Thermochimica Acta, 7 (1973) 95–101

A SIMULTANEOUS ELECTRICAL CONDUCTIVITY–DIFFERENTIAL THERMAL ANALYSIS APPARATUS

Z. HALMOS* AND W. W. WENDLANDT**
Department of Chemistry, University of Houston, Houston, Texas 77004 (U.S.A.)
(Received 1 May 1973)

ABSTRACT

A highly sensitive simultaneous electrical conductivity–differential thermal analysis apparatus is described. The apparatus can simultaneously record both the electrical conductivity and differential thermal analysis curves of a sample under the same conditions of furnace heating rate and atmosphere. Application of the apparatus is illustrated by curves of $CuSO_4 \cdot 5H_2O$, $[Co(NH_3)_5H_2O]Br_3$ and Cu_2HgI_4.

INTRODUCTION

The thermal analysis technique of electrical conductivity (EC) has proven to be a convenient method for the detection of quadruple points (i.e., the temperature at which four phases are present in the system) in metal salt hydrate systems[1,2]. Since differential thermal analysis (DTA) has also been used for quadruple point detection[3], the combination of these two techniques into a single apparatus should be most useful. Thermal measurements can then be made on the same sample under identical conditions of temperature change and furnace atmosphere.

Simultaneous EC–DTA instruments have been described by David[4] and Berg and Burmistrova[5] while EC–DSC (differential scanning calorimetry) measurements can be made using the sample holder developed by Carroll and Mangravite[6]. Chiu[7] described an apparatus in which EC curves could be obtained along with DTA (and other measurements) but two or more separate samples had to be employed.

The purpose of this investigation is to describe a simultaneous EC–DTA apparatus which provides essentially the same experimental conditions as are found in a typical DTA apparatus yet has the capability of obtaining EC data as well. Both types of data are obtained from the same sample under identical controlled temperature and furnace atmosphere conditions. A temperature range of 25–555°C can be covered using a highly sensitive DTA system and EC detection system ($I = 10^{-2}$ to 10^{-7} μA).

---

*Present address: Department of Analytical Chemistry, The Technical University, Budapest, Hungary.

**To whom correspondence should be addressed.

EXPERIMENTAL PART

Description of apparatus

A cross-sectional view of the sample holder is shown in Fig. 1. The sample (and reference) container was constructed from a platinum crucible, 5 mm in diameter and 5 mm in height, which made contact with the junction of a thermocouple on the bottom. Since the thermojunction was in direct contact with the sample, it was coated with a thin layer of teflon (from an aerosol spray container). This limited the temperature maximum to about 320–340 °C; however, without the teflon the maximum temperature limit was about 550 °C. To measure the electrical conductivity of the sample, one electrode was welded to the sample container while the other was a platinum wire which was introduced into the sample through a hole in the teflon cover. The depth of sample contact by this electrode was adjustable by means of a screw device. Two modes of operation were used; in one, no cover was used for the sample container while the other was a tight fitting cover for self-generated atmosphere studies. The reference holder was similar to the above in order to maintain the same heat capacity but contained aluminum oxide rather than a thermally active sample.

