Journal of Thermal Analysis, Vol. 28 (1983) 49–57

MICROWAVE ENHANCEMENT OF EVAPORATION OF A POLAR LIQUID. II.

Theoretical approach

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

The evaporation of a polar liquid at low pressure upon exposure to microwave radiation has been investigated. The conventional theories previously developed to describe the non-equilibrium conditions of the evaporating interface are found to be in poor agreement with the experimental results. It is possible to take into account the influence of microwave fields on the evaporating surface by modifying the expression for the entropy production. Another approach, based on the concept that microwaves would increase the pressure, has also been found to be satisfactory.

In a previous paper we reported some experimental results concerning the evaporation of ethyl alcohol under low pressure during microwave irradiation of the interface between the gas and the liquid.

We established empirical relations giving the evaporation rate and the temperature of the phases (gas and liquid) in contact with the interface as functions of the applied microwave power. The evaporation rate is linearly dependent on the microwave power only above a given field intensity. The temperature of the liquid phase increases linearly, and that of the gas does not vary. These results also suggest that there is no heat transfer across the interface.

In this paper we attempt to specify the behaviour of the interface at which the liquid is transformed into gas, without considering the adjacent phases: the liquid column which is, of course, heated by microwaves and exchanges heat with the surroundings; and the column of flowing gas, which also exchanges heat with the walls of its container.

In order to compare the validity of the different relations that we will test in this paper, we shall refer to a set of 30 labelled experimental results, obtained with a range of initial conditions as different as possible:

$\pi_i = 0; 10; 20; 40; 50$ in Watts;

$T_{cp} = -2.7; 1.8; 5.6; 9; 11.5; 14$ in °C.

T_{cp} is the temperature of the exterior bath which determines the pressure of the gas $P_c = P_s(T_{cp})$; P_c is a constraint of the system. π_i is the incident wave power level, which determines the field intensity $(E_i \cong \sqrt{\pi_i})$. $\overset{\circ}{m}$ is the rate of surface mass evaporation (mg s^{-1} mm^{-2}). T_g and T_l are the temperatures of the phases, measured quite near the interface; we also define the reduced temperatures by

$$\delta_g = \frac{1}{T_{cp}} - \frac{1}{T_g} \quad \text{and} \quad \delta_l = \frac{1}{T_{cp}} - \frac{1}{T_l}$$

Lack of agreement with the classical interface relations

If we could verify a relationship giving the evaporation rate as a function of the thermal and chemical characteristics of the interface, ignoring the value of the electric field, we would then be able to conclude that the action of the field is restricted to the heating of the condensed phase. This, in fact, is not the case.

(a) The formula of Hertz–Knudsen (given in [1]), even if it takes into account the exact temperature of the liquid phase at the surface, does not correctly represent the $\overset{\circ}{m}$ data (see Fig. 1). At least the coefficient K must be dependent on the microwave field.

