ELECTRIC CHARGE IN BINARY MIXTURES OF NON-POLAR MOLECULES CRYOCONDENSED AT LOW TEMPERATURES

BOGDAN SUJAK AND JANUSZ CHRZANOWSKI

Institute of Experimental Physics, University of Wrocław, Cybulskiego Street 36, 50-205 Wrocław (Poland)

It was found that during the cryocondensation of binary mixtures of non-polar vapours surface charges are generated on the free surface of the condensate. This phenomenon can be explained by postulating the existence of molecular complexes exhibiting effective instantaneous dipole moments trapped within the cryocondensate layer.

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1. INTRODUCTION

Studies of polar molecule cryocondensates carried out since the early 1970s have demonstrated the possibility of charge generation on the free surface of the condensates[1-6].

It has been observed that at low temperatures an electric current is generated during the process of cryocondensation of a beam of polar molecules. The current generated can be measured with an electrometer coupled to a metal substrate used for the condensation. It has been found that the electret effect (*i.e.* the density of the surface charge and its sign) is not influenced by an external electric field, by the flow rate of the gaseous phase or by the material of the condensation surface. These results suggest that the charge generation on the free surface of a polar molecule condensate is due to the polarization of the polar molecules condensing in the cryocondensation process. For non-polar gases or vapours no electret effects have been observed.

The studies of condensates of binary mixtures of polar molecules that have been carried out recently have shown that if there is a low concentration (a few per cent) of one of the components in the gaseous phase mixture a simple additivity of electret effects is observed[7]. However, for condensates comprising binary mixtures of polar molecules with high concentrations of both components, the electret effect is not simply the sum of the individual contributions. An especially interesting problem is therefore the condensation of binary mixtures of non-polar components, *i.e.* components with no permanent dipole moment ($\mu = 0$). Specific intermolecular interaction may occur in some cases.

2. EXPERIMENTAL

Details concerning the measuring equipment used in our experiments have

been given previously[4, 5] and the system (Fig. 1) only is briefly described here.

A heat exchanger with a parallel plate capacitor for measurements was positioned inside the vacuum chamber. The lower electrode of the capacitor was fixed to the heat exchanger and was used as the substrate. It was connected to a vibrating reed electrometer to measure the charges generated during the deposition of the gaseous phase to be studied. A dosimetric system allowed the admission of a strictly controlled amount of gas. The entire heat exchanger was shielded with a thermal screen (at 295 K) to ensure that the condensation process took place only on the measuring electrode. In some runs the upper electrode of the capacitor was polarized by applying a high voltage in order to detect possible ion currents in the condensing molecular beam due to free charge carriers. The substrate was cooled to
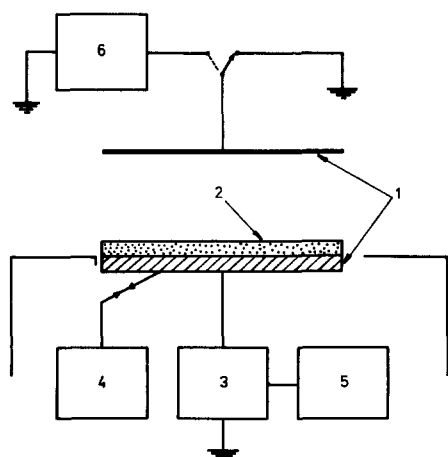

Fig. 1. The system for electrical measurements: 1, parallel plate capacitor for measurements; 2, cryocondensed layer; 3, vibrating reed electrometer; 4, sample heating–cooling system; 5, self-recording compensator; 6, high voltage supply.
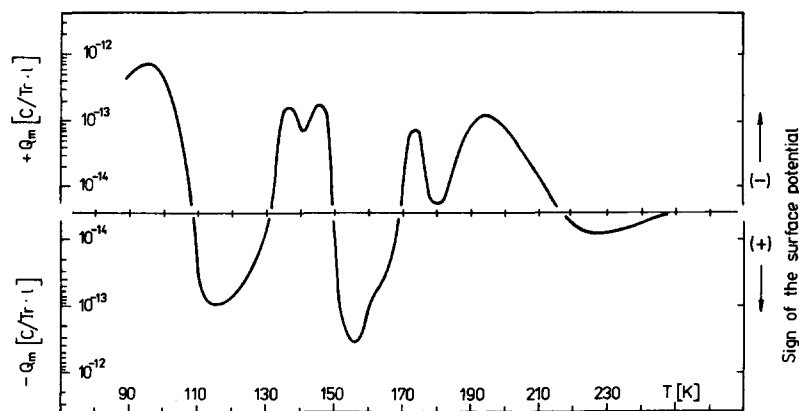

Fig. 2. The charge generation curve Q_m vs. T_s for the cryocondensates of a C_6H_6–1,4-$C_4H_8O_2$ vapour mixture with concentrations approximately in the ratio 50:50 (mol.%).

the required temperature and then deposition of the gaseous phase was carried out under a vacuum of 5×10^{-4} Pa.

The experimental procedure was based on measurements of the charge generated during the deposition of the gaseous mixtures under study as a function of the substrate temperature. Curves of Q_m *versus* T_s were drawn, where T_s is the substrate temperature and Q_m is the charge measured during a complete condensation cycle for a constant mass.

The relation between the surface charge Q_s appearing on the free surface of the condensate and the measured charge Q_m is given by

$$Q_m = -Q_s \frac{x}{\varepsilon d}$$

where x is the thickness of the condensate layer, d is the separation of the electrodes and ε is the dielectric permittivity of the condensate. This relation was developed from molecular orientation studies[2,5] and holds for $x \ll d$.

