Heat Dissipation in Small Drops on Free-Standing Membranes Studied Using Thin Film Thermopiles

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The thermal response to electrical and chemical heating of thermally isolated drops of liquid with volumes between 5 and 35 μl was studied. A thermopile transducer made from 76 bismuth/antimony thin film thermocouples was used to measure temperature differences between the drop/sensor interfaces and the surroundings. The time constant of the sensor arrangement alone is about 0.35 s. By placing a drop onto the sensor surface, two time constants are obtained corresponding to the heat exchange between the drop and the membrane and the heat flow from the sensor-drop complex to the surroundings. These time constants depend on the drop volume. Different thermoelectric transients were observed during the heating and evaporation of pure and binary liquids. The decay of the thermoelectric potential of fast exothermic chemical reactions such as neutralization corresponds well to the time constant of the sensor arrangement in contact with the drop. Different thermoelectric potential time characteristics were found for chemical reactions with more complex reaction mechanisms and lower overall rates, such as inorganic and enzymatic redox reactions. The investigations prove that the arrangement of small drops on thin film membranes is suitable for both microanalytical applications and micro-calorimetry.

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1.   Introduction

The measurement of enthalpies of chemical processes is a universal method in the characterization of materials, because most chemical processes are accompanied by consumption or production of heat. The measurement of heat as an analytical method has a very broad applicability, because the method is independent of the electrical conductance or the optical transparency of the sample. Microcalorimetric experiments for microanalytical tasks were first performed using "thermistors". The electrical resistivity of these transducers changes depending on temperature, which changes during an exothermic or endothermic chemical or biochemical process.[1,2]

Resistive sensing elements require electric current during the measurement process, which supplies electrical power, in addition to the chemical power to be detected. Current-free microcalorimetric measurements are possible using the thermoelectric principle. The application of a series of thin film thermocouples (a "thermopile") in the detection of reaction enthalpies was tested in chemical and biochemical analytical experiments.[3-5]

In most experiments, the analyte has a small-area contact with the bulk material. This contact causes intense heat flow between the reacting area with the "hot" thermojunctions and the reference zone with the "cold" junctions of the thermopile. Thus, the time constants of the heat exchange between hot and cold junctions are small, much smaller than the reaction rates of many analytical reactions. This kinetic mismatch results in comparatively low thermoelectric potentials, typically in the range of $0.01 - 1$ mV. The use of an arrangement with a thermally isolated drop of analyte, situated in the central region of a free-standing thin film membrane not in geometrical contact with the bulk material of the sensor frame, leads to significantly higher thermoelectric potentials (up to 50 mV), corresponding to higher temperatures of the drop during chemical reactions.[6] Here, we report investigations on the thermal behavior of drops on free-standing membranes in cases of external heating, endothermic physicochemical effects and exothermic chemical and biochemical reactions.

2.   Experimental

2.1 *Preparation of sensors*
A modified layout of a standard infrared absolute radiometer developed by IPHT Jena was used as the transducer.[7] It was prepared using anisotropic silicon wet etching in order to obtain a free-standing thin film membrane of a $Si_3N_4/SiO_2/Si_3N_4$ multilayer system. A BiSb/Sb thermopile consisting of 76 thermocouples (approx. 10 mV/K) was used as the detection transducer. Electrical heating was realized using a thin Ag resistor ($70-120$ ohms). The electrical layers and the surface were electrically insulated by cured photoresist layers.

2.2 *Measurement arrangement*
Liquid drops were applied on the center of a free-standing membrane carrying the thermoelectric, insulating, and heating films. Wetting of the outer parts of the free-

SENSOR, CROSS SECTION

(a)

resist, hydrophobic

liquid

hydrophilic surface

heating layer
insulating layer
thermopile layer
carrier membrane

Si-frame

MEASUREMENT ARRANGEMENT

(b)

