T)$. The ratio 1.6 moles of acetic acid to 1 mole of triethylamine was found to be constant whatever the temperature (having been tested through numerous experiments).



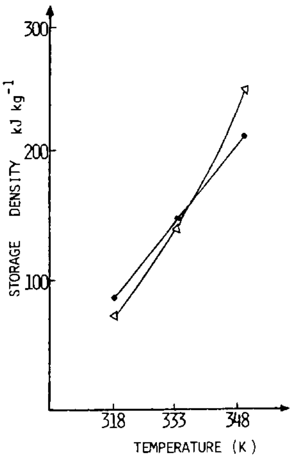


Fig. 1. Extent of reaction of acetic acid + triethylamine (1.6 : 1) at different temperatures.

Fig. 2. The evolution in the storage density of the mixture acetic acid + triethylamine (1.6 : 1) (△) together with the evolution in the same quantity of water (■) within the same temperature interval.

The enthalpy of an equilibrium reaction is given by

$$\left(\frac{\partial \Delta H}{\partial T}\right)_{\mathrm{p}} = \Delta C_{\mathrm{p}} \tag{2}$$

As the value of the heat capacity C_p is constant, ΔC_p is equal to zero in the temperature interval explored. Consequently from eqn. (2) the enthalpy of this equilibrium reaction is constant. Equation (1) can be used to calculate the number of moles of the complex produced at different temperatures. As the temperature increases, the number of moles produced decreases with the decrease in heat released by the reaction.

Figure 1 gives the extent of the reaction $\alpha(T)$, which was found by the relation

$$\alpha(T) = \frac{Q(T)}{Q(298)} = \frac{n_c(T)}{n_c(298)} \tag{3}$$

at 318, 333 and 348 K with respect to the reference state at 298 K. This figure also shows the reaction's theoretical reversibility which can be used for the calculation of useful energy between 298 and 348 K, and shows that 87% of the reaction's heat can be utilized between these temperatures.

It is clear that whenever the temperature is increased in such a system, the amount of sensible heat (the energy due to the specific heat of the components) that can be stored within a temperature interval ΔT must be taken into account. A DSC 111 differential scanning calorimeter was used to determine the specific heat of this liquid complex C_p, (equal to 1.8 J g^{-1}

TABLE 1

Physical and thermodynamic parameters for the mixture acetic acid + triethylamine (1.6 : 1)

Molecular weight ($g\ mol^{-1}$)	Specific heat ($J\ g^{-1}\ K^{-1}$)	Density ($kg\ m^{-3}$)	Enthalpy of reaction ($kJ\ mol^{-1}$)	Heat density ($kJ\ kg^{-1}$)	Storage density ($kW\ h\ m^{-3}$)
196.27	1.8	975	−32.7	235	63.6

K^{-1}). The density of this complex was determined at room temperature by means of a pycnometer, resulting in a value of 975 kgm^{-3}.

RESULTS

Certain physical constants of the complex are given in Table 1, which summarizes the thermodynamic parameters and the energy aspects of the reaction.

Figure 2 shows the evolution in storage density of this reaction as well as the evolution of water within the same temperature interval.

The storage density of such a system may be given by

$$\frac{[1-\alpha(T)]}{\Delta T}\frac{\Delta H}{M_c} + C_p(\text{complex}) \qquad (\text{J g}^{-1}\ \text{K}^{-1}) \tag{4}$$

where ΔH is in J mol^{-1}, M_c is in g mol^{-1}, and C_p is in J g^{-1} K^{-1}.

DISCUSSION

The 1.6 : 1 ratio in the reaction between acetic acid and triethylamine is explained by a secondary phenomenon known as self-association in addition to the main phenomenon of H-bonding.

Most of the discussions involving H-bonding have stressed the existence of complexes formed by one donor molecule and one acceptor molecule (a 1 : 1 ratio); yet such molecules can self-associate through H-bonds in two or more different ways to form various complex species which may coexist in various series of complicated equilibria [1].

It is obvious that the analysis of such systems requires the determination of many equilibrium constants. Rigorous treatments using IR absorption measurements are possible in principle but difficult to carry out [9]. However, this aspect of the reaction is not within the scope of the present study.

We attempted to draw the binary phase diagram (melting curve) of the mixture acetic acid/triethylamine by means of a DSC 111 differential scanning calorimeter. This study can also give us other indications, such as the nature of the complex which may be present corresponding to the top of the melting curve, and the phase or the phases existing in such a phase diagram.

We were unable to crystallize the samples down to 153 K at different molar fractions x: $x(\mathrm{AH}) = 0.9$–0.6. This inability to crystallize can be accounted for by the increase in the complex viscosity due to the increase in molecular weight arising from the formation of the H-bonding [1] and also by the small size of the sample tested (about 100 mg), which was kept in a closed system black box, where the shaking of the sample to speed up solidification was impossible.

An experiment was carried out using approximately 10 g of the mixture acetic acid + triethylamine (1.6 : 1) contained in a test tube immersed in a low temperature thermostatic medium (from room temperature down to about 83 K). A phase transition from liquid to paste, then to the solid state (about 103 to 93 K), was observed. The transition from liquid to the paste state was determined by DSC 111 thermal analysis (Fig. 3). Three different molar fractions x were used in this test: $x(\mathrm{AH}) = 0.615$, 0.75, 0.83. In each case the same form of thermal analysis curves (thermograms) was found. The shape of these curves in differential thermal analysis (DTA) represents the second order transition [10], which means that no phase change occurs in this type of transition. The main characteristic of this transformation is that no two phases are ever present simultaneously.

Our interpretation of the results obtained with the DSC 111 is different from the results given by Kohler [7,8] which show a phase separation in the interval of molar fraction $x(\mathrm{AH})$ between 0.6 and 0.8, approximately the aggregation of 3 moles acetic acid + 1 mole triethylamine. This is due to the strong attractive interaction between a 1 : 1 complex acid + amine and the cyclic dimer of acetic acid.

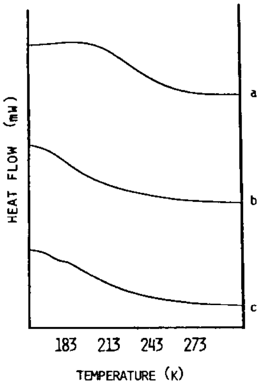


Fig. 3. Thermograms of the compositions (a) x(acetic acid) = 0.615, (b) x(acetic acid) = 0.75, (c) x(acetic acid) = 0.83.

Figure 2 shows the storage density evolution of the reaction in comparison with that of water. It can be seen that between 323 and 348 K ($\Delta T = 25$ K) about 65% of the reaction heat will be used, that is 41 kW h m^{-3} can be used from this system, while only 29 kW h m^{-3} can be used in the case of water for the same temperature interval.

CONCLUSIONS

The study of this type of interaction is still at laboratory level. We are looking for other pairs of carboxylic acid–tertiary amines or diamines; these reactions have the advantage in thermal energy storage of requiring only one storage tank for the mixture. Neither differential pressure nor reagent separations as chemical heat pump are required [11]. In this respect, it is similar to storage systems using sensible or latent heat.

The pair considered in this investigation produces a liquid complex (both reagents and product still in their liquid state). Another reaction between formic acid and N,N,N',N'-tetramethylethylenediamine, however, produces a solid complex which can be used as phase change material in thermal energy storage [12]. The use of the phase diagram provides interesting indications which will be the subject of another paper.

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