Superheating Effects Associated with Microwave Dielectric Heating

David R. Baghurst and D. Michael P. Mingos*

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, UK

Fluoroptic temperature measurements have established that organic solvents in a microwave cavity superheat by 13–26 °C above their conventional boiling points at atmospheric pressure; this behaviour is interpreted using a model of nucleate boiling that emphasises the importance of the wetting properties of the solvents.

In recent years, the acceleration of a wide range of chemical reactions by microwave heating techniques have been reported.[1–3] When the reactions are performed in closed vessels then the boiling point elevation associated with the increase pressure accounts for the observed rate enhancements. For example, superheating by 100 °C results in a rate enhancement of *ca.* 10^3. The results of reactions carried out at atmospheric pressure have been the subject of more controversy. While the majority of experiments have indicated some rate enhancement,[4–6] more detailed kinetic measurements have indicated that the rates in the microwave cavity are identical to those observed under conventional conductive heating conditions.[7,8] The accumulation of reproducible results in this area has been hampered by difficulties associated with the rapid and reliable measurement of the reaction temperature inside a microwave cavity. Such measurements are required in order to estimate the relative importance of localised microwave heating effects such as those observed in carbon fibre–epoxy resin composites,[9] and general superheating of the bulk reaction mixture.[10–13] Recently, Hoopes and coworkers have tackled these problems using thermal imaging techniques.[14] Their results have indicated that in the initial stages of heating the temperature rise is localised in particular parts of the reaction vessel and that most organic solvents are superheated above their boiling points. Here, we present our independent observations on microwave heating of solvents and propose a model to account for the observed behaviour.

We have used fibre-optic techniques[15,16] to monitor the temperature in four spatially defined parts of a round-bottomed glass flask during solvent heating. The round-bottomed flask is connected to a reflux condenser, which passes through the roof of the microwave oven *via* a port.[4] The output from the four fibre-optic channels was acquired in real time onto an IBM PC-XT computer. The initial rates of heating of a range of inorganic and organic solvents and mixtures have been studied using this technique and the results for water, methanol and ethanol are illustrated in Fig. 1.

In the initial stages of heating of 150 cm^3 of solvent with full power (650 W) the rate of temperature increase is very nearly linear for all the solvents studied. Large differences in the individual probe temperatures were not observed for most solvents, because the solvents' penetration depths were sufficiently large to lead to efficient volumetric heating. Three classes of general behaviour were observed and may be illustrated by reference to specific examples from each class. In the first class ethanol is heated above its boiling point without boiling commencing. The temperature continues to rise and passes through a maximum at point A [Fig. 1(*a*)]. Here the ethanol bumps and begins to reflux vigorously. The temperature at this point drops down to a plateau region (B) where the reflux temperature is maintained typically to within ±3 °C. This temperature, which is still *ca.* 20 °C higher than the normal boiling temperature, may be maintained for many hours and as such an equilibrium is established between