micropipettes

temperature controlled box

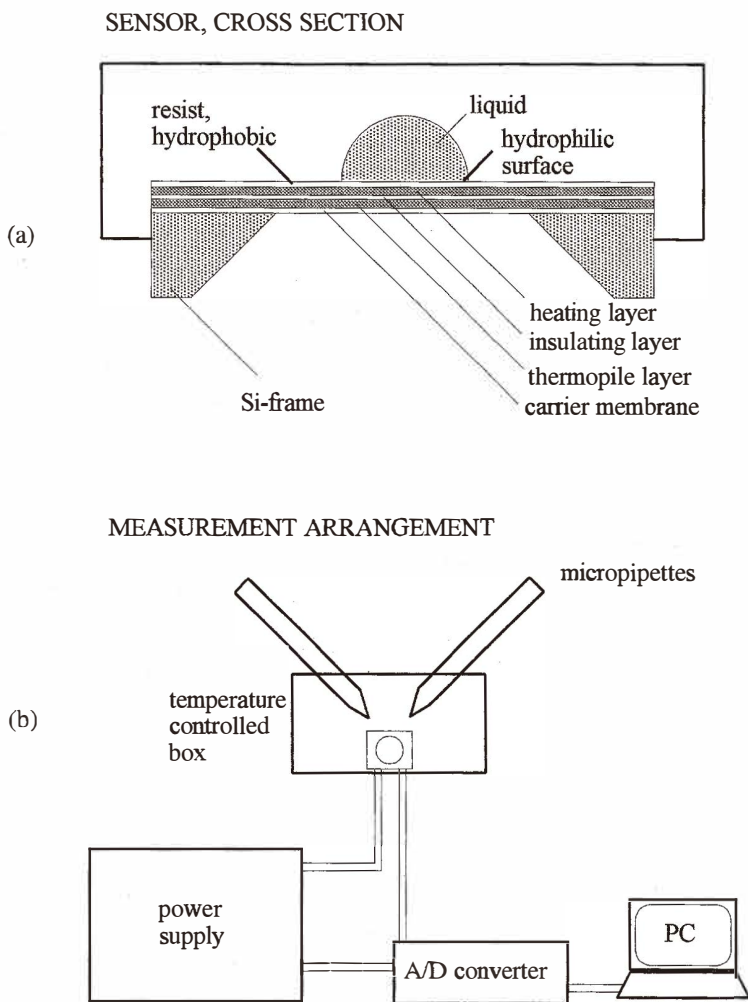power supply

A/D converter

PC

Fig. 1.   Principle of measurement arrangement: cross section (a) and experimental setup (b).

standing sensor surface was restricted by hydrophobization of the outer parts of the surface (Fig. 1 (a)).

The sensor was fixed on a socket and electrically connected to a programmable power supply (potentiostat PS 4 and variator PV3 Meinsberg) to provide the heating current and an analog/digital (A/D) converter (ASO 1600 Keithley) to register the thermoelectric potential and heating current by means of a personal computer (PC). The sensor and socket were placed in a temperature-controlled glass box with two movable micropipettes. The use of this box improved the thermal stability of the measurement arrangement and considerably reduced the noise caused by air convection (Fig. 1 (b)).

2.3 *Measurement procedure*

In the case of physical and physicochemical experiments, drops were placed on the sensor surface and allowed to stand for thermal relaxation for at least 3 minutes before the potential measurement was performed. In the case of chemical reactions, liquid drops were successively placed on the sensor surface using micropipettes, after beginning the registration of the thermoelectric potential.

The thermoelectric potential was recorded on a PC, and the range of A/D conversion was adjusted to the expected maximum voltages in order to obtain sufficient voltage resolution. Integration times between 150 ms and 3.6 s were chosen depending on the recording time.

3. Results

3.1 *Theoretical estimation of thermoelectric response in presence of drops*

The dynamics of the thermal system consisting of the free-standing thin film system and the liquid drop are mainly controlled by the heat flow from the drop to the surroundings Q_r, by the heat flow inside the drop Q_r' and the thermal capacitance of the thermal system C_p.

In the case of drops with volumes of 1 μl or greater, the heat capacitance of the liquid is much greater than the heat capacitance of the thin film system. Therefore, the heat capacitance of the whole system is given approximately by the product of the liquid volume V, the specific weight ρ, and the specific heat capacity C_s of the liquid.

$$C_p = V \times \rho \times C_s \tag{1}$$

The time constant τ is given by the ratio of C_p to the heat conductance G_r of the surroundings.

$$\tau = C_p / G_r \tag{2}$$

The heat conductance G_r was calculated for the sensor without liquid using the geometrical and material parameters of the thin film stack, i.e., the thermoelectric potential U in heating experiments, the number of thermocouples n, the Seebeck coefficient α and the applied heating power P.

$$G_r = n \times \alpha \times P / U = n \times \alpha / S \tag{3}$$

(S: responsivity)

A Seebeck coefficient of 135 μV/K for the BiSb/Sb thermocouples used and a n value of 76 gave a thermopower α_n ($\alpha_n = n \times \alpha$) of 10.3 mV/K (c.f. ref. 7). A very simplified geometrical model was used in the estimation of the heat transport through liquid drops. It is assumed that the liquid forms a cylinder of a volume V, of which the radius r is equal to the height h (Fig. 2).
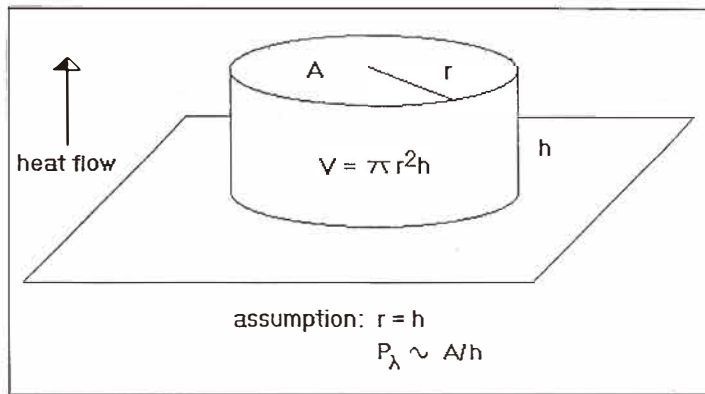
Fig. 2.   Simplified geometrical model for the estimation of heat transfer from the thin film system to the surface of a liquid drop (assumption: cylindric shape with height h, cross-sectional area A, radius r and volume V).

