Study on Dropwise Condensation Curves*

(Dropwise to Filmwise Transition of Propylene Glycol,
Ethylene Glycol and Glycerol Vapors on a Copper Surface
Using a Monolayer Type Promoter (Part 1))

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In order to clarify the mechanisms of transition from dropwise to filmwise condensation heat transfer, dropwise condensation curves on a copper surface adsorbing a common monolayer type promoter, trilauryl trithiophosphite, were measured precisely for the substances having various physical properties, i.e. propylene glycol, ethylene glycol and glycerol vapors, at several reduced pressures and vapor forces.

As the condensing surface subcooling increases in steady states, an abrupt change from drop type to film type occurs and the dropwise condensation curves of all the vapors become discontinuous at comparatively high vapor pressures, although the curves are continuous for propylene glycol and glycerol vapors at low vapor pressures. The surface subcoolings at the points, where these discontinuities start, are also shown and discussed.

Key words: Phase change, Dropwise condensation curve, Transition, Organic vapor

1. Introduction

The object of the research is to clarify the dropwise condensation curve, i.e. the relation between the heat flux and the surface subcooling in dropwise condensation. There are unknown factors in understanding the heat transfer mechanisms and characteristics of the dropwise condensation curves. For example, although two modes of transition from drop type to film type are observed, i.e. the continuous dropwise condensation curve(1) and the discontinuous one (2,5), the conditions determining the transition modes are not clarified. The reason and the effect also of the condensing material physical properties in determining the heat flux limit are not clear.

The dropwise condensation curves of propylene glycol vapor on a thin PTFE coated copper surface were measured at several reduced pressures and vapor force conditions in the former report(1). In this study, the dropwise condensation curves of propylene glycol vapor, the same substance as used in the former report, on a copper surface using a monolayer adsorbing type promoter used in the measurements for steam in many cases until now were measured and compared.

Furthermore, in order to gain more knowledge on the dropwise condensation curves, measurements were carried out with other organic vapors having different liquid physical properties which are considered as the important controlling factors. Specifically speaking, trilauryl trithiophosphite ($(C_{12}H_{25}S)_3P$, melting point, $23^\circ C$) was used as the common adsorbing type promoter on the copper surface, and three kinds of organic vapors, propylene glycol, ethylene glycol and glycerol were used as the condensing vapor. The vapor pressure and the vapor force were selected as the parameters for the measurement.

2. Selection Test of the Effective Promoter for Dropwise Condensation of Organic Vapors

Because only a few promoters were used in realizing dropwise condensation for organic vapors unlike steam in the past, the effective promotion methods are not established well.

The methods realizing dropwise condensation for organic vapors can be divided into two groups. One is a method utilizing the fluorocarbon polymers (mainly polytetrafluoroethylene, PTFE). The observation (3) and the measurement (4) for aniline, ethylene glycol and nitrobenzene, and the dropwise condensation curve measurement for ethylene glycol (5) and propylene glycol (1) are reported. With this method, it is easy to realize dropwise condensation for the liquids having comparatively high surface tension because of its low surface energy and high chemical stability. The other method is a method using a surface adsorbing type promoter.

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Table 1 Test results of dropwise condensation promoter

Promoter Organic vapor	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Acetophenone	*		*							*				*
Anisole	*		*	*						*				*
Bromobenzene	*	*	*	*	*	*	*	*	*	□	*	*	*	*
Benzoic Acid Methyl Ester	*		*							*				*
Cyclohexane	*	*	*	*	*	*	*	*	*	□	*	*	*	*
Epichlorohydrin	*		*	*		*	*		*	*	*		*	□
Ethylene Glycol	○		○		*	*	○	△	○		○			○
Methyl Salicylate	*		*							*				*
Morpholine	*		*							*				*
o-Nitroanisole	*	*	*	*		*	*		*	*	*	*	*	*
o-Nitrotoluene	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Propylene Glycol	□	◇	□	◇	△	△	*	△	*	□	*	◇	*	○
Quinoline	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Toluidine	*		*							*				*
Glycerol														○

