Journal of Thermal Analysis, Vol. 28 (1983) 37–47

MICROWAVE ENHANCEMENT OF EVAPORATION OF A POLAR LIQUID. I.
Experimentation

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(Received January 25, 1983; in revised form May 9, 1983)

The evaporation of a polar liquid at low pressure and exposed to microwave radiation has been investigated, as an example of an endothermic reaction. A fixed, high column of liquid was irradiated in a waveguide with 2.45 MHz-CW microwave radiation. The temperatures of the gas and the liquid in contact with the interface and the evaporation rate were measured as functions of the non-equilibrium gas pressure and the microwave field.

Empirical equations relating the dynamic non-equilibrium parameters to each other are given. The results show that microwave heating offers the possibility or reversing a temperature difference between the two phases at a gas-liquid interface. Other special features of the action of microwaves are discussed.

Among the many industrial applications of microwave power is its use in the areas of drying, freeze-drying and defrosting. All these examples fall into the class of endothermic processes, changes which require energy for their occurrence. The use of microwaves is an elegant solution, because they can rapidly supply much energy, inside any dielectric material.

In the classical method of carrying out these processes, heat is conducted to the interface by thermal contact with one or both phases. Theoretical approaches deal mainly with the problems of mass and heat transfers, but few articles treat what happens at the interface and how to describe, at least numerically, the mechanism of the reaction itself. The need for such information is especially manifest when microwaves are used to accelerating a process.

Whether microwave irradiation exerts an influence only via thermal action or whether there are field-specific interactions is now a fundamental question we must answer. According to the laws of thermodynamics, the microwave electric field might introduce an external parameter at the interface and could modify the equilibrium or the rate of the reaction.

It is the purpose of the present two papers to investigate these problems by studying the evaporation of a polar liquid, the surface of which is exposed to a known microwave field intensity.

Parameter inventory for describing the interfacial reaction rate

It is well known that the observed evaporation rate of a liquid into vacuum differs significantly from that indicated by the Hertz–Knudsen equation, which is derived from the classical kinetic theory of gases

$$J_K = \alpha \frac{P_s(T_{cp}) - P_c}{\sqrt{\pi MRT_{cp}}} \tag{1}$$

where $P_s(T_{cp})$ is the saturated vapour pressure at the absolute temperature T_{cp}, and P_c is the pressure at which the experiment occurs. In this publication, the constraint parameters are denoted by the subscript c. The introduction of the coefficient α, described by Knudsen as the "evaporation coefficient", to obtain better agreement with experiment is questionable [1–3]. The relation proposed by Hickman [4].

$$J_H = \frac{1}{\sqrt{2\pi MR}} \left(\frac{P_s(T_i)}{\sqrt{T_i}} - \frac{P_c}{\sqrt{T_{cp}}}\right) \tag{2}$$

to take into account the value of the temperature of the interface, T_i (which differs from the temperature T_{cp}), also fails in many cases. Erikson [5] found it convenient to correlate his data with the expression

$$J_E = -k \log \frac{P_c}{P_s(T_{cp})} \tag{3}$$

which introduces the ratio of the pressures as a measure of the deviation of the chemical potential from its equilibrium value.

A more general approach has been proposed by Bertrand et al. [6, 7] and Mokhlisse [8]. They have found that the temperature of the liquid in contact with the evaporating surface is never that of the bulk, but lower. Following the usual methods of analysing irreversible processes, they describe the relationship between heat and mass transfers. The rate of evaporation is then the direct sum of two independent terms:

$$J_M = -A \log \frac{P_c}{P_s(T_l)} + B\left(\frac{1}{T_g} - \frac{1}{T_l}\right) \tag{4}$$

or

$$J_M = A'\left(\frac{1}{T_{cp}} - \frac{1}{T_l}\right) + B'\left(\frac{1}{T_{cp}} - \frac{1}{T_g}\right) \tag{4'}$$

in which the differences in temperature between the two phases (T_l for the liquid temperature at the interface, T_g for the vapour temperature at the interface) and the external temperature T_c are introduced separately to specify how far the stationary state is from the equilibrium.