The transported heat power P_λ is proportional to the ratio of cross-sectional area A and h, the temperature difference ΔT and the heat conductivity λ of the liquid.

$$P_\lambda = \Delta T \times \lambda \times A / h \tag{4}$$

Using this approximation and $\Delta T = 1$ K, a P_λ of 2.2 mW is obtained for 5 μl drops of water, and a P_λ of 0.66 mW for 5 μl drops of ethanol. These values are related to their specific heat conductances of 0.6 W/(Km) and 0.18 W/(Km).[8] The electrical power P is dissipated by heat flow through the membrane, IR radiation and convective cooling of the back of the membrane (summed as the physical dissipation power P_p) and by heat flow through the drop P_λ and its successive dissipation by heat exchange at the drop surface. Two possible cases of the control of heat dissipation from the drop surface are distinguished.

(A) The rate of heat dissipation from the drop surface is controlled by heat exchange at the drop surface and the temperature gradient in the drop is low. In this case, the surface temperature of the liquid should be equal to the temperature of the sensor. The dissipation of energy from the liquid surface should be mainly dependent on the rate of evaporation, which is a physicochemical process controlled by an activation energy ΔH_e following an Arrhenius relation:

$$P = P_p + P_o \times e^{-\Delta H_e / RT} \tag{5}$$

(R: universal gas constant)

with $\qquad\qquad\qquad\qquad P_p = \lambda_p \times \Delta T. \tag{6}$

P_o and ΔH_e can be estimated from a logarithmic plot of the difference between the electrical heating power P and the physical dissipation power P_p against the inverse absolute temperature under the assumptions that the surface temperature is equal to the transducer temperature and λ_p to the value of the empty transducer:

$$\ln(P - \lambda_p \times \Delta T) = \ln(P_o) - \Delta H_e / RT \tag{7}$$

with
$$\Delta T = U / \alpha_n \tag{8}$$
and
$$T = T_s + \Delta T \tag{9}$$
(T_s: absolute temperature of the surroundings).

(B) The intensity of heat dissipation from the drop surface is controlled by heat transport through the drop, and the temperature gradient in the drop is high.

$$P = P_p + P_\lambda \tag{10}$$

Then the temperature difference ΔT should be nearly linearly dependent on the electrical heating power P.

$$\Delta T = P / (\lambda_p + \lambda \times A / h), \tag{11}$$

and for the cylindric shape model with $r = h$,

$$\Delta T = P / (\lambda_p + \lambda \times \pi \times \sqrt[3]{(V/\pi)}). \tag{12}$$

The distinction between cases A and B is apparent in experiments due to the functional dependence of U on P. The time taken for complete evaporation of drops depending on P provides additional information about the heat transport.

3.2 *Heat dissipation of sensor without liquid*

A thermoelectric potential can be observed if the transducer is heated by the thin film resistor, as is recognized in the unmodified absolute radiometer.[7] The responsivities S were found to be 2.6 V / W ... 3.4 V / W in sensors constructed as described above. The empty sensors used in dissipation experiments had S of 3.16 V / W. The time constant of heat dissipation after switch-off varies slightly between individual transducers and was found to be in the range between 0.3 s and 0.42 s. The two sensors used in experiments with drops had S values of 2.6 and 2.9 V / W.

The heat conductances G_r can be estimated from S and α_n using eq. (3).

$$G_r \text{ (exp.)} = \alpha_n / S = 10.3 \text{ mV} / \text{K} \times 0.316 \text{ mW} / \text{mV} = 3.25 \text{ mW} / \text{K} \tag{13}$$

The heat capacitance can be calculated from G_r and the time constant τ using eq. (2).

$$C_p = G_r \times \tau = 0.98 \text{ mJ}/\text{K} \ (\tau = 0.3 \text{ s})$$
$$= 1.37 \text{ mJ}/\text{K} \ (\tau = 0.42 \text{ s}) \tag{14}$$

Heating powers of up to 0.25 W were applied in heating experiments with sensors without liquid. The stability of the thin film components and the supporting membrane is high enough to realize many heating cycles up to this power without any change in the thermoelectric response. The maximum temperatures on the surface of the thin film stack are expected to be about 100°C ($\Delta T = 77$ K; room temperature 23°C) as predicted from eq. (13). The maximum thermoelectric potential was found to be 0.71 V in this experiment, which is slightly less than the expected maximum thermoelectric potential of 0.79 V.

3.3 *Heat dissipation in the presence of drops*

In the presence of drops, the thermal relaxation of the thermally insulated system is more complex. The time constant is generally considerably higher due to the high heat capacity of the drop in comparison with the heat capacities of the thin film stack. This results in a slow saturation of thermoelectric potential after both switch-on and switch-off of the heating power (Fig. 3).

The response time of the transducer ($S = 2.6\text{V}/\text{W}$) in the presence of a 20 μl drop of water was found to be about 33 s. This corresponds roughly to the time constant given by eq. (2) using the specific heat of water (4.2 J/gK):

