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# MEASUREMENT OF CONTACT ANGLES UNDER CONDENSATION CONDITIONS. THE PREDICTION OF DROPWISE–FILMWISE TRANSITION

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**Abstract**—Values of contact angles for the systems benzene, carbon tetrachloride, methanol and aniline on P.T.F.E. measured under condensation conditions are presented. The results confirm the role of surface properties in controlling the mechanism of condensation on solid surfaces and with the exception of methanol the contact angles increased as predicted with decreasing pressure. The results indicate that under practical working pressures filmwise condensation of benzene and carbon tetrachloride will always take place on P.T.F.E. surfaces. The pressure at which the contact angle attained the critical value for transition from filmwise to dropwise condensation agreed with previous experimental observations on this system.

## NOMENCLATURE

M = mass L = length
T = time t = temperature

$T$, temperature [t];
$\theta$, contact angle;
$\gamma$, surface free energy $[ML^{-2}T^{-2}]$;
$\gamma_c$, critical surface tension $[MT^{-2}]$;
$\pi_e$, equilibrium film pressure $[ML^{-2}]$;
$S$, spreading coefficient $[ML^{-2}T^{-2}]$.

Subscripts
$L$, liquid;
$S$, solid;
$SL$, solid–liquid;
$V$, vapour.

## INTRODUCTION

THE USE of surface coatings to promote dropwise condensation and thus increase the rate of heat transfer has been the subject of many investigations. The application of polytetrafluoroethylene, P.T.F.E., coatings for this was first reported by Topper and Baer [1]. It was shown to be effective for condensing water, ethylene glycol, nitrobenzene and aniline. P.T.F.E. has the advantage that it can be used up to 500°F and the increase of the overall heat transfer coefficient for these systems is high enough to outweigh the cost of the coating. In evaluating the use of P.T.F.E. with other systems however, Mizushina *et al.* [2] found that for carbon tetrachloride, benzene and methanol, film condensation occurred and the coating was apparently ineffective.

It has been shown by Davies and Ponter [3] that the mechanism of condensation can be predicted from the surface properties of the solid and liquid phases. Thus by considering the equilibrium of a droplet on a solid surface the surface free energies of the film free solid $\gamma_S$, liquid $\gamma_L$ and solid–liquid interfaces $\gamma_{SL}$ may be related to the contact angle of the liquid droplet $\theta$ and equilibrium film pressure $\pi_e$

$$\gamma_S - \gamma_{SL} = \gamma_L \quad \cos\theta + \pi_e. \qquad (1)$$

The condition for the liquid to spread over the surface (the conditions for filmwise condensation) may be described by the spreading coefficient $S$,

$$S = \gamma_S - \gamma_{SL} - \gamma_L. \qquad (2)$$

Introducing the contact angle $\theta$ into equation (2)

$$S = \pi_e + \gamma_L(\cos\theta - 1). \qquad (3)$$

When $S \leqslant 0$ dropwise condensation results.

Since Fox and Zisman [4] have shown that on low energy surfaces such as P.T.F.E. the equilibrium film pressure for pure liquids is negligible, $S$ now becomes

$$S = \gamma_L(\cos\theta - 1). \qquad (4)$$

That is, the spreading coefficient is controlled solely by the contact angle and the surface free energy of the liquid. For this to be zero (the limiting condition for dropwise condensation) then since $\gamma_L$ must always be finite, the mechanism of condensation for a particular system on any low energy surface is controlled by the contact angle alone.

Analysing the results of previous workers [1, 2, 5] it is apparent that dropwise condensation of most organic systems on P.T.F.E. can only be achieved under reduced pressure conditions. From this it was suggested [3] that for condensation of pure vapours of benzene, carbon tetrachloride and methanol the contact angle would increase as the pressure was reduced and might even reach the limiting value for dropwise condensation. Other factors influencing contact angle, surface roughness and temperature have already been discussed by Ponter and Davies [6, 7]. To test these predictions it is necessary to have information on contact angles under conditions prevailing during condensation and as no data is available a programme of work was undertaken.