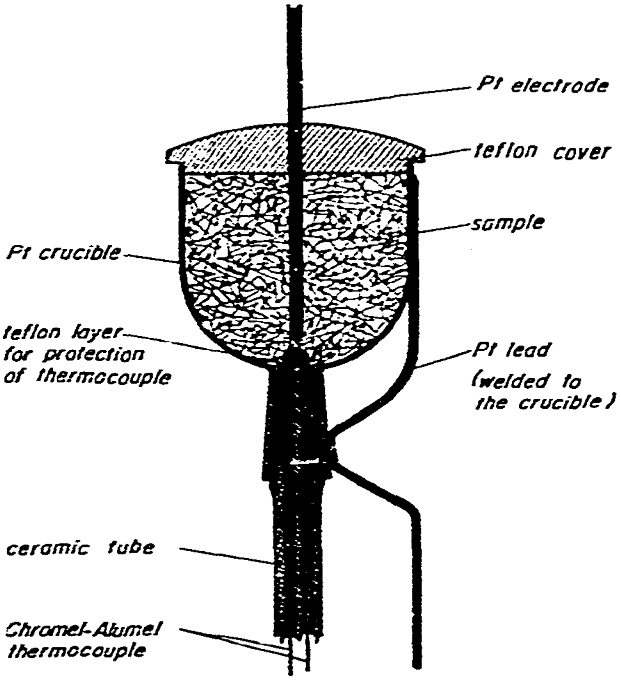

Fig. 1. EC–DTA sample holder cross-section.

A cross-sectional view of the complete EC–DTA cell is shown in Fig. 2.

The heater block (8), which was machined from aluminum, contained a 500 W heater cartridge (11) located in the center of the block. Two cylindrical chambers located on each side of the heater housed the sample and reference container, res-

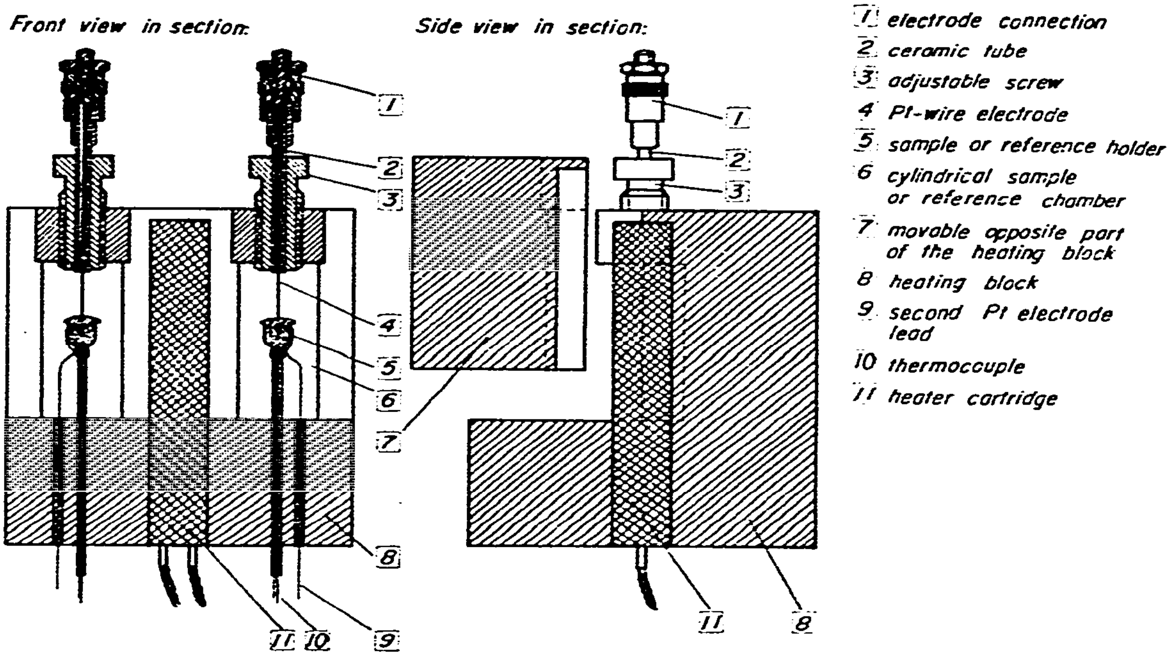

Fig. 2. Cross-section of EC–DTA cell.

pectively. Care was taken to position each container at exactly the same distance from the heater. It was found from previous DTA studies[8] that the diameter of the container cavities greatly influenced the DTA curves obtained. In this cell, they were 18 mm in diameter by 38 mm in depth.