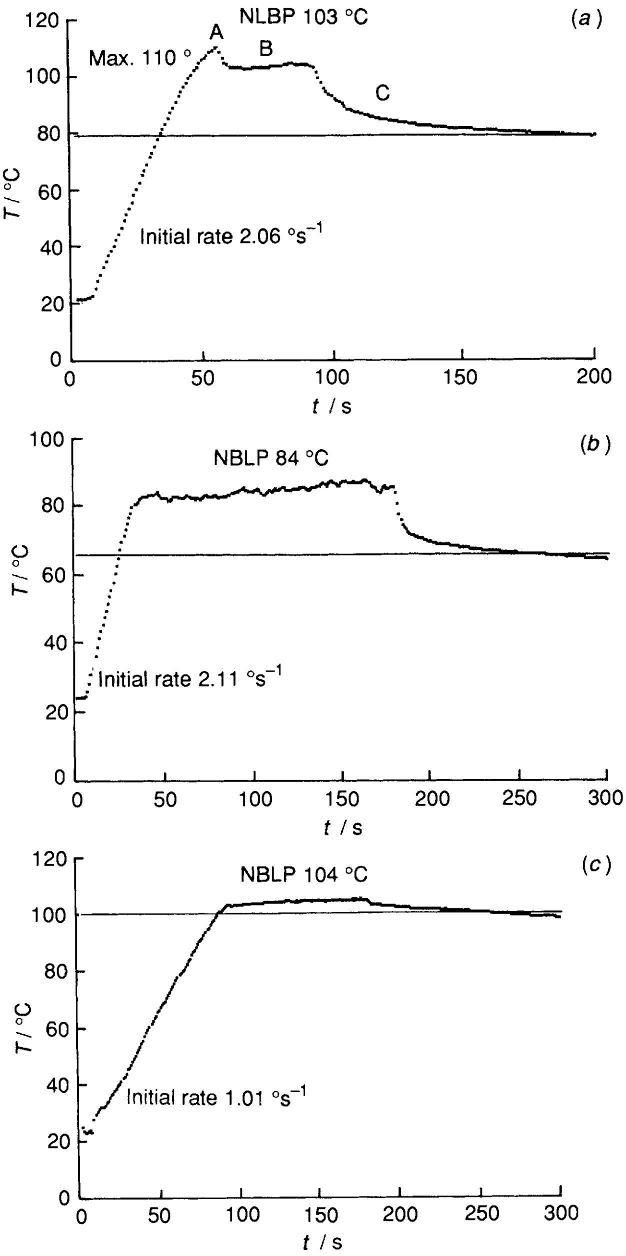


Fig. 1 Microwave heating of (*a*) ethanol, (*b*) methanol and (*c*) water

microwave energy input and a range of heat loss mechanisms. Since the system is at equilibrium conventional superheating is an inappropriate term for this boiling temperature. For reasons discussed below, this temperature will be referred to as the nucleation limited boiling point (NLBP). Removal of microwave power leads to a rapid drop in the observed temperature (C) down to close to the conventional boiling point. In the second class of behaviour [Fig. 1(*b*)] solvents such as methanol are heated to beyond the conventional boiling point but begin to reflux without bumping. As a result there is no drop in temperature observed (A). The majority of organic solvents show NLBP's 13–26 °C above their conventional boiling points (see Table 1) and this accounts for the rate enhancements observed in organometallic and organic microwave syntheses. The efficiency of microwave absorption can be estimated from the initial heating rates and the heat capacities and lies between 50 and 95%. In the final class [Fig. 1(*c*)] very little boiling point elevation is observed and water, for example, shows a NLBP of only 104 °C.

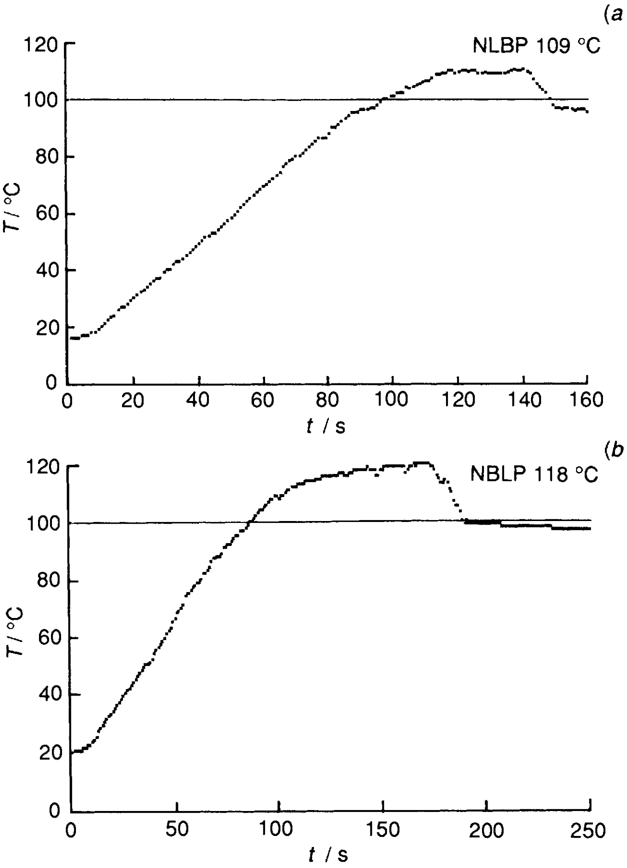


Fig. 2 Nucleate boiling (*a*) 0.27% (volume) Decon 90, (*b*) 0.13% (volume) Triton X100

These observations may be understood within the framework of conventional boiling theory. While some energy no doubt will be lost to the surroundings through convective air flow around the bottom of the flask and through radiation from the surface of the liquid the largest source of energy loss is the act of boiling itself. The most likely source of boiling in our experiments is nucleate boiling.[17] The stages of nucleate boiling are illustrated in Fig. 2.

