Thin Solid Films, *103* (1983) 417–421
GENERAL FILM BEHAVIOUR

ELECTRIC CHARGE GENERATION IN BENZENE–WATER MIXTURES DURING CONDENSATION AT LOW TEMPERATURES

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(Received February 7, 1983; accepted February 25, 1983)

It was found that, during the condensation of binary benzene–water mixtures from the gas phase, electric charges are generated. Several processes which may be responsible for this phenomenon are discussed. It seems that one of these may be a hypothetical chemical reaction in the condensate layers producing ethanol molecules.

1. INTRODUCTION

Electrical polarization occurring during the condensation of molecules which have a dipole moment has recently been studied by several researchers[1–7]. The accepted mechanism accounting for the observed effects is based on a polarization of molecular dipoles. This explains why no electret effects have been observed in the case of non-polar molecules.

Sujak and Chrzanowski[6] have recently reported that the condensation of binary mixtures of vapours of some non-polar liquids onto a substrate cooled to liquid nitrogen temperatures results in the generation of electric charges in the condensates. This suggests that some specific intermolecular forces are operating and that molecular complexes with a non-zero instantaneous dipole moment are produced. When these complexes are trapped within the condensate layer they give rise to a metastable dipole moment in the condensate. The observed effects are then similar to the phenomena arising during the condensation of gases whose molecules have a permanent dipole moment.

Because no electrization effects are observed for condensates of pure non-polar vapours but an electret effect does occur in the condensation of mixtures of non-polar molecules, we are led to consider the nature of the electrical properties of the "polar" plus "non-polar" mixture in the condensed state. This solid solution of a polar substance in a non-polar medium can produce an electrolyte with electrical properties which differ from those of the liquid mixture. Since electrification processes are known to occur during the flow of liquid hydrocarbons contaminated with water[8], mixtures of benzene and water were studied under various conditions.

In the present paper the electret effect that occurs during the condensation of benzene–water vapour mixtures is reported.

0040-6090/83/$3.00

2. EXPERIMENTAL DETAILS

The condensates of benzene–water mixtures were formed by "freezing" of a molecular beam onto substrates at temperatures of 90–273 K. The system for the electrical measurements, the vacuum apparatus used in the experiments and the experimental method have been given elsewhere[7]. The condensation of the gaseous benzene–water mixture occurs on the cooled electrode (copper plate) of a measuring parallel plate capacitor. The electric current which flowed during condensation of the molecules was measured with a vibrating reed electrometer connected to the condensation substrate and coupled with a self-recording compensator. This compensator recorded the temporal variation in the current $J(t)$ generated during the condensation of the vapour mixture under investigation. The generated charge Q was determined from the relation

$$Q = \int_{t=0}^{t=t(m_0)} J(t)\,\mathrm{d}t$$

where $J(t)$ is the current *versus* time curve and m_0 is the mass of the condensed vapour mixture.

3. RESULTS AND DISCUSSION

High purity liquids I (i.e. benzene and water) were used as vapour sources for the condensation. Carefully prepared benzene, contaminated with no water or other polar pollutants, gave no electret effect in any experiment in which pure vapour was used. Curves of Q *versus* temperature T for condensates of mixtures of benzene and water with four concentrations of water are shown in Fig. 1.

The $Q(T)$ curves represent quantifiable evidence of the charge generation process. A low concentration of one of the components in the mixture under investigation had a marked effect on the measured charge Q. It was observed that even a very low concentration of water (approximately 0.001 mol.%) in the condensing benzene vapour led to charge generation in the condensate. To investigate the possibility of modification of the electrification processes in the condensates investigated, the condensation was performed in an external electric field. An electrostatic filter held at a different potential relative to earth was also used to exclude possible ion currents. However, it was found that the dispersion of the measured Q values usually did not exceed the maximum experimental error. This suggests that the process of charge generation in the condensates investigated occurs during condensation of the molecular mixture onto the cold substrate. This process (or processes), which is independent of external electric fields and takes place in the condensate layer, must be very intense, *i.e.* the intensity of the internal electric fields in the condensate far exceeds that of the external applied field.