Promoter
 1: Di-n-Decyl Disulfide
 2: Di-n-Octadecyl
 3,3'-Thiodipropionate
 3: Di-tert-Dodecyl Disulfide
 4: Lauryl Mercaptan
 5: n-Octadecane
 6: n-Octadecylamine
 7: Oleic Acid
 8: Paraffin
 9: Palmitic Acid
 10: Perfluoro-n-Butylic Acid
 11: Stearic Acid
 12: Stearyl Mercaptane
 13: Tetraethylthiuram Disulfide
 14: Trilauryl Trithiophosphite

In this method, since the promoter material must have very low dissolution to the condensate and have strong adsorptive power to the surface, few effective substances are available. Up to now, dropwise condensation of seven kinds of organic vapors: isooctane, decaline, ethanol, carbontetrachloride and others on the perfluorinated acid adsorbed surface within a short period of duration (6) and that of ethylene glycol and glycerol vapors on the cupric oleate promoted surface (7) are observed. The quantitative measurements so far done are only for ethylene glycol on the oleic acid promoted copper surface (5,8).

Referring to the above mentioned cases and previous research on steam promoters and others, (9,10) empirically determined three-stage tests described below were carried out to find out effective adsorbing type promoters for organic substances having relatively large liquid surface tension. The test surface material was restricted to copper with high conductivity generally used in many studies.

(1) Solubility: For the first stage, solubilities were tested after the organic liquid and the promoter were mixed and heated by hot water. The combination showing no solubility was passed to the next stage.

(2) Adsorptivity and hydrophobic ability: The copper plates were painted with the promoters and soaked in organic liquids. The combinations maintaining enough hydrophobic power were sent to the next stage.

(3) Condensation test: Condensation states were tested using a newly manufactured condensation test apparatus at reduced pressure.

The test results of the aforementioned method are shown in Table 1, where the symbols △, □ and ○ denote the successful cases passing the first stage, the second stage and the third stage, respectively. The symbol * denotes the case of failing at the first stage, and ◇ the case where no test at the third stage was made although it successfully passed the second stage. It was clarified through

the test that many of the promoters useful for steam were not effective for the organic vapors but that trilauryl trithiophosphite, 14th promoter in Table 1, was effective for propylene glycol, ethylene glycol and glycerol vapors. These three combinations were adopted for the measurement because the viscosity and the surface tension differ widely, which conforms to the object of this study.

3. Experimental Apparatus and Procedures

The experimental apparatus are shown in Figs.1(a), (b), (c). Since these apparatus are almost the same as those presented in the former report, only the major points and the modified parts will be described below.

The configuration of the whole apparatus is shown in Fig.1(a). The pressure and velocity of vapor passing through the condensing chamber located at the upper part of the apparatus can be kept constant by adjusting the valve opening while continuing vacuum suction of a container placed right next to a glass condenser. Fig.1(b) shows a cross section of the condensation apparatus viewed from below. The cover of the condensation apparatus is made of glass in one-piece construction. The front part in particular (upper part of the figure) uses an optical ground glass for observation. The vapor flows through a rectangular duct (18 mm width) surrounded by a condensing surface and a teflon insulator on one side, a glass cover on the opposite side and two fixed teflon walls. The flow direction is horizontal and is parallel to the vertical condensing surface. The duct height can be changed in two ways to adjust the flow rate and flow velocity of the vapor. Jets of heating oil, water, water with ice (plus salt) and ethanol cooled by liquid nitrogen are used in the order of cooling intensity for cooling the condensing surface. Fig.1(c) shows the condensing block used in the measurement, which is installed at the center of the condensing chamber. The heat transfer surface is designed to be in a

relatively small size (the end surface of the 8 mm diam. cylinder), and is surrounded by a teflon insulator to avoid significantly different condensation states and heat flux between the upper and the lower parts of the condensing surface. The surface is finished using chromium oxide particles (about $0.5\ \mu\text{m}$) to make it mirror-smooth. Five $0.5\ \text{mm}$ diam. holes parallel to the condensing surface are drilled in the heat transfer block, and constantan wires of $0.1\ \text{mm}$ in diameter with teflon coating are inserted and soldered at the center of each hole with a copper wire soldered at the root of the block. Thermocouples are formed by these wires, and the surface temperature and the heat flux are determined from these thermocouple e.m.f.s and the distances from the top. It was certified that the temperature

distributions in the block maintained enough linearity. The sheath thermocouple placed in front of the condensing surface in the vapor duct is used to measure the vapor temperature. In the preliminary tests, it was observed that the condensate did not flow smoothly at the end of condensing surface because of the hydrophobic teflon insulator used. Thus the hydrophilic tracing paper smoothly connecting to the condensing surface was fixed on the teflon insulator in the measurement.