$$\tau = C_p/G_r = 84 \text{ mJ}/\text{K}/3.96 \text{ mW}/\text{K} = 21.2 \text{ s}. \tag{15}$$
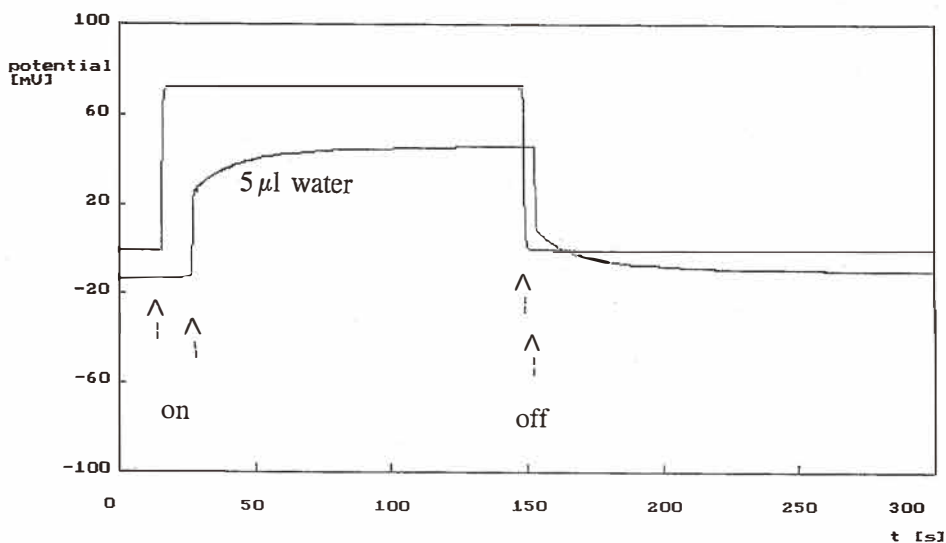

Fig. 3. Thermoelectric response of the thermopile in the presence of a 5 μl drop of water during electric heating with a heating power of 10 mW.

The time constant of thermal relaxation of drops depends strongly on drop size. Figure 4 shows that a small drop (5 μl) cools much faster than a large drop (35 μl). In the case of both small and large drops, a fast decay of thermoelectric potential is observed immediately after switching off the heating voltage. This decay has a time constant of about 0.1 s, which is considerably faster than the time constant of the empty sensor (Fig. 5). The time constant of this fast decay shows no significant dependence on the drop size. In contrast, the decay reflects a higher temperature difference in the case of small drops. This decay is interpreted in terms of the heat exchange between the thin film stack and the interior of the drop.

The thermoelectric response was studied over a large range of electrical heating power in order to obtain information about heat flux control in the thermal system in the presence of liquids. Using 5 μl drops of water, we observed no significant change in the ratio of thermoelectric potential to heating power over a range of 2.5 orders of magnitude of heating power (Fig. 6). At the highest heating power investigated, the evaporation of water from the drops can no longer be neglected, because the temperature of the transducer is just below the boiling point of the liquid. The observed behavior implies that the heat flux is dominated by the heat conductance in the interior of the drop. Case B (see section 3.1) seems to be consistently valid for drop sizes of 5 μl and larger studied in the experiments reported here. This finding is supported by the observed period for complete evaporation of drops, which depends not only on the activation energy of evaporation but also on the heat flux through the drop.
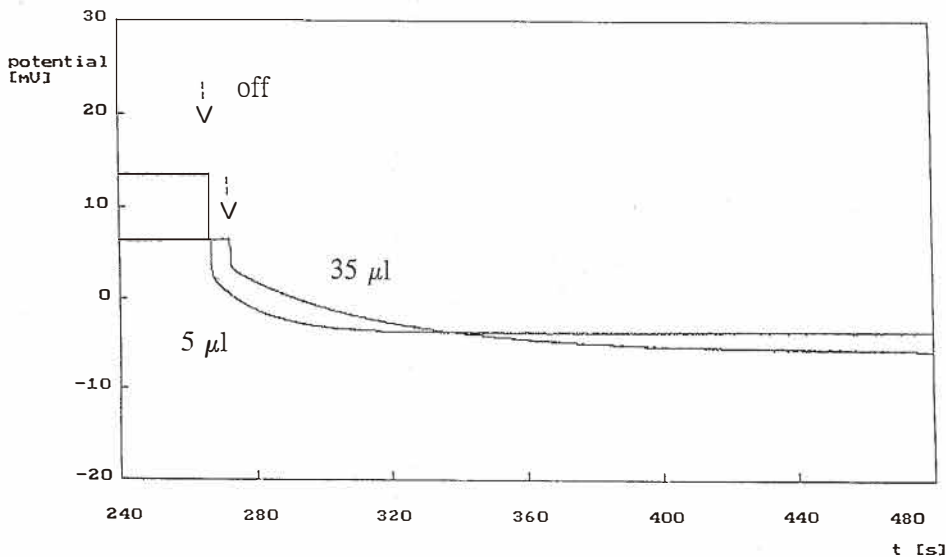