A change in the concentration of water in the mixture to be condensed significantly affected the shape of the observed $Q(T)$ curves. A change in the substrate material (copper or silver) or the replacement of the substrate by a dielectric film did not affect the observed electret effect. It should be noted that the $Q(T)$ curves for the mixture investigated represent mean values of the results obtained in many experimental runs for a rather large dispersion in the observed Q values.

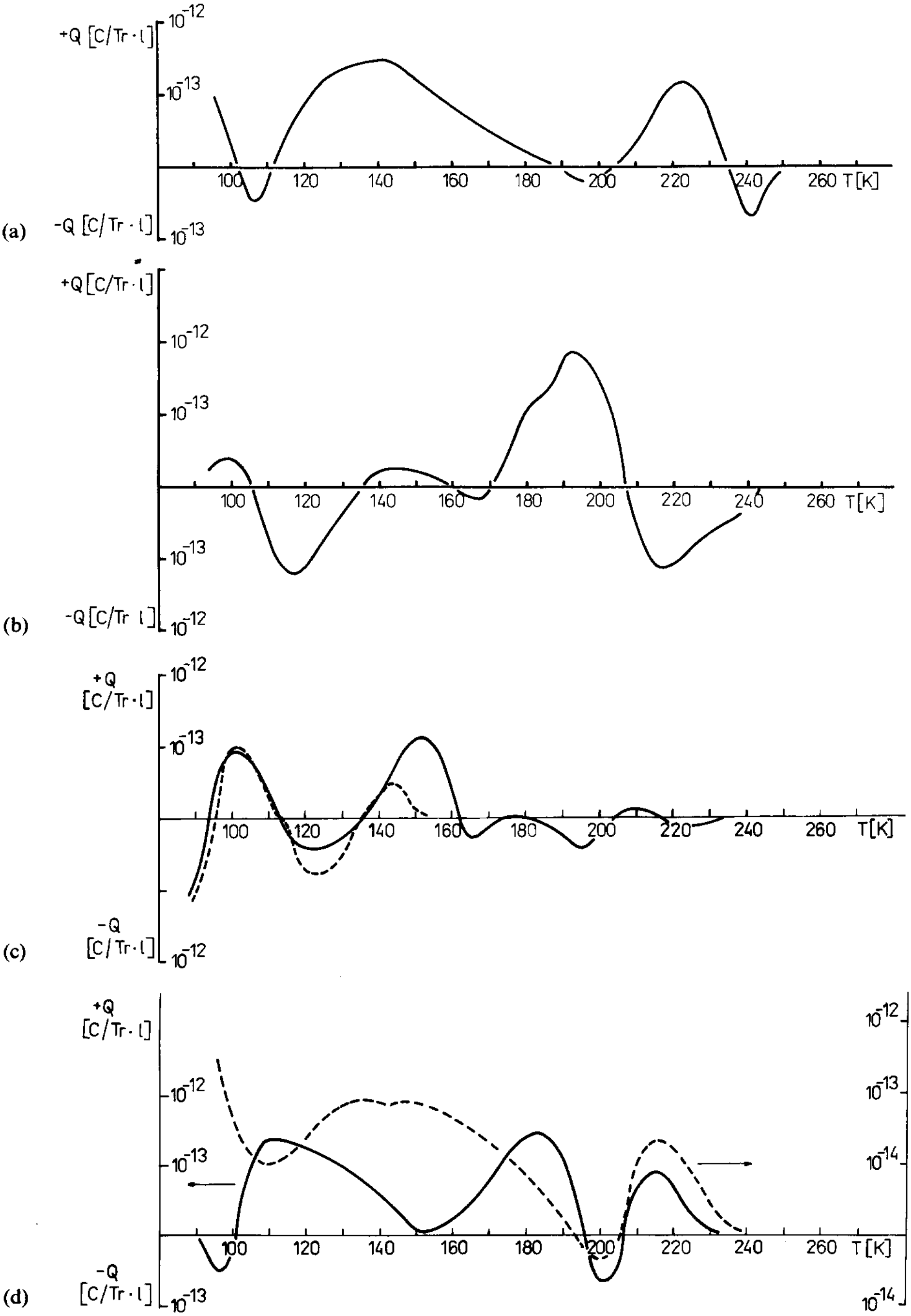

Fig. 1. Charge generation curves $Q(T)$ for condensates from benzene–water mixtures: (a) benzene plus 0.005 mol.% water; (b) benzene plus 0.025 mol.% water; (c) benzene plus water in the molar concentration ratio of approximately 100:20 (---, $Q(T)$ curve for pure ethanol); (d) water plus 0.025 mol.% benzene (---, $Q(T)$ curve for pure water).