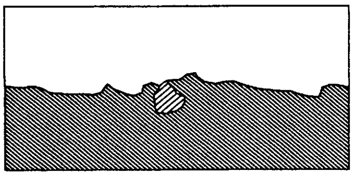
Conventional nucleate boiling relies on the existence of cavities, pits and scratches on the surface of the vessel in contact with the liquid[18] in which bubbles can form. Bubble inception further relies on the existence of a vapour embryo trapped inside the crevice by the bulk liquid. When the temperature of the surrounding liquid is at least equal to the saturation temperature corresponding to the pressure in the vapour embryo then bubble growth occurs. In the simplest model of bubble growth it is proposed that evaporation occurs all around the bubble to liquid interface. The energy for evaporation is supplied by a superheated liquid layer, which surrounds the bubble. Once the forces holding the bubble in place are overcome the bubble is released from the cavity and boiling occurs. As the volume of the superheated liquid layer is increased the number of active embryo sites increases[19] because the layer temperature approaches the saturation temperature of more and more sites.

This model emphasises the importance of available crevices with dimensions of the order of microns and a superheated layer adjacent to these crevices. In conventional heating thermal energy is supplied to the vessel walls themselves by a heating mantle or oil bath *etc.* The walls of the vessel in turn heat the liquid in the vessel. In some regions superheated layers will exist adjacent to embryo sites. Thus, boiling occurs from the surface of the containment vessel at suitable nucleation sites. The inversion of the temperature profile

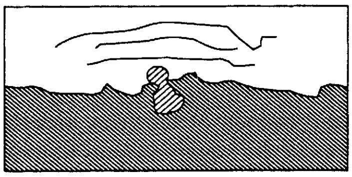
Table 1 Nucleation limited boiling points and heating rates for a range of solvents (% power absorption to nearest 5% assuming full power = 650 W)

Solvent	B.p./ °C	NLBP/ °C	NLBP − b.p./+ °C	Heating rate/°C s^{-1}	Initial power absorption/%	Type
Water	100	104	4	1.01	>95	III[c]
Ethanol	79	103	24	2.06	90	I[a]
Methanol	65	84	19	2.11	>95	II[b]
Dichloromethane	40	55	15	2.16	75	I
Tetrahydrofuran	66	81	15	2.04	—	II
Acetonitrile	81	107	26	2.36	>95	II
Propan-2-ol	82	100	18	2.11	>95	I
Acetone	56	81	25	2.23	90	II
Butanol	118	132	14	1.87	80	II
1,2-Dimethoxyethane	85	106	21	2.54	—	II
Diglyme	162	175	13	2.17	—	II
Ethyl acetate	78	95	17	1.78	70	I
Acetic anhydride	140	155	15	1.97	—	I
iso-Pentyl alcohol	130	149	19	1.92	85	II
Butan-2-one	80	97	17	2.57	—	II
Chlorobenzene	132	150	18	2.63	90	I
Trichloroethylene	87	108	21	1.54	45	II
Dimethylformamide	153	170	17	2.18	>95	II
Chlorobutane	78	100	22	2.59	>95	I
iso-Propyl ether	69	85	16	1.90	50	II

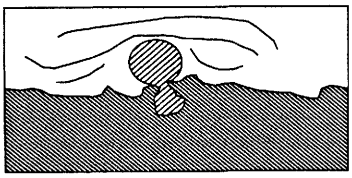
[a,b] Types I and II indicate significant superheating with type I giving a peak in heating before boiling commences. [c] Type III behaviour indicates little superheating.



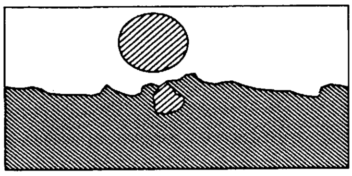
(*a*) Embryo trapped by solvent



(*b*) Hot zone forms around embryo. Embryo growth



(*c*) Bubble growth approaches critical size



(*d*) Bubble detaches. Boiling commences

Fig. 3 Increasing the NLBP of water

observed when the vessel is heated by microwaves accounts for the observation of high NLBPs. In microwave heating the outer walls of the flask are continuously cooled by convective air flow. The layer of solvent immediately adjacent to the walls then may be somewhat below the temperature of the bulk liquid. When the bulk temperature rises to the NLBP heating of the layer of liquid adjacent to the walls of the vessel approaches the saturation temperature of embryo sites.

A consequence of this model is that the differences in behaviour observed for water and the common organic solvents may be explained. The number of vapour embryos trapped in the surface of the vessel is determined in part by the ability of the solvent to wet the surface.[20] Most organic solvents wet the surface of glassware well and diminish the vapour trapping/retention capabilities. As a result the number of nucleation sites is small and a high NLBP is required before boiling can occur. On the other hand, water wets surfaces poorly and there will be large numbers of active sites available.