The upper electrode (4) was electrically insulated from the block by a ceramic tube (2) and sleeve (3) and was attached to an adjustable screw device (1) and an electrical connector. To aid in sample loading and to remove the spent sample, one half of the block (7) was removable. It was always placed into position when EC–DTA measurements were made.

The cell block was supported by three 5 mm diameter ceramic rods which were attached to a 12 mm thick circular aluminum base. To insulate the cell, a Marinite enclosure was used which was approximately 10 mm thick. It could be placed over the entire cell during the heating cycle and could be removed to aid in the cooling of the cell back to room temperature. All electrical connections were made on a connector located on the base of the cell. Due to the cell construction, it was not possible to control the furnace atmosphere in any manner, hence, most of the runs were made in the self-generated atmosphere mode.

A schematic diagram of the entire EC–DTA apparatus is shown in Fig. 3.

The DTA system components were conventional and consisted of a Leeds and Northrup Model 9835-B d.c. microvolt amplifier and a Hewlett–Packard Model 135A X–Y recorder. For the EC system, a 1–25 V variable voltage regulated d.c. power supply was used along with an E–H Research Laboratories Model 240 record-

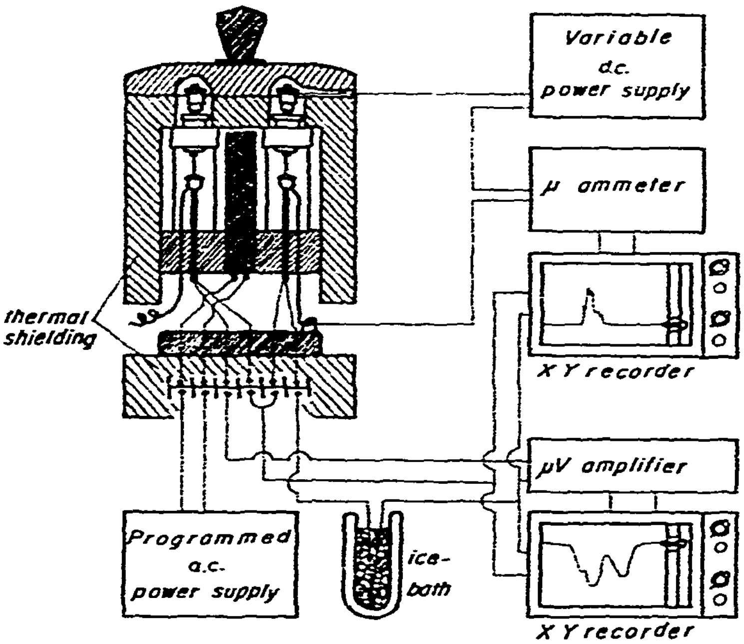

Fig. 3. Schematic diagram of entire EC–DTA apparatus.

ing micro-microammeter and a Hewlett-Packard Model 7035B X–Y recorder. The furnace temperature programmer was a motor driven variable voltage transformer type which permitted the use of linear heating rates from 2 to 20°C min^{-1}.

The DTA baseline of the system could be reproduced to ±0.06°C and gave a very flat, stable recorded curve. At d.c. current levels less than 1×10^{-8} μA, the EC curve showed some electrical noise; at higher current levels, no noise appeared in the curve. Typical EC and DTA baselines are illustrated in Fig. 4.

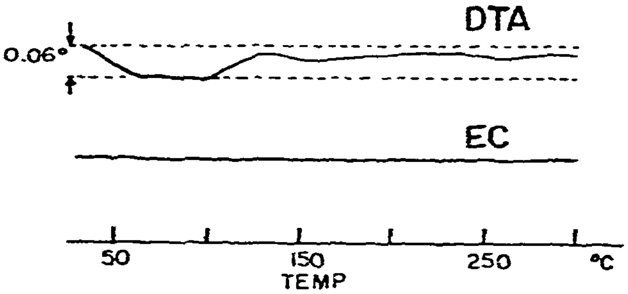

Fig. 4. Typical EC and DTA baselines for apparatus.