The experimental procedures and the method are as follows:

(1) After grinding the surface and cleaning it with solvents, the promoter was adsorbed on the condensing surface by soaking the surface in a solution of approximately one percent trilauryl trithiophosphite in carbon tetrachloride for about 15~20 minutes.

(2) Suction by the vacuum pump and heating of the steam generator were started after the experimental apparatus was set up. The excess promoter on the condensing surface was washed by the condensate as done with the steam and oleic acid combination. The molecules contacting the copper surface were tightly adsorbed and the condensation was stable. Although a special test for the promoter life was not performed, it was certified that the promoter can be kept in good condition for more than twenty hours.

(3) Measurements were started after the conditions of the experimental system became stable, i.e. constant vapor velocity and pressure. Both the steady state measurement and the quasi-steady state measurement lowering the cooling medium temperature very slowly were conducted. Special care was taken in the quasi-steady state measurement in the transition region to realize a state close enough to the steady state; that is, the cooling temperature variations were kept at $0.001\sim0.004\ \text{K/s}$ using the natural cooling of the cooling medium. In carrying out the measurement, the cooling intensity was always increased because the subject of the study was the transition from dropwise condensation to film condensation.

4. Results and Discussions

4.1 Propylene glycol vapor

The measured results of the propylene glycol vapor on the trilauryl trithiophosphite adsorbed copper condensing surface are given in Figs.2(a)~(e) and the experimental conditions corresponding to the figures are in Table 2. Realizing the steady state or quasi-steady state, measurements were performed keeping the vapor saturation temperature and the vapor mass velocity constant. The vapor superheat was measured by the same method as in the former report to determine the vapor saturation temperature. These methods are also the same for ethylene glycol and glycerol vapors. The measurements were performed for the five conditions presented in the table; three vapor pressures and two vapor forces (expressed using the mass

(a) Outline of the experimental apparatus

(b) Condensation apparatus

(c) Condensing block (copper)

Fig.1 Experimental apparatus

velocity and the departing drop diameter). These conditions are similar to those in the former report. The variations of the departing drop diameters measured using a video recorder set are shown in Fig.2(a). Although the departing drop diameters depend on the condensing surface subcooling ΔT and decrease with an increasing ΔT , it is seen that they center around two values (i.e. groups of data points denoted by symbols Δ , $\circ$, $\bullet$ and those by $\square$, $\blacksquare$). The departing drop diameter is used as the indicator for vapor force here. Figures 2(a) and (c) show the change of the heat flux q and the heat transfer coefficient h with the surface subcooling for relatively small vapor forces, respectively. Figures 2(d) and (e) are for relatively large vapor forces. The solid line, single dotted broken line, dotted line and double dotted broken line in the figures express the previous results for the PTFE surface. These lines correspond to the present results denoted by symbols $\circ$, $\bullet$, $\square$ and $\blacksquare$, respectively. The shapes of the dropwise condensation curves greatly differ from one another depending on the surface properties.

Two remarkable differences can be cited which depend on the surface characteristics. One is that the dropwise condensation curves of the trilauryl trithiophosphite adsorbed surface moved to the smaller subcooling region, and the heat transfer coefficients in the relatively small subcooling region (the region where the heat transfer coefficients show almost constant value) are 2~5 times greater than those for the PTFE coated surface. These results are similar to the results of the

Table 2 Experimental conditions for propylene glycol vapor

	P kPa	T _S K	m kg/m ² s	D mm	
△	16.0	408	3.1	0.9	Present work
○	6.5	388	2.1		
● ▲	1.9	363	0.8		
□	6.5	388	8.1	0.2	
■ ◇	1.9	363	5.2		
—	6.5	388	3.0	0.7	Utaka et al. (1) (PTFE surface)
- - -	1.9	363	1.6		
- - -	6.5	388	6.8	0.2	
- - -	1.9	363	3.2