## APPARATUS

The apparatus used is illustrated in Fig. 1 and consists of a 1 litre still with a cell mounted vertically above it in which the P.T.F.E. specimen was mounted. The still is fitted with a thermometer pocket, condensate return line and liquid feed line. The cylindrical cell (15 cm × 10 cm o.d.) is split into two sections, the bottom section being fitted with two optical flats situated on opposite sides of the cell for viewing the surface of the specimen. The P.T.F.E. specimen (5 cm × 3 cm) is supported horizontally on glass mounts fused into the walls of the cell. Above this a small reservoir is positioned and liquid from the still is fed into this through a stainless steel capillary tube (0·093 in. i.d.) using a D.C.L. micropump. The still and cell are heated electrically, the power input being controlled by two Variacs. The whole apparatus is lagged with asbestos rope to minimize heat losses. Vapour from the cell is condensed in a glass helical coil condenser and returned to the still. Vacuum is applied on the vapour line, two cold traps are inserted between the condenser and vacuum pump to condense out traces of vapour passing from the condenser. The operating pressure is measured using a mercury manometer. The P.T.F.E. specimen was carefully prepared. The surface was first smoothed and then pressed between two plate glass surfaces. The surface roughness, measured by a Talysurf meter, was of the order of $1 \times 10^{-6}$ in. The specimen was then washed in boiling distilled water, degreased with acetone and finally again thoroughly washed with boiling distilled water. The glass apparatus was all washed in chromic acid, distilled water and dried before assembly. Care was taken to ensure that the plate was horizontal. To achieve this, the vertical cross wire in a travelling microscope was aligned against a thin plumb line. The goniometer eyepiece was then rotated through 90° and the specimen plate adjusted until its surface lay parallel to the new position of the cross wire. Variations of plate inclination of up to $\frac{1}{2}$ degree to the horizontal did not