A typical procedure for a run consisted of the following: A powdered sample of 20–100 mg in mass was placed in the sample container and lightly packed in place. The container cover and upper electrode were then put into position and the cell assembled and enclosed by the Marinitec over. A d.c. voltage of about 6 V was used in the electrical circuit for the EC measurements. After allowing the electrical system to come to equilibrium, the programmer was activated using a heating rate of 5°C min^{-1}. The EC and DTA curves were recorded simultaneously using the two separate X–Y recorders. After completion of the heating cycle, the insulating cover was removed and the cell permitted to cool to room temperature at which time the spent sample was removed from the sample container.

RESULTS AND DISCUSSION

The operation and use of the apparatus are illustrated by the EC–DTA curves of $CuSO_4 \cdot 5H_2O$, $[Co(NH_3)_5H_2O]Br_3$ and Cu_2HgI_4. The EC–DTA curves of $CuSO_4 \cdot 5H_2O$ are shown in Fig. 5.

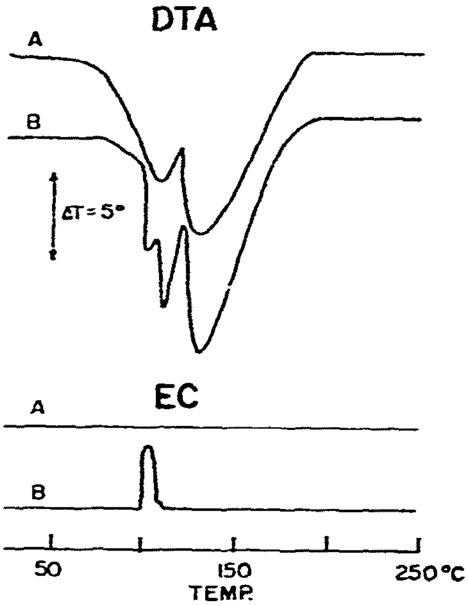

Fig. 5. EC–DTA curves of $CuSO_4.5H_2O$; (A) Non-self-generated atmosphere; (B) Self-generated atmosphere.

Two modes of operation of the apparatus are indicated: mode (A) which is an open sample container or non-self-generated atmosphere; and mode (B) which is a self-generated type of atmosphere. In mode (A), only one major peak and a shoulder peak are indicated in the DTA curve while no EC curve peaks are evident. Due to the limited maximum temperature employed, the curve peaks are those due to the deaquation reactions involving the loss of four moles of water per mole of salt, as previously described[1,9]. In mode (B), the self-generated atmosphere causes the formation of a liquid water phase which appears as another shoulder peak on the DTA curve and also a EC curve peak. The system under these conditions exhibits a quadruple point which has previously been reported[1,3,9,10].

Another example of a system which exhibits a quadruple point is that of [Co $(NH_3)_5H_2O]Br_3$, which is illustrated in Fig. 6. This compound has been previously studied by several investigators[9,11] who explained the DTA curve in terms of a deaquation–anation reaction. Evolution of the coordinated water is shown by the shoulder peak on the DTA curve and also by the EC curve peak which occurs in the

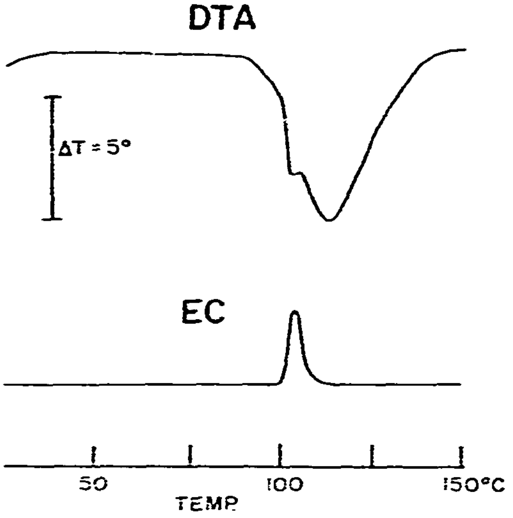

Fig. 6. EC–DTA curves of $[Co(NH_3)_5H_2O]Br_3$.