(a) Departing drop diameter and surface subcooling

(b) Heat flux and surface subcooling (D=0.9 mm)

(c) Heat transfer coefficient and surface subcooling (D=0.9 mm)

(d) Heat flux and surface subcooling (D=0.2 mm)

(e) Heat transfer coefficient and surface subcooling (D=0.2 mm)

Fig.2 Measured results of propylene glycol vapor

measurements done by Nagata and Tanasawa (11) for steam on a silicone resin (0.1~0.2 μm) coated glass surface, where the heat transfer coefficient thereof was 25~30 % of the conventional cases obtained on the oleic acid promoted copper surfaces. By applying the analysis of Hannemann(12) and Hannemann and Mikic(13) to estimate the effect of the thermal conductivity of the condensing surface material, which is the conceivable cause for this difference, the relation between the heat transfer coefficient of the former report (PTFE surface) h' and that of the present report (copper surface) h can be expressed as

$$h' = (0.82 \sim 0.91) \cdot h$$

However, the difference between the two measurements is greater than that predicted by this relationship. It is probable that this difference depends on other surface properties of the condensing surface. Hence this is to be further studied.

The second major difference between them is the changing modes from dropwise condensation to film condensation. Whereas all the curves for the PTFE surface are continuous in all subcooling ranges (in increasing the surface subcooling, the dropwise condensation curve can be expressed as one continuous curve), the heat flux decreases discontinuously and the condensation state changes to the film type almost skipping the region of a decreasing heat flux for the trilauryl trithiophosphate adsorbed copper surface except for the case where the pressure is 1.9 kPa. Hence the heat flux change with the subcooling is expressed by the discontinuous curves. For $P=1.9$ kPa, both continuous and discontinuous curves were measured at two vapor velocities (distinction is made by using different symbols in Fig.2). But, even in the case of the discontinuous curve, the dropwise regions extend to a larger subcooling region. The curves are clearly different from the relatively high pressure cases and are very similar to the continuous ones. Here, the actual saturation temperature for the $P=1.9$ kPa and $D=0.2$ mm case is slightly lower than the T_s value shown in Table 2 because of the larger vapor superheat. The point expressing the maximum surface subcooling in the dropwise region is to be called the jump starting point from drop type to film type. The jump starting points are expressed with arrows in Figs.2(b)~(e). The same applies to the case described later. The surface subcoolings of jumping points are relatively small, being in the range from 11 K to 19 K, and the heat fluxes are in the range from 1.8×10^5 W/m² to 6.5×10^5 W/m².

4.2 Ethylene glycol vapor

Figures 3(a)~(c) show the measured results of the trilauryl trithiophosphate adsorbed copper surface along with a part of the results of the oleic acid promoted surface obtained by Stylianou and Rose. The symbols and the conditions are given in Table 3. The departing drops were selected to be of the same size as seen in Fig.

Table 3 Experimental conditions for ethylene glycol vapor

	P kPa	T_s K	m kg/m ² s	D mm	
○	24.5	428	3.1	0.7	Present work
●	1.6	368	0.6		
▽	19.5	424			Stylianou & Rose ⁽⁵⁾ (Oleic Acid)
◊	11.5	411			
◇	3.8	386

(a) Heat flux and surface subcooling

(b) Heat transfer coefficient and surface subcooling

(c) Departing drop diameter and surface subcooling

Fig.3 Measured results of ethylene glycol vapor

3(c), whereas the pressures were at two substantially different values of 1.6 kPa and 24.5 kPa. As presented in Fig. 3(a) and (b), jumping from drop type to film type is also observed as in the case of propylene glycol excluding the $P=1.9$ kPa condition. The jump starting points are at about $\Delta T=46$ K and $q=7.7 \times 10^5$ W/m² for $P=1.6$ kPa, and $\Delta T=27$ K and $q=2 \times 10^6$ W/m² for $P=24.5$ kPa.

Thus as evidenced, the surface subcoolings of jumping points for ethylene glycol are larger than the those for propylene glycol. A common trend observed for both the propylene glycol and ethylene glycol cases is that the lower the pressure is, the larger the surface subcooling of jumping point becomes.