In order to confirm this hypothesis a number of additional heating experiments were performed with the same glass vessel, volume of solvent and microwave source. First, the wetting ability of water was increased by adding small quantitites of commercially available detergents, Decon 90 and Triton X100. The resulting heating curves clearly exhibit higher NLBPs even for low detergent concentrations (Fig. 3). Indeed, with both of these detergents there appears to be a limit to the boiling point elevation that can be achieved by adding larger quantities (+10 °C, for Decon 90 and +18 °C for Triton X100). When the wetting properties of the glass surface were reduced by silylation with Me_3SiCl then the NLBP of water was reduced to 102 °C.

The ability of ethanol to wet the glass surface was reduced by adding water. When 10% by volume was added the stable boiling temperature was reduced to 98 °C from 103 °C. Addition of 20% reduced it further to 86 °C. The number of available crevices can be dramatically increased by the addition of nucleating materials to the glass vessels. Following heating to 83 °C a sample of ethanol gave a stable boiling temperature identical to that found conventionally (79 °C) when anti-bumping granules were added. It is apparent from these results that the degree of rate enhancement associated with microwave assisted reactions depends on the condition of the glass surface and the wetting properties of the solvent. Unless the NLBP is measured in the reaction this could give the impression of irreproducible results.

Drs D. Kenning and P. B. Whalley, Department of Engineering, Oxford are thanked for their many helpful discussions. Dr Ed Neas of the CEM Corporation is thanked for the loan of the fluoroptic thermometry equipment and for providing us with his results prior to publication. The AFOSR and the SERC are thanked for financial support.

Received, 6th January 1992; Com. 2/00068G

References

1 D. M. P. Mingos and D. R. Baghurst, *Chem. Soc. Rev.*, 1991, **20**, 1.
2 R. Gedye, F. Smith and K. Westaway, *J. Microwave Power and Electromagn. Energy*, 1991, **26**, 3: R. N. Gedye, W. Rank and K. C. Westaway, *Can. J. Chem.*, 1991, **69**, 706.
3 S. T. Chen, S. H. Chiou and K. T. Wang, *J. Chin. Chem. Soc. (Taipei)*, 1991, **38**, 85.
4 D. R. Baghurst and D. M. P. Mingos, *J. Organomet. Chem.*, 1990, **384**, C57.
5 W.-C. Sun, P. M. Guy, J. H. Jahngen, E. F. Rossomando and E. G. E. Jahngen, *J. Org. Chem.*, 1988, **53**, 4414.
6 J. Berlan, P. Giboreau, S. Lefeuvre and C. Marchand, *Tetrahedron Lett.*, 1991, **32**, 2363.
7 E. G. E. Jahngen, R. R. Lentz, P. S. Pesheck and P. H. Sackett, *J. Org. Chem.*, 1990, **55**, 3406.
8 S. D. Pollington, G. Bond, R. B. Moyes, D. A. Whan, J. P. Candlin and J. R. Jennings, *J. Org. Chem.*, 1991, **56**, 1313.
9 A. Bouazizi and A. Gourdenne, *Eur. Polym. J.*, 1988, **24**, 889.
10 C. R. Buffler and T. Lindstrom, *Microwave World*, 1988, **9**, 10.
11 J.-M. Thiebaut, P. Collin and G. Roussy, *J. Therm. Anal.*, 1983, **28**, 37.
12 G. Bond, R. B. Moyes, S. D. Pollington and D. A. Whan, *Chem. Ind.*, 1991, 686.
13 B. F. Armstrong and E. D. Neas, *Sep. Sci. Technol.*, 1990, **25**, 2007.
14 T. Hoopes, E. Neas and G. Majetich, *Abstr. Pap. Am. Chem. Soc.*, 1991, **201**, 231.
15 Model 755 multichannel fluoroptic thermometer by the Luxtron Corporation, Mountain View, CA 94043.
16 K. A. Wickersheim, M. H. Sun and D. H. Rall, *Microwave and High Frequency, Int. Conf.,* Nice, 8–10 Oct., 1991, 183.
17 V. K. Dir, *Proc. 9th International Conference on Heat Transfer*, Jerusalem, 1990, **1**, 129.
18 H. B. Clark, P. S. Strenge and J. W. Westwater, *Chem. Eng. Prog. Symp. Ser.*, 1959, **55**, 103.
19 R. F. Gaertner and J. W. Westwater, *Chem. Eng. Prog. Symp. Ser.*, 1960, **56**, 39.
20 S. P. Liaw and V. K. Dhir, *ASME J. Heat Transfer*, 1989, **111**, 731.