This point of view was supported by the direct observation of the temperature differences evoked in this treatment. With water and ethyl alcohol the evaporating liquid first coexists in equilibrium at some specified temperature T_c. The pressure of the system is then decreased from $P_s(T_c)$ to a value P_c. The parameters T_g, T_l, and the rate of evaporation are measured during the stationary state which then occurs.

In these papers, we consider similar experiments under microwave irradiation to ascertain whether the microwave action involves or not purely thermal heating of the bulk. In fact, we conclude that relation (4) no longer holds when the microwave field is applied.

A description of the experimental device

The experimental arrangement is presented in Fig. 1. The applicator is part of a standard waveguide WR 340 in which a tube of pure silica (ϕ 10 mm) is centrally located in the broad face. The liquid fills the tube and is connected to a mercury column. The level of the evaporating surface can be moved up or down or be stabilized at a specified height in the guide by an electronic servomechanism. The position of the surface is optically determined by two photodiodes in front of a lamp. The signals then control the pressure as an automatic gas burette would do, by operating an electric valve.

The upper outlet of the tube is connected to a thermostat, the temperature T_{cp} of which determines the pressure P_c of the gas by the relation

$$P_c = P_s(T_{cp}) \tag{5}$$

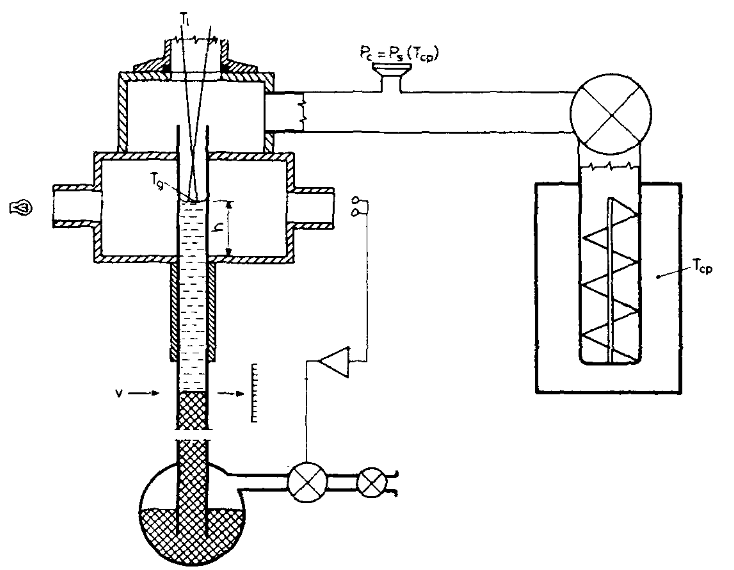

Fig. 1 Experimental design used to study the evaporation

The microwave set-up (see Fig. 2) includes, as usual, a generator (Microtron 200), a circulator and a means of measuring the levels of the incident, the reflected and the transmitted powers (π_i, π_r, π_t). A water load closes the end of the guide. The absorbed power is $\pi_a = \pi_i - \pi_r - \pi_t$.

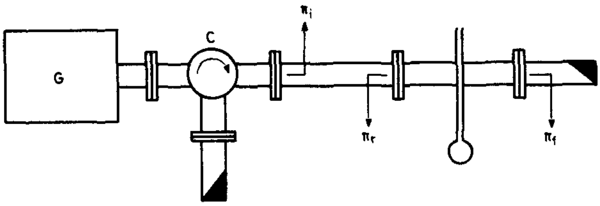

Fig. 2 Microwave circuit

The rate of evaporation is deduced from the speed v of the liquid mercury meniscus, which is projected onto a metric scale. Small thermocouples are placed in the gas and in the liquid regions outside the waveguide. We also measure the pressure P_c directly with a gauge. The tube which connects the applicator to the thermostat is of large cross-section so that the gas flow is unimpeded.

The temperature of the liquid in contact with the interface is determined by a radiothermometer (Heitmann KT 14) which is focused on it.