Fig. 4. Decay of thermoelectric potential after switching off the heating current for two different drop sizes (5 μl: fast decay; 35 μl: slow decay).
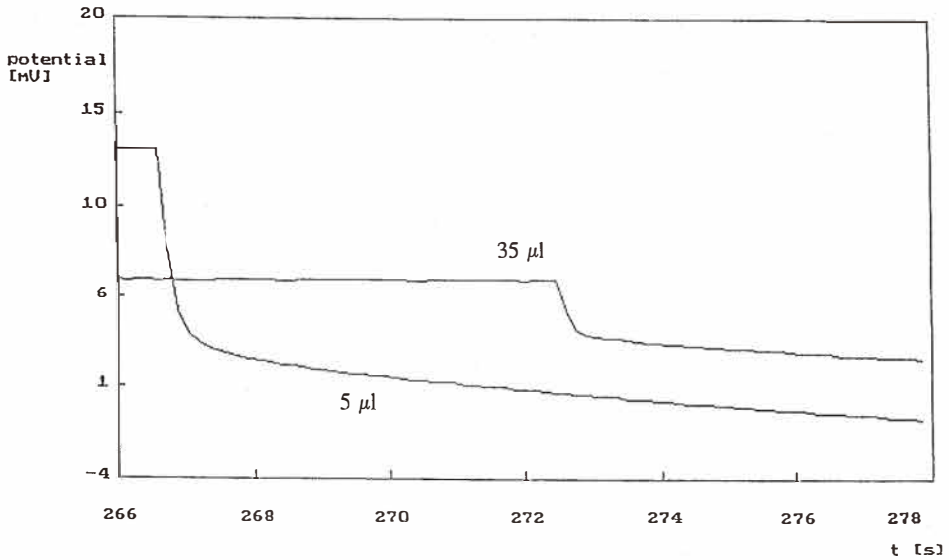
Fig. 5. Decay of thermoelectric voltage in the first seconds after switching off the heating current for two different drop sizes (5 μl: fast decay; 35 μl: slow decay; enlargement of part of the curves in Fig. 4).
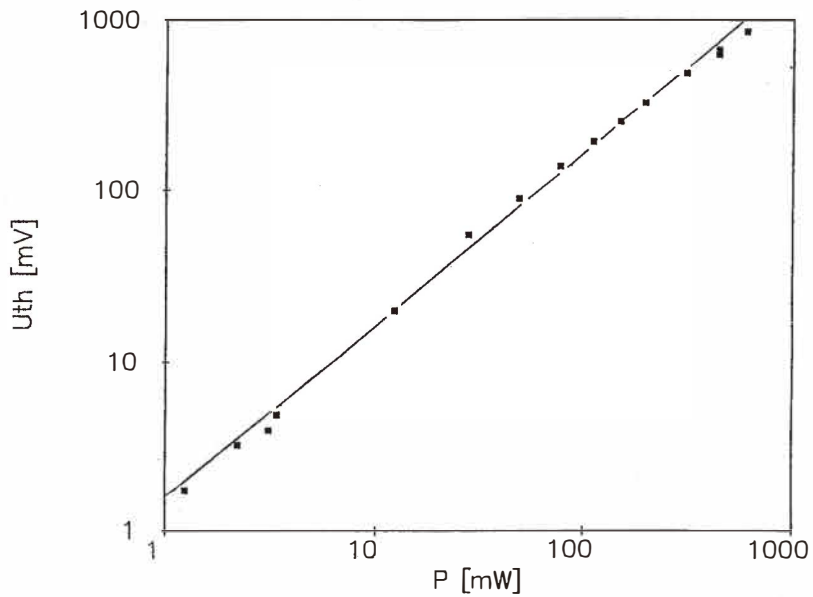

Fig. 6. Dependence of the thermoelectric potential U_{th} during the heating of 5 μl of water on the heating power P (double logarithmic plot).

3.4 *Thermoelectric transients in the case of drop evaporation*

The applicable electric power (up to 0.77 W) for the thin film heater is sufficient to evaporate drops of water with volumes between 5 μl and 25 μl completely within a few minutes. In all cases, a thermoelectric potential in the range between 0.7 and 1.1 V was observed, reflecting temperatures close to the boiling point of water.

The heat dissipation characteristics clearly indicate the existence of thermal transient states in the cases of binary liquid mixtures. We used a mixture of water with ethanol in 5 μl drops as test samples (Fig. 7). The thermal voltages in the transient states are dependent on the ethanol concentration. The lowest transient thermoelectric potential was obtained with the highest alcohol fraction (Fig. 8). The duration of the transient state increases with decreasing ethanol concentration. It is assumed that the changes in surface and interface tensions, which depend on the concentration, affected the time behavior due to modified drop shape and wetting, in addition to the lower heat capacity, the lower boiling point and the lower evaporation enthalpy of ethanol in comparison with water.

3.5 *Calorimetric experiments*

Microcalorimetric experiments were carried out without electric heating during the measurement process. Only the heat-producing or heat-consuming chemical and physico-chemical processes contributed to thermoelectric power in these investigations.   The expected temperatures and the resulting thermoelectric potentials were much lower than those in most dissipation experiments which use electrical heating.   In calorimetric experiments, electric heating was used only for calibration procedures.
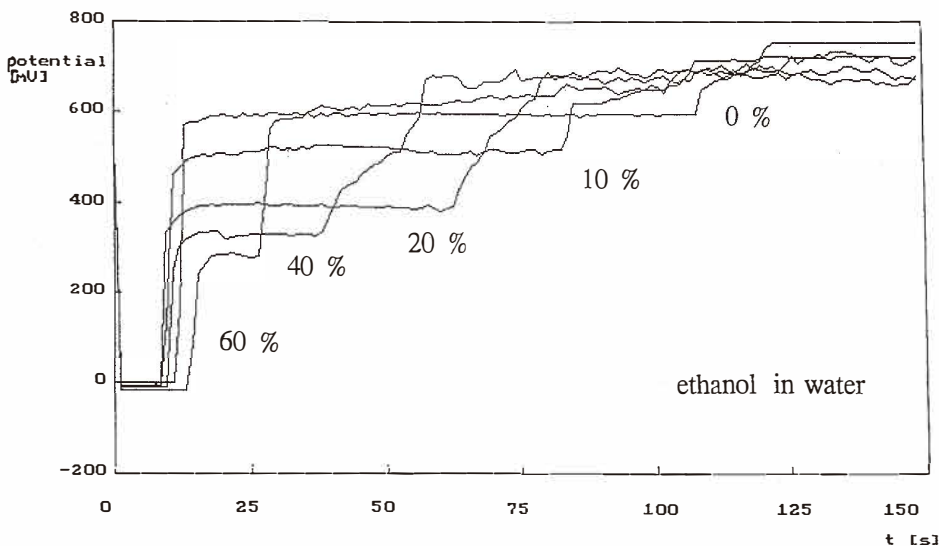