When the results of this study are compared with the data of Stylianou and Rose, the shapes of dropwise condensation curves resemble each other. Although strict comparison is difficult because of the differences in the promoter used, the condensing surface size and the pressure value, the jumping point subcooling and the heat fluxes of this study are some-what larger than those of Stylianou and Rose. It seems that the heat flux differences between the two studies are caused by the difference in the steam velocity because the measurement by Stylianou and Rose is done in almost stagnant vapor. However, as described by Stylianou and Rose, the oleic acid adsorbed copper surface loses the

hydrophobic property at about 423 K. The case expressed by ∇ in Fig. 3 is near this temperature limit and the promoter effect is considered to have weakened. The promoter used in this research was tested to have full effect up to the vapor temperature of 443 K.

4.3 Glycerol vapor

The results of glycerol, which has the largest liquid viscosity and surface tension among the three substances, are shown in Figs. 4(a) and (b). Considering the heat resistance limit of the apparatus, the comparatively low pressure conditions given in Fig. 4 were adopted because glycerol is a liquid with relatively high temperature boiling point. The vapor forces were selected at about the same values as in sections 4.1 and 4.2. Because it was difficult to maintain a constant pressure over a wide subcooling range at $P=0.35$ kPa due to the limit of the apparatus capacity and valve adjustment range, the measurements were performed in a relatively large subcooling range (it is easy to keep the vapor velocity and the pressure constant because the change of condensation rate is small in this region). As seen in Figs. 4(a) and (b), the continuous shift from drop type to film type appeared at $P=0.35$ kPa, as was the case with propylene glycol at $P=1.9$ kPa. Both results of the two measurements expressed a continuous curve. The discontinuous shift is observed in the $P=0.6$ kPa case as was obtained in all cases of three organic vapors excluding the above condition. In this case the subcooling of the jumping point is largest at about 82 K, and the heat flux is about 1×10^6 W/m². Although the method of quasi-steady measurement described in chapter two is used in all measurements near the jump starting points shown in this chapter, full care is taken to achieve steadiness in the measurement. Furthermore, since the condensation states and the e.m.f.s of thermocouples in the block did not change when lowering of the temperature of the cooling medium was stopped and a constant temperature was kept at a point just before the jumping point, it was confirmed that the quasi-steady measurement method adopted was close enough to the steady state method.

5. Conclusions

The measured results of dropwise condensation curves under various vapor pressure and vapor velocity conditions on a trilauryl trithiophosphite adsorbed copper condensing surface were shown for three kinds of organic vapors; propylene glycol, ethylene glycol and glycerol. The results obtained are summarized as follows.

In case of the condensation surface using the same adsorbed type promoter, the characteristics of dropwise condensation curves are affected by the vapor substances and the vapor pressure conditions. As the surface subcooling increases while keeping the steady state, in some cases, the liquid

(a) Heat flux and surface subcooling

(b) Heat transfer coefficient and surface subcooling

Fig. 4 Measured results of glycerol vapor

film suddenly grows rapidly and completely covers the surface. The dropwise condensation curves for these cases are expressed as discontinuous curves which jump from drop type to film type. The surface subcoolings and the heat fluxes at these jump starting points depend greatly on the vapor kinds and the system pressures. The results demonstrate the tendencies that the subcooling of jump starting points increases in the order of propylene glycol, ethylene glycol and glycerol and of lower pressure.

There were cases where the jump phenomena did not appear, wherefore the dropwise condensation curves are continuous, when the pressure is lowest for propylene glycol and glycerol vapors in the experiment. The subcooling of condensing surface covered with the liquid film is larger than the subcooling of jumping point appearing at higher pressure of the same vapor.

The characteristics of the dropwise condensation curves are affected by the surface properties even when the propylene glycol vapor is used as the common substance. The heat transfer coefficients of the trilauryl trithiophosphite adsorbed copper surface are greater than those of the PTFE coated surface. In addition, although all of the dropwise condensation curves on PTFE surface are continuous, a jumping phenomenon from drop type to film type exists in the case of adsorbed surface. It is considered that the phenomena described above are controlled by the hydrophobic property concerned with the heat transfer surface and the condensate as

well as the liquid physical properties. In the next report, the relation among the states of condensate on the condensing surface and them will be investigated.

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