Measurement of the gas temperature

The experimental device fails to measure the temperature (T_g) of the gas near the interface directly. It is not possible to place a thermocouple inside the guide, as this would interfere with the microwave beam, thereby inducing measurement errors or modifying the field distribution. The gas temperature adjacent to the surface is obtained by measuring it to within a certain distance, and then extrapolating. Such a procedure is possible because the profile of the temperature as a function of the distance from the interface can be determined [9].

When the gas flow is stationary, the equations of conservation of the mass, the linear momentum and the energy of a differential element dx of the gas hold. It follows that

$$\rho u = v = C_1 \tag{6}$$

$$P + vu = C_2 \tag{7}$$

$$\rho \frac{\mathrm{d}}{\mathrm{d}t}(C_V T) + \frac{\mathrm{d}}{\mathrm{d}x}\left(Pu - \lambda \frac{\mathrm{d}T}{\mathrm{d}x}\right) = -k(T - T_c) \tag{8}$$

where u is the speed of the centre of mass; ρ is the specific mass of the gas; P and T are the local pressure and temperature; C_V, C_p and λ are the heat capcities and the thermal conductivity coefficients of the gas; T_c is the surrounding temperature; and k is the thermal conductivity coefficient of the wall. It follows that

$$\frac{d^2T}{dx^2} - \frac{v}{\lambda} C_p \frac{dT}{dx} = \frac{k}{\lambda}(T - T_c) \tag{9}$$

Only the solution corresponding to the negative root has a physical meaning, so that

$$T = T_c + (T_g - T_c) \exp(+ s_1 x) \tag{10}$$

with

$$s_1 = \frac{vC_p}{2\lambda}\left(1 - \sqrt{1 + 4\frac{k\lambda}{vC_p}}\right) \tag{11}$$

The profile is exponential, but the reciprocal length constant is a function of the rate. The exponential dependence of the temperature at the distance x from the surface has been observed by measuring $T(x)$ directly when the microwave field is off (see Fig. 3). From these curves the unknown parameter k can be estimated and substi-

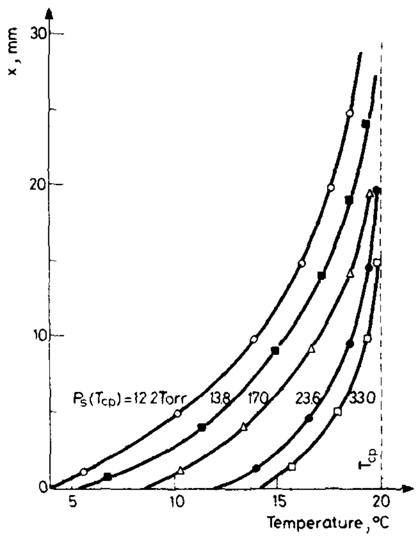

Fig. 3 Gas temperature profile above the evaporating surface

tuted back into relations (10) and (11) to determine T_g when the microwave field is on (from the measurement of the speed v and a value $T(x)$ at the distance x). Relation (11) has also been verified with a fixed value of $\lambda = 3.11 \cdot 10^{-6}$ cal/mm s deg and with $k = 4.26 \cdot 10^{-7}$ cal/mm^2 s deg (see Fig. 4), these values being unaffected by microwave application.

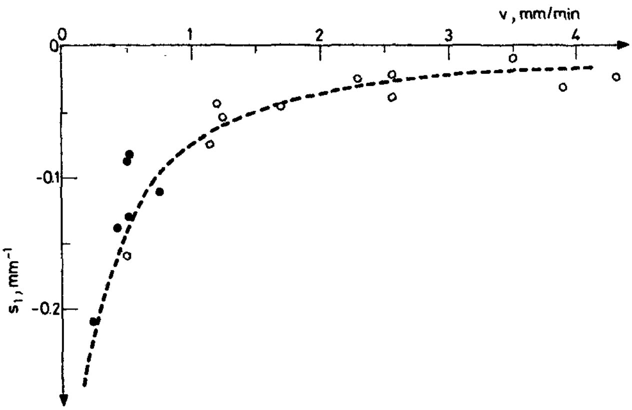

Fig. 4 S_1 versus v. The experimental points • are deduced from the fitting of the experimental profile $T_g(x)$ recorded when the field is off. The experimental points ○ are obtained by comparison of two temperature measurements ($T_g(x_1)$ and $T_g(x_2)$) at two distances x_1 and x_2 when the microwave field is on. The dotted curve corresponds to the best fit of equation (11)

Electric field on the surface

It is generally difficult to determine the electric field configuration (in direction and in intensity) when microwaves irradiate a specimen.