Fig. 7.   Transient thermoelectric potentials during the evaporation of 5 μl drops of water-ethanol mixtures with a heating power of 0.36 W.
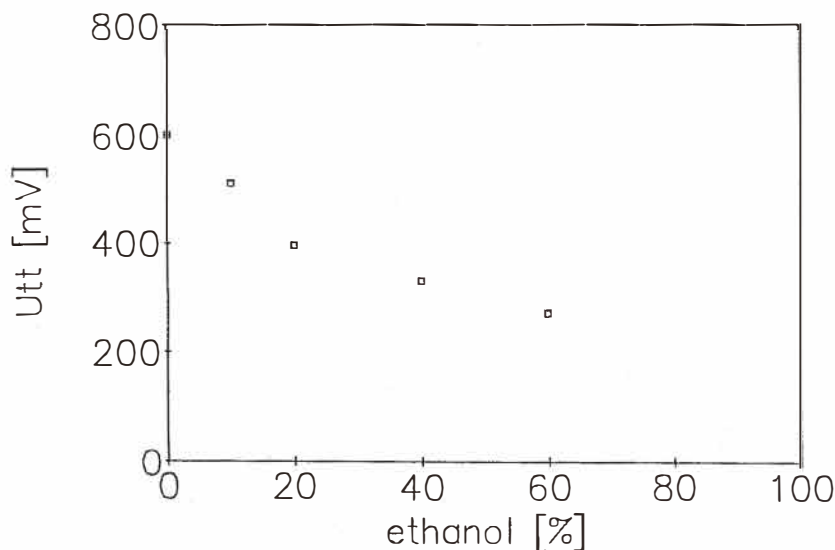
Fig. 8.   Transient thermoelectric potentials U_{tt} during the evaporation of 5 μl drops of water-ethanol mixtures with a heating power of 0.36 W relative to ethanol concentration.

First, the influence of a drop of water on the thermoelectric potential was tested. When drops were applied, a negative thermoelectric potential was observed. The potentials increased with increasing drop size and increasing convection in the surrounding atmosphere. The potentials could be reduced by creating a more humid atmosphere using a chamber which contained a small puddle of additional water. Therefore, the negative thermoelectric potential in the presence of water drops on the sensor surface can be well understood by the influence of evaporation cooling. A typical case is shown in the upper curve in Fig. 9. A decrease in the potentials after a water drop was placed on the transducer surface was recorded.

We observed a modified potential if a dissolution process took place after the water drop was introduced. The lower curve in Fig. 9 was recorded after dropping 20 μl of water onto the transducer surface, where about 3 mg of solid KCl had been placed previously. In this case, a significantly lower thermoelectric potential is found after the application of water. This higher level of heat consumption can be explained by the dissolution of the salt. This dissolution process consumes energy because the lattice energy of the solid KCl is higher than the energy of dissociated ions. The increase in thermoelectric potential after 5–10 s indicates a decrease in the rate of dissolution corresponding to a reduction in the salt crystal surface area and an increase in salt concentration. After about 3 minutes, the salt is dissolved completely, and the thermoelectric potential is similar to that obtained in experiments without salt.

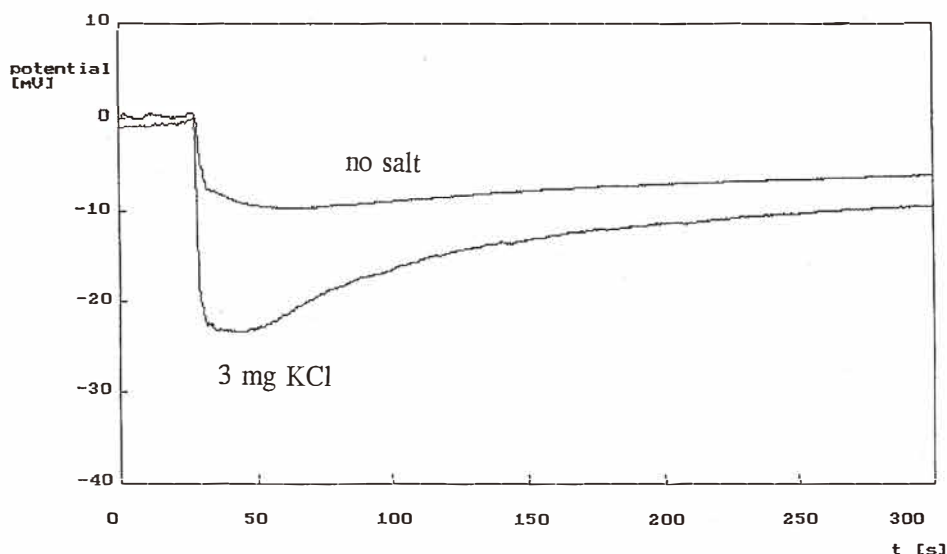Exothermic chemical reactions can be monitored by the evolution of a positive thermo-