3. RESULTS

High purity non-polar liquids such as benzene (C_6H_6), 1,4-dioxane ($C_4H_8O_2$) and carbon tetrachloride (CCl_4) were used as vapour sources for condensations. No electret effects were observed in any of the experiments using pure vapours provided that some residual (background) charges (of the order of 10^{-15} C Torr^{-1} l^{-1} for 1,4-dioxane) probably resulting from contamination by water were neglected.

The curves of Q_m *versus* T_s for the condensates of a mixture of C_6H_6 and 1,4-$C_4H_8O_2$ are shown in Fig. 2. The concentrations of the components in the vapour phase mixture were approximately in the ratio 50:50 (mol.%). Figure 2 gives quantifiable evidence of the charge generation process. The cryocondensation was performed in an external electric field of the order of 200 V cm^{-1} at various flow rates with no effect either on the sign or on the values of the measured charge. Furthermore, it can be seen that the amount and the sign of the measured charge are dependent on the condensation temperature in a similar way to those of the pure polar molecule condensates (see refs. 2, 4 or 5).

A similar charge generation effect for mixtures of CCl_4 and C_6H_6 is shown in Fig. 3. A curve of Q_m *versus* T_s was recorded for vapour mixtures of components with concentrations approximately in the ratio 50:50 (mol.%). Within the temperature range 90–215 K only positive charges are observed. Above 215 K some negative charge is generated. It is important to note that the curves Q_m *versus* T_s presented in Figs. 2 and 3 represent mean values of results obtained in many experimental runs. We observed a rather large dispersion in the values Q_m, especially at higher temperatures of condensation.

4. DISCUSSION

The electret phenomena of polar molecule condensates, as hitherto observed, can be explained on the basis of the model of molecular polarization[2,4-6] taking into consideration only the interaction between the molecules and the condensation surface. According to this model no electret effects are to be expected for non-polar molecules and none were observed.
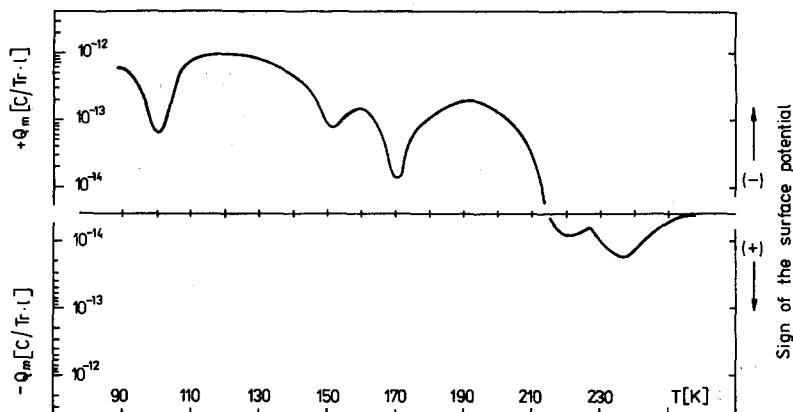
Fig. 3. The charge generation curve Q_m vs. T_s for the cryocondensates of a C_6H_6–CCl_4 vapour mixture with concentrations approximately in the ratio 50:50 (mol.%).

The electret phenomenon we observed during the condensation of binary gaseous mixtures of non-polar molecules suggests that intermolecular interactions are, in some cases at least, very important.

The results for binary mixtures of non-polar compounds such as C_6H_6–1,4-$C_4H_8O_2$ or C_6H_6–CCl_4 suggest that weak intermolecular forces (i.e. van der Waals' interactions) between the non-polar molecules may generate molecular complexes of short lifetime with a non-zero dipole moment.

During condensation at low temperatures the times of the accommodation processes of gaseous molecules are very short ($\approx 10^{-10}$ s). The molecular complexes with virtual dipole moments may therefore be "frozen" in less than the lifetime of the polar complexes. This leads to a metastable dipole moment of the condensate.

If we accept the hypothesis of molecular polarization of the condensed dipoles, the different signs of the surface charges may be explained by there being opposite orientations of the complexes to the substrate in different temperature ranges (not considering the mechanism of this polarization). Local oscillations in surface charge values may be caused by various phase transitions within the condensates or by changes in the intensity of the interaction between the polar complex and the substrate.

The effective dipole moment of the cryocondensate depends on the bond energy of the complexes and on the condensation temperature. An increase in the condensation temperature increases the accommodation time and acceleration of the relaxation processes inside the condensate may take place. This may reduce the lifetime of the polarized complexes in the condensate and may result in lower values of the surface charge.

The instantaneous dipole moment of the complex has no immediate influence on the surface charge, the value of which depends strongly on the degree of polarization of the complexes (i.e. on the components of the dipole moments which are normal to the substrate surface).

The observed phenomenon may also be caused by chemical reactions between impurities within the condensates. These reactions, by generating free charge

carriers, could produce a surface charge in the condensate; however, it is assumed that this mechanism is less probable.

Studies of the cryocondensation of binary systems may yield interesting information about intermolecular interactions, particularly for complexes of low bond energy and short lifetime (*e.g.* complexes of the "charge transfer" type). During cryocondensation on a cold surface "freezing" of the polarized complexes occurs; their existence can therefore be detected. The sensitivity of this method is limited by the value of the measured charge generated during cryocondensation and by the purity of the gaseous phase sources used in the experiments.

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