The configuration depends on the shape of the sample because the continuity conditions of the electric field vector, on passing from one dielectric to the other, discriminate between the normal and the tangential components. The electric field inside a massive dielectric stub placed in a rectangular guide is not modified, however,

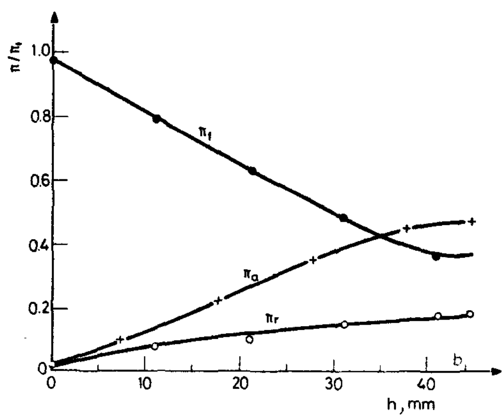

Fig. 5 Variations of the microwave power levels vs height of liquid exposed to microwaves

because the cylindrical surface limiting the dielectric specimen is parallel to the electric field vector. It is also homogeneous throughout the sample and its intensity is directly related to that of the incident wave [10, 11].

In our case, when the column of liquid is not as wide as the guide, the field is slightly distorted. We verified that the distortion is independent of the height (h) of the liquid introduced in the guide, by measuring π_i, π_t and π_r as functions of h and verifying that they are linearly dependent (see Fig. 5). We conclude that the field intensity on the surface is proportional to the square root of π_i, and does not depend on h. Finally, we noted that the product $h \cdot \pi_i$ certainly represents the power π_a absorbed by the column of liquid.

Experimental results

The first set of results concerns the evaporation process as a function of the incident microwave power, the pressure P_c being fixed [12]. They are the following:

(a) The temperature of the liquid phase adjacent to the interface is a linear function of the power π_i (see Fig. 6).

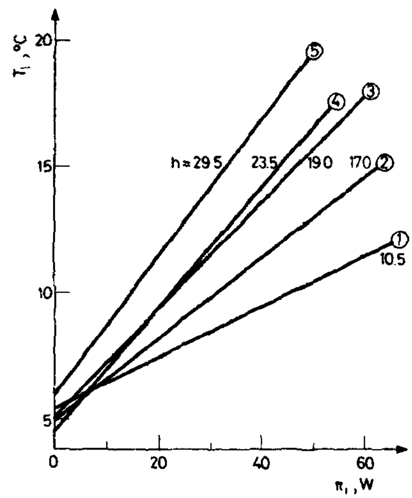

Fig. 6 Temperature of the liquid in contact with the surface vs microwave field and height of liquid column

(b) The evaporation rate is proportional to the incident power, but only above a given level. For a low power level, the rate tends to a non-zero limit, in a non-linear fashion (see Figs 7 and 8).