Fig. 9.   Thermoelectric voltage after applying a drop of water (20 μl) to an empty transducer surface (upper curve) and that in the presence of solid KCl (lower curve) without any electric heating.

electric potential during the reaction and dissipation of heat (Figs. 10 and 11). Ten μl of 2.5 M sulfuric acid were neutralized by NaOH solutions of different concentrations. A steep increase in thermoelectric potential was observed immediately after mixing the two compounds at the transducer surface. The potential depends strongly on the hydroxide concentration. The observed decay of the thermoelectric potential does not depend on the concentration, but corresponds to the purely physical relaxation of the thermal system. This is to be expected in the case of chemical reactions in which the decay of the reaction rate is faster than the thermal relaxation. The time-integrated potential is directly related to the reaction enthalpy. The experimentally estimated reaction enthalpies for this standard reaction agree with the values in the literature (67 kJ / mole [9]).

The overall kinetics of chemical reactions can be recorded in the case of slower chemical reactions. We studied the redox reaction between malonic acid and bromate in highly acidic media in the presence of Ce(IV) as a redox catalyst (c.f. ref. 6). The speed of this complex reaction is dependent on the catalyst concentration (Fig. 11). The higher the catalyst concentration the steeper the increase in thermoelectric potential after the start of the reaction, the higher the exothermic peak U_{max} and the faster the postpeak decay. In this case, the thermoelectric decay is not dependent on the (physical) thermal relaxation, but on the rate of the chemical reactions.

The transducer is also suitable for detecting biochemical reactions. Exothermic peaks can be found using the drop method for the free-standing thin film transducer in the enzymatic oxidation of glucose with glucose oxidase and in the decomposition of the
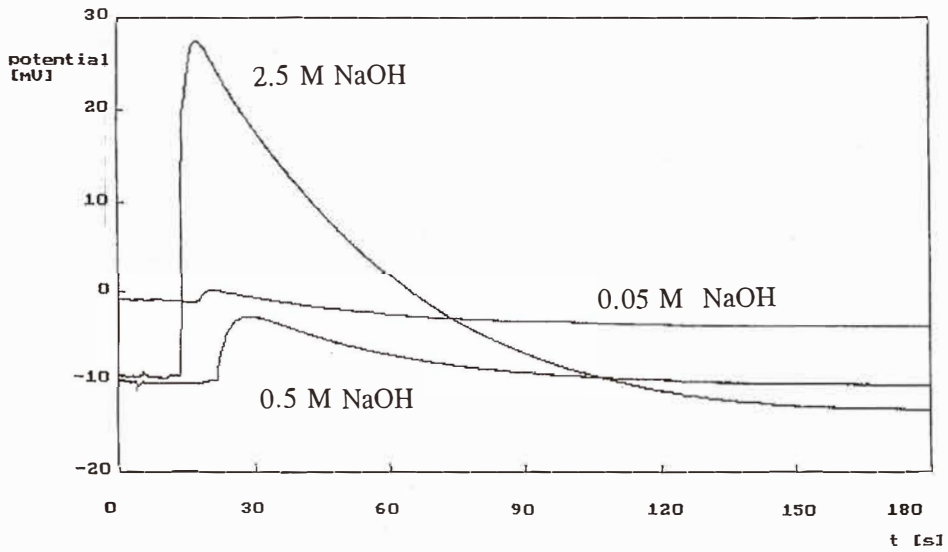
Fig. 10.   Evolution of thermoelectric potential after the reaction of 10 μl 2.5 M sulfuric acid with 10 μl of 50 mM, 0.5 M and 2.5 M NaOH (no electric heating).

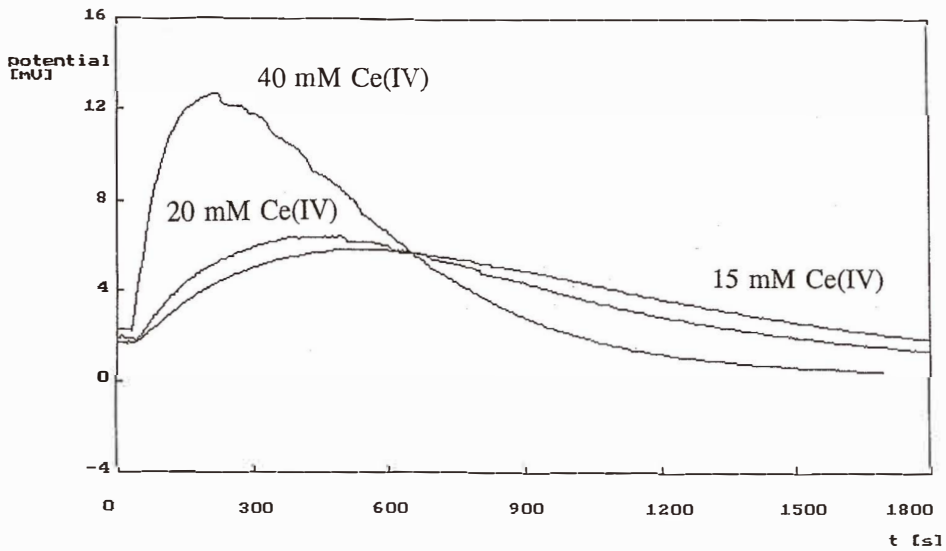
Fig. 11.   Evolution of thermoelectric potential during a complex redox reaction of 10 μl of solution A (6 M sulfuric acid, 0.6 M NaBrO$_3$, 0.4 M malonic acid) with 10 μl of 15 mM, 20 mM and 40 mM solutions of Ce(NH$_4$)$_2$(NO$_3$)$_6$ (no electric heating).