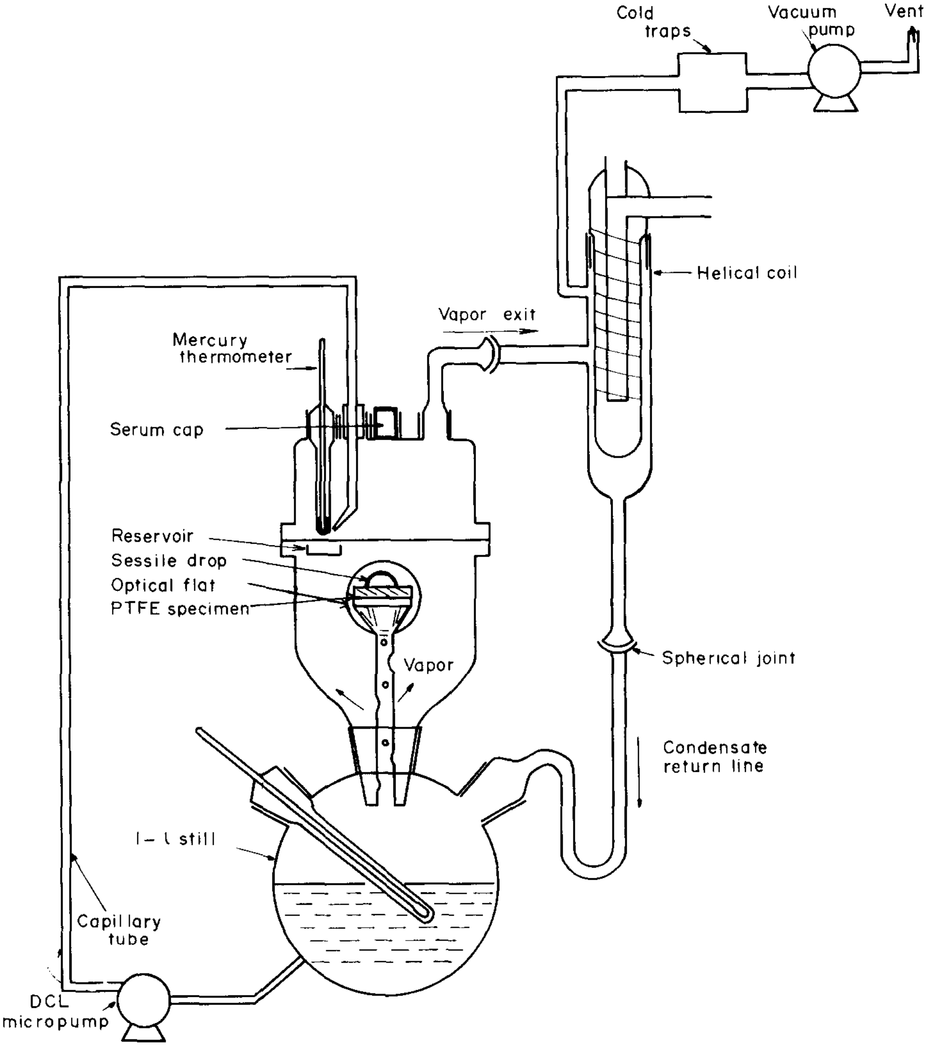

FIG. 1. Contact angle cell.

affect the value of contact angle obtained. The liquids used were "Analar" grade and were redistilled before use. The physical properties, density and surface tension were measured and compared with tabulated data.

The apparatus was allowed to reach equilibrium. The contact angle $\theta$ of a drop condensed on the surface of the specimen was then measured using a travelling microscope fitted with a goniometer eyepiece. Liquid could be added to the drop from the reservoir using an Agla Syringe fitted through the serum cap. Sufficient liquid was added, if necessary, to establish an equilibrium drop height on a flat surface [8]. Measurements were taken of droplets formed well away from the edge of the P.T.F.E. specimen to avoid edge effects. This procedure was repeated several times under each set of conditions. Values were reproducible to ±1°.

## RESULTS AND DISCUSSION

The variation of contact angle with applied pressure is shown in Figs. 2 and 3. With the exception of methanol, in the systems studied the contact angle increased with decreasing pressure. For methanol it was impossible to form a sessile drop on the surface during condensation, a film of condensate being formed at all pressures studied down to 60 mm Hg, i.e. the contact angle was zero over this range. For benzene and carbon tetrachloride the contact angle increased to 47° and 35° respectively at 100 mm Hg and therefore in practice filmwise condensation would still take place in these systems. In aniline however $\theta$ increased to the limiting value for transition to dropwise condensation at a pressure of 80 mm Hg. This agrees well with the data of Topper and Baer who reported dropwise condensation of aniline on P.T.F.E. at 68 mm Hg pressure thus confirming the determining role of surface properties on the mechanism of condensation. Furthermore the results establish that dropwise condensation could never be attained for methanol, benzene and carbon tetrachloride on P.T.F.E. at realistic working pressures extending the previous data which was measured only at atmospheric pressure.

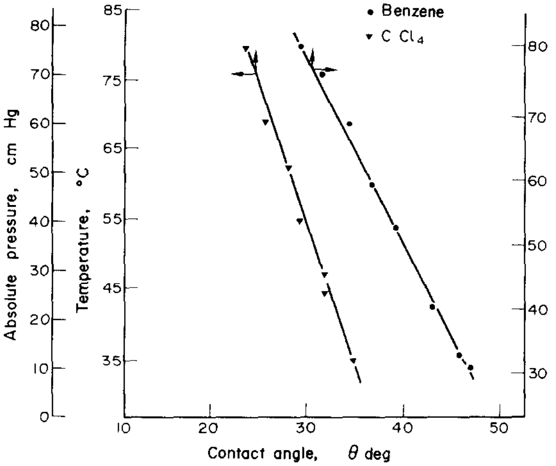

FIG. 2. Condensation on P.T.F.E.

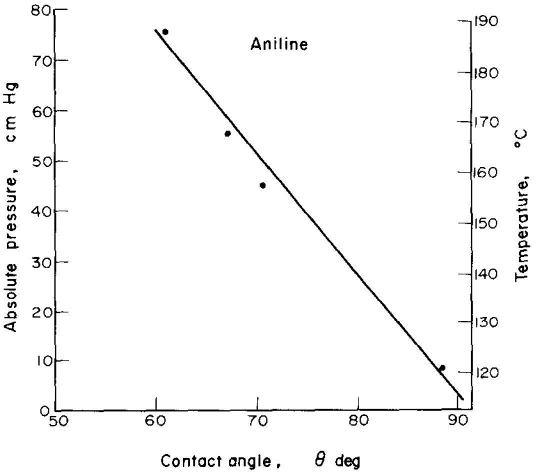

FIG. 3. Condensation on P.T.F.E.