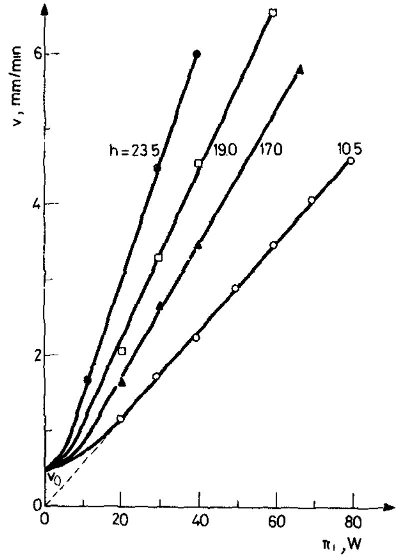

Fig. 7 Evaporation rate vs microwave field and height of liquid column

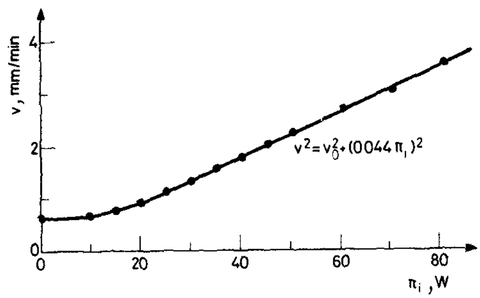

Fig. 8 Test of the equation giving v vs π_i

(c) The temperature of the gas in contact with the interface remains constant and is independent of the microwave power, although the evaporation rate is largely enhanced.

Results "*a*" are described by the relation

$$T_l = T_{l0} + \alpha\pi_i \quad (12)$$

Moreover, the coefficient α is linearly dependent on the height of the liquid inside the guide, so that (see Fig. 6)

$$T_l = T_{l0} + \alpha'\pi_a \quad (13)$$

which suggests that the liquid is simply heated by microwaves.

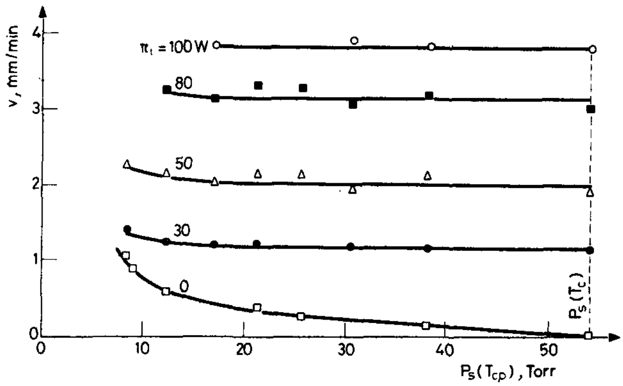

Fig. 9 Dependence of the evaporation rate on the pressure

The curves given in Fig. 7 are easily represented by the relation

$$V^2 = V_0^2 + \beta\pi^2 = V_0^2 + \beta'\pi_a^2 \tag{14}$$

as is shown in more detail in Fig. 8. In these equations v_0 and T_{l0} are the rate of evaporation and the temperature of the liquid in the absence of a microwave field.

It follows that the system (including the two phases and the column) can be described numerically by simple equations under microwave irradiation, provided that its behaviour is known when the field is off.

However, it is difficult to justify the equation giving the rate of evaporation, because it is not a linear function of the absorbed power. This means that the mass fluxes are not additive when the liquid is heated simultaneously by microwaves and thermal conduction. In this case, the squares of the mass fluxes are additive quantities.

From a practical viewpoint, it is clear that the system does not use the heat it obtains from the outside by thermal conduction in the same way as that which it obtains from the microwave field.

Other features are to be noted. When the field is off, the rate of evaporation is largely accelerated by decreasing the pressure (see formulae (1), (2), (3) or (4) given in the first section). In contrast, when the field is on, the rate of evaporation does not depend on the pressure (Fig. 9). This is true at least in the range of the experimental values studied and even in the neighbourhood of the equilibrium pressure. If it were also true in microwave freeze-drying, then we would conclude that the rate of evaporation was not increased by reducing the gas pressure or increasing the efficiency of the vacuum system. However, the temperature of the gas and that of the condensed phase are decreased (see Fig. 10).

Point *c*: the temperature of the gas in contact with the surface, T_g was found to be independent of the microwave field, although the temperature profile of the gas column changes because the speed of the flow varies and although the temperature of the liquid phase increases. The situation is summarized in Fig. 11.