The results presented suggest that the process (or processes) of electrification is very intense in the condensates investigated. The nature of the process is probably a consequence of intermolecular interaction between benzene and water molecules. The intensity of the process depends only on the condensation substrate temperature T. It is worth noting that a local phase transformation in the condensates may affect the value of the observed charges as a consequence of a change in the dielectric permittivity. This is a result of the method used to detect the charges.

The observed effect of electrification in the condensates investigated may be caused by several different processes. Some of these are discussed briefly below.

(1) The free surface of the condensate may be an interface at which the ions H^+ and OH^- can be produced during the condensation and can separate. Some water molecules may also accumulate there and then generate an electric double layer in a similar manner to that predicted by Flatcher[9] for pure ice. The thickness and the dipole moment of the layer may vary as the temperature of the condensation process changes.

(2) During the condensation process the dissociation of water molecules can occur:

$$H_2O \rightleftharpoons H^+ + OH^-$$

or

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

The variation in the yield of these processes with temperature may produce the oscillations in the magnitude of the observed charges. The alteration in the sign of the charge may be the result of the different activation energies for diffusion of the ions. This process depends on the internal structure of the condensate layer. The ions diffusing to the colder interface with various mobilities can produce the separation of charge of varying magnitude[10].

(3) Strong intermolecular interaction between benzene and water molecules (or ions) may produce molecular complexes of the hydrogen bond or "charge transfer" type. Some of these complexes can exhibit effective instantaneous dipole moments. This may lead to a metastable dipole moment of the condensate.

(4) Good dispersion of water molecules in the benzene matrix and therefore the intense molecular interaction between the benzene and water molecules (ions, radicals) and the accompanying evolution of heat of condensation can lead to the dissociation of some of the benzene molecules too. These processes may give rise to chemical reactions between the products of the dissociation. A large number of structural defects in the condensate, perturbing the electrical structure of the layer, may also be an important factor facilitating the chemical reaction by acting as centres of the reaction.

Although the occurrence of such a hypothetical reaction seems rather difficult to accept completely (*i.e.* disintegration of benzene molecules), taking into account the extreme conditions inside the condensate—very strong (10^6–10^7 V cm^{-1}) and inhomogeneous local electric fields—as well as some recent results reported in papers dealing with chemical reactions at low temperatures[11,12], we admit the possibility of such a process. The products of the hypothetical reaction would be polar molecules, *e.g.* of ethyl alcohol ($\mu = 1.6$ debye), which when trapped within the condensate layer may be a source of the observed electret effect.

It is known[11] that the chemical reactions taking place in condensates are particularly intense in temperature ranges where transformations occur in the condensate. The analysis of the results obtained suggests that the maxima of the $Q(T)$ curves shift as the concentration of water in the condensed mixture is varied. For high concentrations of water in the mixture the maxima in $Q(T)$ appear at temperatures near to the temperature ranges at which phase transformations in ethanol layers have been observed[13], namely 96 and 123 K. In Fig. 1(c) the $Q(T)$ curve for pure ethanol condensates is also presented. As is seen, both curves are similar in shape. Above 160 K the electrical processes that occur in the condensates investigated may be of a different nature because the electret effect in the ethanol cryocondensates was observed only below 160 K [3,7].

The similarity in the range 90–160 K of the $Q(T)$ curves for ethanol and for the mixture investigated is not of course evidence that the discussed chemical reaction really occurs. Proof that the reaction actually takes place could be obtained from an analysis of the condensate components. Unfortunately, we were not able to perform this analysis. However, we intend to carry out such a study.

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