intermediately formed hydrogen peroxide with catalase (Fig. 12). Only a short duration, small potential was observed when buffer solution alone was added to the enzyme solution. Significantly higher and broader peaks representing the biochemical reaction were observed when glucose was present in the buffer solution. Thus, the maximum potential is affected mainly by the concentration of the biocatalysts. In contrast, the amount of substrate (glucose) affects the duration of the reaction, and thus the shape of the reaction peak. This observed behavior agrees well with the known mechanisms of enzymatic processes. Different concentrations of glucose (substrate) can be well distinguished; therefore the method is, in principle, applicable to biosensors.

4. Conclusions

The system which involves adding of a drop on thermally isolated membranes with thermal thin film sensors has two time constants. The time constant for the thermal relaxation of the whole system (thin film stack plus drop) is much higher than the time constant for the sensor alone, which can be explained by the dramatically increased heat capacity of the system due to the presence of the drop. In addition, a fast heat exchange process is observed, which is interpreted as heat flow from the thin film stack to the interior of the drop.
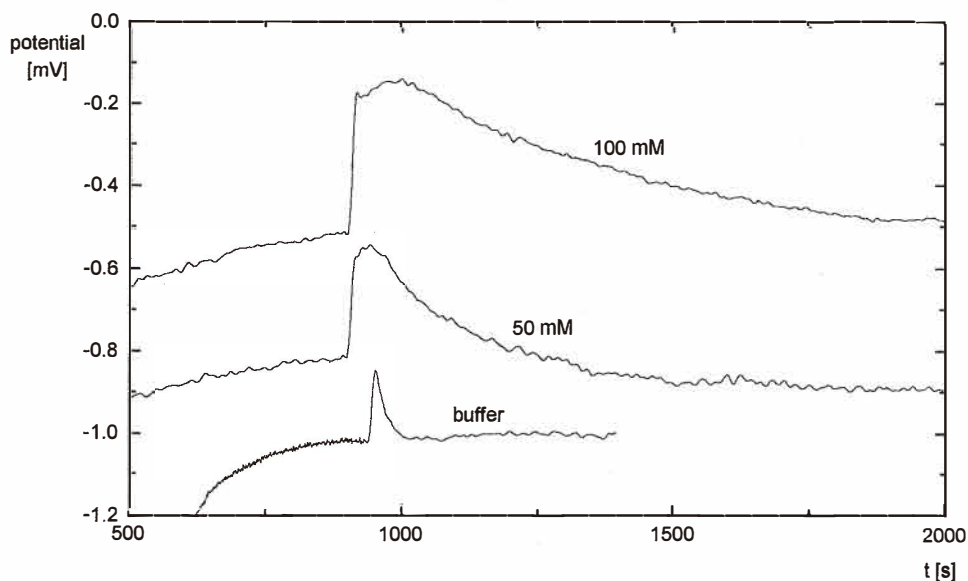

Fig. 12. Evolution of thermoelectric potential during a biochemical reaction of 10 μl of an enzyme (5 U/μl glucose oxidase and 5 U/μl catalase) with 10 μl of 100 mM and 50 mM glucose in phosphate buffer solution and pure phosphate buffer solution.

Evaporation from the drop surface has a cooling effect on the sensor. Evaporation cooling can be detected as a negative thermoelectric potential, which, as expected, depends on the surface size of the drop.

Using thin film resistors, it is possible to apply high heat flux densities to the drops. At high electrical heating power, a considerable temperature gradient evolves inside the drop. The energy is consumed by fast evaporation of liquid in the case of water or ethanol, which leads to the complete evaporation of drops with volumes of 10 μl within a few minutes or even seconds. The disappearance of liquids from the surface by evaporation is marked by a marked change in the thermoelectric potential in the case of constant heating power.

The thermal isolation of drops means that the system is suitable for detecting small amounts of chemical substances in inorganic, organic and biochemical reactions. The thermal relaxation of a fast reaction such as neutralization is mainly dependent on the time constant of the sensing system. However, it was shown that the kinetic behavior of slower and more complex chemical reactions such as the catalytic oxidation of malonic acid by bromate in the presence of cerium can also be accurately represented by the thermoelectric potential with respect to time. Quantitative measurements are also possible in the detection of biochemical processes. The influence of concentration of biochemical substrates on the time-integrated thermoelectric potential and the influence of the enzyme concentration on the thermoelectric potential correspond well with the known basic mechanisms of enzymatic reactions.

Further work is necessary in order to evaluate the influence of parasitic and perturbation effects on the thermal flow between thermally isolated drops and their surroundings. If the physical limit of Nyquist noise (approx. 25 nV) can be determined by controlling the disturbance of heat flow in the measurement apparatus, it might be possible to realize microcalorimetry, microthermokinetic measurements and microscanning calorimetry with analyte concentrations in the picomole range, which would be very important in environmental analysis, biotechnology and medical analysis.

Acknowledgments

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