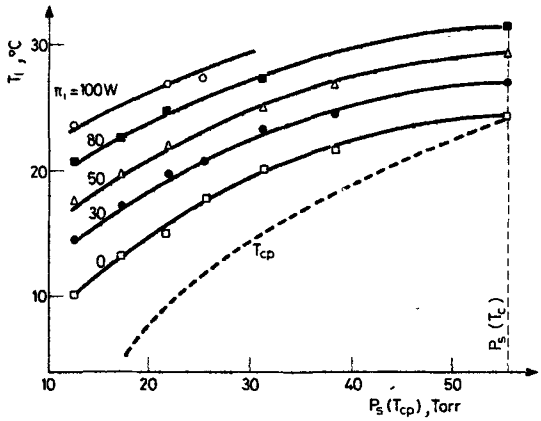

Fig. 10 Dependence of the liquid temperature on the pressure

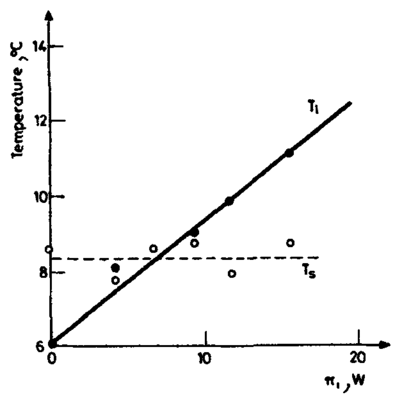

Fig. 11 Liquid and gas temperatures at the surface

Our results confirm that microwave fields do not interact significantly with a gas; moreover, the interface does not conduct heat. Our results suggest that the interface does not conduct heat in any direction, because the sign of the difference $(T_g - T_l)$ can be reversed without inducing any variation of T_g. It is therefore difficult to accept that gas could supply thermal energy to the interface to accelerate the evaporation as the liquid phase could do. It should be noted that relation (4′) implies that the heating effects from the two sources are additive.

When the energy required for the evaporation is supplied by a thermal conduction process, T_l is always lower than T_g. When the microwave field is on, vapour can be produced which is at a lower temperature than that of the liquid.

These experiments seem to show that microwave heating impedes the conductive heat transfers which occur between the interface and its surroundings in the absence *of a field, so that the microwaves supply the greater portion of the energy required by* the evaporating interface.

We also note that the interface cannot be described by either relation (4) or (4'), which were directly derived from the laws of classical thermodynamics, because the second term would then decrease the rate of evaporation.

We shall see in a later paper that a correction of formula (4) can be proposed to explain this apparent inconsistency.

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Zusammenfassung — Die Verdampfung einer bei niedrigem Druck der Einwirkung von Mikrowellenstrahlung ausgesetzten polaren Flüssigkeit wurde als Beispiel einer endothermen Reaktion untersucht. Eine fixierte, hohe Flüssigkeitskolonne wurde mit 2.450 MHz-CW-Mikrowellen bestrahlt. Die Temperature der mit der Grenzfläche in Kontakt befindlichen Gas- und Flüssigkeitsmenge und die Verdampfungsgeschwindigkeit wurden in Abhängigkeit vom Nichtgleichgewichts-Dampfdruck und Mikrowellenfeld gemessen. Empirische Gleichungen werden angegeben, die die dynamischen Nichtgleichgewichtsparameter miteinander in Beziehung bringen. Die Ergebnisse *zeigen, dass Mikrowellenheizung die Möglichkeit bietet, die Temperaturdifferenz zwischen den* zwei Phasen einer Gas-Flüssigkeits-Grenzfläche umzukehren. Andere spezielle Züge der Wirkung von Mikrowellen werden diskutiert.

Резюме — Исследовано, как пример эндотермической реакции, испарение полярной жидкости при низком давлении и выдержанной под микроволновым излучением. Фиксированная, высокая колонка жидкости была облучена волноводом с микроволновой частотой 2.450 МГц-ЦВ. Температура газа и жидкости на границе раздела и скорость испарения *были измерены в зависимости от неравновесного давления газа микроволнового поля.* Приведены эмпирические уравнения, связывающие друг с другом динамические неравновесные параметры. Результаты показали, что микроволновой нагрев оказывает возможность обратимости различия температуры между двумя фазами на границе раздела газ — жидкость. Обсуждены другие специфические черты микроволнового облучения.