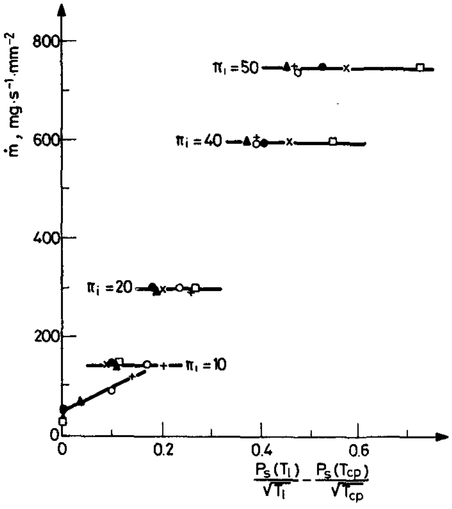

Fig. 1 Hertz–Knudsen representation of the results

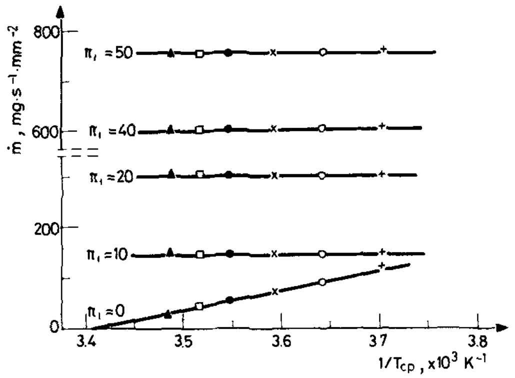

Fig. 2 Erikson representation of the results

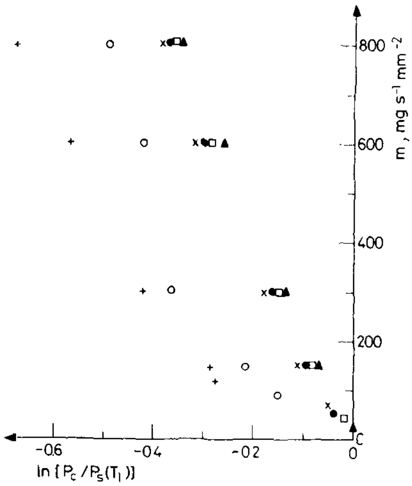

Fig. 3 *Modified Erikson representation of the results*

(b) The first of Erikson's formulae [1] states that the mass rate is proportional to the logarithm of the pressure P_c, or to $1/T_{cp}$. It is numerically found acceptable (see Fig. 2) for zero microwave field only, although heat transfers are not explicitly taken into account in this formula. The modified form, which introduces the exact value of the temperature of the liquid, is not a better representation (Fig. 3).

(c) To evaluate the performance of formula (4) given in [1]

$$\overset{\circ}{m} = A'\left(\frac{1}{T_{cp}} - \frac{1}{T_l}\right) + B'\left(\frac{1}{T_{cp}} - \frac{1}{T_g}\right) \qquad (1)$$

we give the results in Fig. 4 by representing

$$\frac{\overset{\circ}{m}}{\dfrac{1}{T_{cp}} - \dfrac{1}{T_g}}$$

as a function of

$$\frac{\dfrac{1}{T_{cp}}-\dfrac{1}{T_l}}{\dfrac{1}{T_{cp}}-\dfrac{1}{T_g}}.$$

We would obtain a single straight line if the formula agreed with the experimental results. We observe a large discrepancy, which is evidently associated with the dispersion of the experimental points for a given value of T_g. The dashed line is the representative curve for the zero microwave field experiments. We observe that the discrepancy becomes increasingly greater as the field increases.

Finally, formula (1) must be corrected in order to give a satisfactory description of the behaviour of the evaporation rate of a liquid exposed to microwaves, although it is deduced directly from thermodynamics laws. This means that the action of the field does not involve purely a heating process of the liquid.

It also means that the electric field is an additional independent thermodynamic parameter, which cannot simply be integrated into the temperature in order to describe the behaviour of the interface.

Correction to formula (1)

Formula (1) takes into account two thermodynamic forces in order to calculate the entropy production at the interface: the chemical potential and the temperature discontinuities. Two phenomenological coefficients, A' and B', are consequently introduced. Both can be calculated by fitting the experimental data, when the microwave field is off (see dashed line of Fig. 4):

$$A' = -50 \text{ mg s}^{-1} \text{ mm}^{-2}, \quad B' = 227 \text{ mg K s}^{-1} \text{ mm}^{-1}$$

However, the quantity $\mathring{m} - B'\left(\frac{1}{T_{cp}}-\frac{1}{T_g}\right)$ appears to be fit better by a relation such as $C\pi_i + A''\left(\frac{1}{T_{cp}}-\frac{1}{T_l}\right)$ than by $A'\left(\frac{1}{T_{cp}}-\frac{1}{T_l}\right)$ (see Fig. 5).

The graph shows the experimental points to lie on straight and parallel lines. They are shifted proportionally to the incident power value.

Thus, when the electric field is on, an additional term appears to be necessary to complete the relation between forces and fluxes. Moreover, the coefficient A' (which describes the chemical transfer) changes, while the thermal transfer coefficient B' remains constant.

The best fit of the data gives

$$\mathring{m} = \left[A'_0 + A'_1 \exp\left(-\frac{\pi_i}{\alpha}\right)\right]\left[\frac{1}{T_{cp}}-\frac{1}{T_l}\right] + B'\left(\frac{1}{T_{cp}}-\frac{1}{T_g}\right) + C\pi_i \qquad (2)$$