The results allow an insight into the comparative effects of temperature and pressure on this phenomenon. The effect of temperature on contact angle has been well documented [7, 9], the most recent review being given by Petke and Ray [10]. Accepting a temperature coefficient of contact angle on smooth low energy surfaces to be +0·06 degrees/°C the increase in contact angle attributable to temperature alone, represents at most only 30 per cent of the total measured change. Thus the main effects must be due to the variation in pressure on surface properties with a small contribution due to temperature on the surface free energies of solid and liquid interfaces.

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## MESURE DES ANGLES DE CONTACT SOUS DES CONDITIONS DE CONDENSATION. LA PRÉDICTION DE LA TRANSITION GOUTTES-FILM

**Résumé**—On donne les valeurs mesurées des angles de contact pour les systemes benzène, tetrachlorure de carbone, méthanol et aniline sur le P.T.F.E., sous des conditions de condensation. Les résultats confirment le rôle des propriétés de surface dans le contrôle du mécanisme de condensation sur des surfaces solides et, à l'exception du méthanol, les angles de contact croissent comme prévu quand la pression diminue. Les résultats indiquent que sous des pressions de travail usuelles, la condensation en film du benzène et du tétrachlorure de carbone aura toujours lieu sur des surfaces P.T.F.E. La pression pour laquelle l'angle de contact atteint la valeur critique pour la transition film gouttes de la condensation est en bon accord avec les observations expérimentales antérieures sur ce système.

## MESSUNG VON RANDWINKELN BEI KONDENSATION. BESTIMMUNG DES ÜBERGANGS VON TROPFEN- ZU FILMKONDENSATION

**Zusammenfassung**—Es werden Messwerte von Randwinkeln unter Kondensationsbedingungen wiedergegeben. Die untersuchten Stoffe sind Benzol, Tetrachlorkohlenstoff, Methanol und Anilin auf Polytetrafluoräthylen. Die Ergebnisse bestätigen die entscheidende Rolle, die Oberflächemeigenschaften beim Mechanismus der Kondensation an festen Oberflächen spielen. Die Voraussage, dass die Randwinkel mit fallendem Druck steigen, wurde für alle Stoffe mit Ausnahme von Methanol bestätigt. Die Ergebnisse zeigen, dass bei praktischen Arbeitsdrücken Benzol und Tetrachlorkohlenstoff auf Polytetrafluoräthylen stets als Film kondensieren.

Der Druck, bei dem der Randwinkel den kritischen Wert für den Übergang von Film- zu Tropfenkondensation annimmt, stimmte überein mit früheren experimentellen Beobachtungen.

## ИЗМЕРЕНИЕ КОНТАКТНОГО УГЛА В УСЛОВИЯХ КОНДЕНСАЦИИ. РАСЧЕТ ПЕРЕХОДА ОТ КАПЕЛЬНОИ КОНДЕНСАЦИИ К ПЛЕНОЧНОЙ

**Аннотация**—Представлены результаты измерений контактного угла для стстем бензин. четыреххлористый углерод, метанол и анилин на поверхности из политетрафторэтилена, полученные в условиях конденсации. Результаты подтвержлают роль свойств поверхности в регулиоовании механизма конденсации на твердых поверхностях, а также предположение о том, что за исключением метанола контактный угол увеличивается при уменьшении давления.

Результаты показывают, что при обычных давлениях, встречающихя в практике, на поверхности из политетрафторэтилена всегда происходит пленочная конденсация бензина и четыреххлористого углерода. Величина давления, при котором контактный угол достигает критического значения для перехода от пленочной конденсации к капельной, согласуется с экспериментальными данными, полученными ранее для этой же системы.