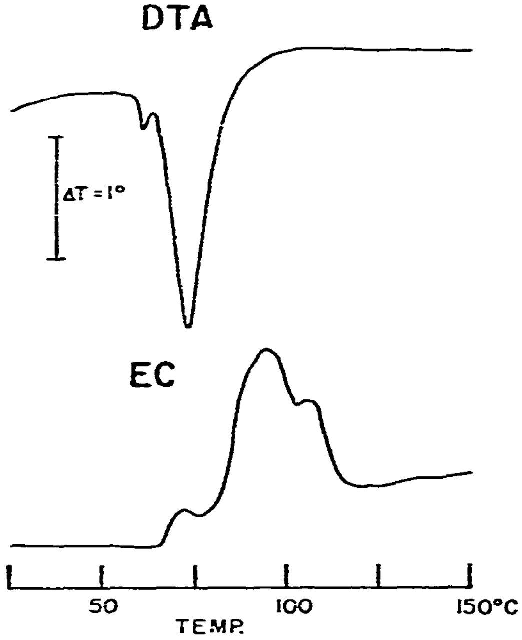

Fig. 7. EC–DTA curves of Cu_2HgI_4.

same temperature range. The DTA shoulder peak is more prominent in this curve than that shown in previous work[9].

To illustrate a different type of phenomenon, the thermochromism of Cu_2HgI_4 was studied using this apparatus. As shown by the EC–DTA curves in Fig. 7, this thermochromic transition, which is caused by an order–disorder crystalline phase transition, results in distinct EC and DTA curve peaks. The EC of this compound has been the subject of a recent investigation[12] and by other earlier studies. With this apparatus it is seen that the color transition is continuous and extends over a fairly large temperature interval. The EC curve reveals the multi-step processes involved and appears to be more useful in this type of investigation than DTA.

CONCLUSIONS

The examples discussed here illustrate the use of the combined EC–DTA apparatus for the study of deaquation and other types of reactions. It is a simple apparatus to construct and to use and since both the EC and DTA curves are obtained, it permits a time saving convenience over separate instruments for each thermal analysis technique. The EC curve can aid in the interpretation of the DTA curve for certain types of systems.

ACKNOWLEDGEMENT

The financial support of this work by the Robert A. Welch Foundation of Houston, Texas, is gratefully acknowledged.

REFERENCES

1 W. W. Wendlandt, *Thermochim. Acta*, 1 (1970) 11.
2 E. L. Simmons and W. W. Wendlandt, *Thermochim. Acta*, 3 (1972) 171.
3 H. J. Borchardt and F. Daniels, *J. Phys. Chem.*, 61 (1957) 917.
4 D. J. David, *Thermochim. Acta*, 1 (1970) 277.
5 L. G. Berg and N. P. Burmistrova, *Russ. J. Inorg. Chem.*, 5 (1960) 326.
6 R. W. Carroll and R. V. Mangravite, in R. F. Schwenker and P. D. Garn (Eds.), *Thermal Analysis*, Academic Press, New York, 1969, Vol. 1, p. 189.
7 J. Chiu, *Anal. Chem.*, 39 (1967) 861.
8 J. R. Williams and W. W. Wendlandt, in H. G. Wiedemann (Ed.), *Thermal Analysis*, Volume 1, Birkhäuser Verlag, Basel, 1972, p. 75.
9 W. W. Wendlandt, *Thermochim. Acta*, 1 (1970) 49.
10 Z. Halmos and W. W. Wendlandt, *Thermochim. Acta*, 5 (1972) 165.
11 R. H. Gore and W. W. Wendlandt, *Thermochim. Acta*, 1 (1970) 491.
12 Z. Halmos and W. W. Wendlandt, *Thermochim. Acta*, 7 (1973) 113.