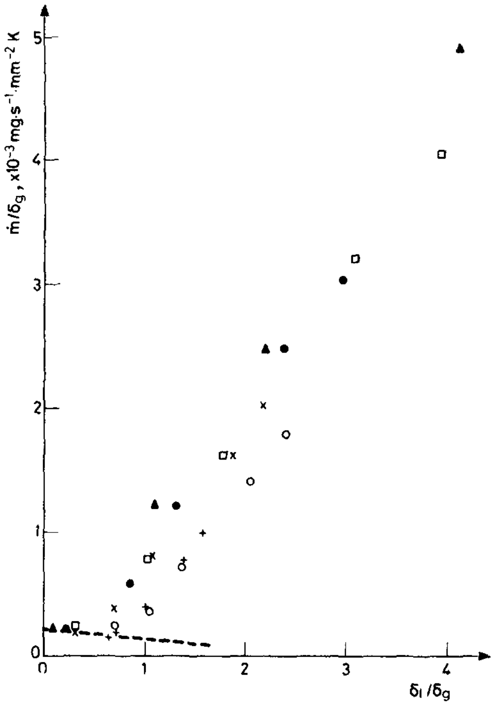

Fig. 4 Misfitting of the results with Mokhlisse's relation

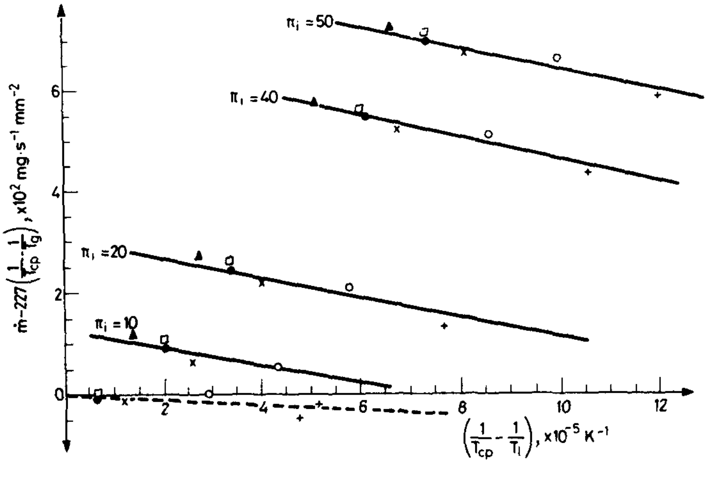

Fig. 5 Representation of the data by $m' = |A'_0 + A'_1 \exp(-\pi_l/\alpha)|\delta_l + B'\delta_g + C\pi_l$

with

$$A'_0 = -250 \text{ mg K s}^{-1} \text{ mm}^{-2}, \quad A'_1 = 200 \text{ mg K s}^{-1} \text{ mm}^{-2}, \quad \alpha = 7.2 \text{ W},$$

$$B = 227 \text{ mg K s}^{-1} \text{ mm}^{-2}, \quad C = 1.75 \cdot 10^{-3} \text{ mg K s}^{-1} \text{ mm}^{-2}\, W^{-1}$$

The coefficient A' changes from the value -50 when $\pi_i = 0$, to a constant value -250 as soon as a field of adequate amplitude is applied. A' describes the chemical transfer as for a coupled activation-saturation process.

Hence, when the field is high, the first two terms are small, and the evaporation rate increases linearly with the power. However, when the field is low, the mass rate is a result of the three terms, which are of similar amplitude. The first two terms correspond to the classical thermodynamics forces.

The last one, $C\pi_i$, corresponds to the enthalpy of alcohol. About 900 Watts is required to evapore 1 g of alcohol per second. This can be written as a function of the absorbed power, π_a, as shown in [1].

Driving pressure

Another way of interpreting the data of Table 1 is to reconsider equations (6)–(11) given in ref. [1]. The flow of gas is due to a driving pressure in the cylindrical column. We can calculate its profile, as soon as the temperature profile is known: $P(x)$ is a solution of the second degree equation

$$P(x) + \frac{\mathring{m}^2 r T(x)}{P(x)} = C$$

in which the value of the constant is obtained, at $x = \infty$, where $P = P_c$ and $T = T_c$. So

$$0 = P^2 - \left(\frac{P_c^2 + m^2 r T_c}{P_c}\right) P + m^2 r \{T_c - (T_c - T_g) \exp s_1 x\}$$

The effective pressure inside the column varies exponentially with the distance

$$P(x) = P_c \left[1 + \frac{m^2 r (T_c - T_g)}{P_c^2} \exp s_1 x\right]$$

It follows that the pressure on the surface is slightly higher than P_c, the relative difference being

$$p = \frac{P\,(x = 0) - P_c}{P_c} = \frac{\mathring{m}^2 r (T_c - T_g)}{P_c^2}$$

p is the reduced driving pressure, which induces the flow of gas. It varies with the square of the rate of mass evaporation.

Equation (14) of reference [1] would mean that the microwave and the heat transfers increase the driving pressure separately.

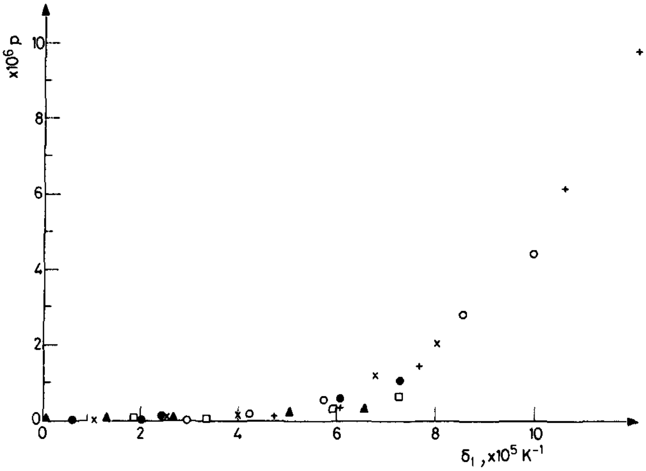

Fig. 6 Representative curve of p as a function of δ_l

The preceding arguments lead us to attempt to relate all the reduced values p, δ_l and δ_g to π_l so as to obtain a description of the interface. By fitting the data numerically, we found that p is a function only of δ_l, as shown in Fig. 6. The best data fit gives

$$p = p_0 \, (\exp \tau\delta_l - 1)$$

where $p_0 = 1.62 \cdot 10^{-8}$, $\tau = 54.700$ K. This is a two-numerical parameter formula. It introduces only one of the three possible variables; but, δ_l being a function of π_a, p could also have been written as a function of the microwave field. Furthermore, the temperature of the gas at the surface is also introduced implicity in the calculation of p. We note immediately that this relation does not refer to any previous non-equilibrium state as do formulae (12) and (14) of ref. [1]. The quantities p_0 and τ_0 would characterize ethyl alcohol and probably the experimental device. p_0 determines a pressure limit: when the interfacial vaporization pressure is lower than p_0, the square of the mass rate is a linear function of the reduced temperature of the liquid δ_l. In contrast, when the pressure is higher than p_0, the logarithmic value of the rate of vaporization is linear with δ_l.

Discussion

Two plausible numerical formulae have been found acceptable to describe how many molecules escape from the evaporating surface when the interface is irradiated by microwaves. The two aspects represented by these formulae are not conflicting, but rather complementary.

One of them considers especially the dynamic behaviour of the gas phase. It establishes a relationship between the pressure gradient in the gas and the liquid temperature at the interface. All quantities introduced are measured with reference to the equilibrium state. In this relation, the microwave field does not appear explicitly. The microwave field heats the liquid phase and the evaporation rate enhancement seems to result from its temperature change.

The second approach, which also gives good agreement between calculated and measured values for the rate of mass evaporation from a liquid under microwave irradiation, starts from the classical analysis of an irreversible process. The microwave field, which acts on both the liquid phase and the interface, is then introduced, and appears in the formula in two separate terms: A conventional one describes the transformation of the liquid into gas at the cost of enthalpy, the energy being supplied by the field. Simultaneously, the microwave field changes the coupling of heat and mass transfers and reduces the portion of thermal energy that the liquid supplies to the interface. According to this theoretical viewpoint, the microwave field would act on the interface in a manner different from pure heating.

In our experimental device, the evaporation is unidirectional and thus, whatever the principal causes of the evaporation process may be, the evaporated molecules cannot be distinguished in the gas phase. The additivity of the mass rates, which is given by formula (2), does not uniquely locate the causal dissipation process at the interface. We even know that the term $C\pi_i$ is of a volumic type.

Our models do not give any precise information about the molecular mechanisms which occur. They give only algebraic relationships between two different sets of system variables. Nevertheless, the experimental study leads to many new important features. We have first proved that it is possible to reverse the thermal gradient between the two phases of an evaporating interface. Furthermore, we have also shown that the heat transfers between the interface and either the liquid or the gas phases are dissymmetric. Finally, the experimental conditions (pressure, temperature of the evaporating surroundings and microwave power levels) have been fully investigated: they have characteristic influences on the behaviour of the system and its non-equilibrium state.

Reference

1 J. M. Thiebaut, P. Colin and G. Roussy, J. Thermal Anal., 28 (1983) 37.

(1) contains all other references cited in this paper

Zusammenfassung — Es wurde die bei niedrigem Druck unter Einwirkung von Mikrowellenstrahlung erfolgende Verdampfung einer polaren Flüssigkeit untersucht. Die früher entwickelten konventionellen Theorien zur Beschreibung der Nichtgleichgewichtsbedingungen der verdampfenden Grenzschicht sind in schlechter Übereinstimmung mit den experimentellen Ergebnissen. Es ist möglich, den Einfluss des Mikrowellenfeldes auf die verdampfende Oberflächenschicht durch Modifizierung des Ausdrucks für die Entropieproduktion in Rechnung zu stellen. Eine andere Näherung, die auf dem Konzept beruht, dass Mikrowellen den Druck erhöhen, wurde ebenfalls als zufriedenstellend gefunden.

Резюме — Исследовано испарение полярной жидкости при низком давлении и облученной микроволновым излучением. Традиционные теории, развитые для описания неравновесных условий испарения на границе раздела, плохо согласуются с экспериментальными данными. Для этого следует учитывать влияние микроволновых полей на поверхность испарения путем изменения выражения для получения энтропии. Найдено удовлетворительным и другое приближение, основанное на концепции погонного пара, что микроволны должны увеличивать давление.