Condensation of Vapors of Immiscible Liquids

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In a system of two immiscible liquids each component will vaporize and exert its own vapor pressure independent of the other component. The total equilibrium pressure is the sum of the vapor pressures of the individual components at the temperature of the system, if the law of additive pressures applies. In a three-phase, two-component system (liquid *A*, liquid *B*, and vapor) the system pressure fixes the temperature T_E. The equilibrium temperature as well as the equilibrium vapor composition can be computed from the pure component vapor-pressure data. Thus if two components are present in separate liquid phases on a condensing surface and the liquid surfaces are in thermal equilibrium, the interface temperature is the eutectic temperature. The temperature drop across the liquid film can then be taken as the difference in the eutectic temperature and the condenser surface temperature.

The Nusselt equation for condensation adequately describes condensation of a pure vapor in a laminar film. However no present theory or modification of Nusselt's equation has been generally successful in accounting for the condensation of a vapor of two immiscible liquids. This is due primarily to the inability to predict and describe the behavior of the two liquid phases on the condensing surface.

A single component normally condenses as a film which completely wets the surface. In the case of two immiscible components a number of phenomena may be observed. Generally the liquid having the lowest surface tension will wet the condensing surface. In water-organic systems the organic will normally wet the surface and form a continuous film. Water will condense as drops in the wetting film (film-drop), as lenses on the wetting film (film-lens), in distinct channels (channeling), or as a more or less continuous film on the wetting phase.

These phenomena can be understood by the introduction of a spreading coefficient. Harkins and Feldman (2) define the spreading coefficient of liquid *A* on liquid *B* as the difference between the work of adhesion and the work of cohesion. From thermodynamic considerations the spreading coefficient can be shown to be equivalent to the following relation:

$$S_{AB} = \gamma_B - \gamma_A - \gamma_{AB} \qquad (1)$$

A positive coefficient indicates that liquid *A* will spread on liquid *B*, and a negative coefficient indicates that it will not spread.

In the cases being considered, film condensation is assumed for one component. If the spreading coefficient for the other component is positive, it will form a film on the first liquid. If the coefficient for liquid A to spread on liquid *B* is positive, then it is seen that the coefficient for *B* to spread on *A* is negative. Therefore *A* cannot spread on *B* if *B* spreads on *A*.

Harkins and Feldman (2) describe the form of water on immiscible organic liquids. They state that for systems in which the organics spread on water ($S_{BA} > 0$) a spherical drop of water forms; the organic liquid rises as it approaches the sphere and spreads as a thin film over the surface. Thus one has a small sphere of water within the organic film. For organic liquids which do not spread on water ($S_{BA} < 0$), water forms lenses on the organic surface and the surface of the organic falls as it meets the water lens.

These ideas may be used to explain the various condensation mechanisms. Consider systems in which the surface is wet by an organic phase with water as the other condensing component. If the spreading coefficient for the organic on water is large ($S_{AB} >> 0$), the water will form small drops within the organic phase. For $S_{BA} << 0$, either film-lens or channeling would be expected. Channeling would be prevalent for high condensation rates or high water-vapor concentrations. If the spreading coefficients are near zero, a combination of drop-lens formation or lens-channeling would be expected because of the great tendency for coalescence of the water phase.

In the case of film-drop condensation the heat transfer coefficient would be expected to follow a Nusselt type of equation with some modification to account for the effects of the drops on the density and thermal conductivity. The film-lens mechanism is somewhat similar. In the case of channeling the surface is in part covered by a Nusselt type of film of the wetting component. On the remainder the nonwetting phase flows as a film over a very thin layer of the wetting fluid. If the thermal resistance of this thin film is much smaller than the nonwetting layer, the overall process can be considered a parallel condensation for the two fluids.

EXPERIMENTAL PROCEDURES

The apparatus consisted of a solid brass cylinder 2½ in. in diam. and 3 in. long. Each end of the cylinder was covered with an inch-thick piece of insulating plastic. Cooling water flowed through water courses within the block and a condensate collector was provided directly below the condensing surface. The condensing section was mounted inside a large clear Dewar flask which was equipped with a heater, thermocouples, and a manometer. The unit, shown schematically in Figure 1, could be rapidly assembled, sealed for vacuum use, and put into operation.

First the equipment was assembled and evacuated and one or two liquids were added to the Dewar. The heater and condenser cooling water were then turned on. In all cases where two immiscible liquids were used, at least 1 in. depth of each liquid phase was present in the boiling section. The heater was immersed in the lower phase so that bubbles generated on the heater rose through the less dense liquid phase and caused a rather high degree of mixing. Vapors were exhausted from the system to eliminate inert gases. For a series of runs the condenser surface temperature as measured with imbedded thermocouples was held constant to within 0.1°F. and the heat input varied. The heat input, the liquid temperature, the bulk vapor temperature, the cooling water flow rate and composition, and the system pressure were measured. These measurements provided checks on all the system variables.

In this mode of operation a steady state condition could be reached, but thermal equilibrium between the vapor and liquid phases was seldom approached. In general the liquid temperature was 10° to 20°F. higher than the vapor temperature. The vapor temperature was in turn 5° to 20°F. higher than the eutectic temperature as computed from the total pressure measure-

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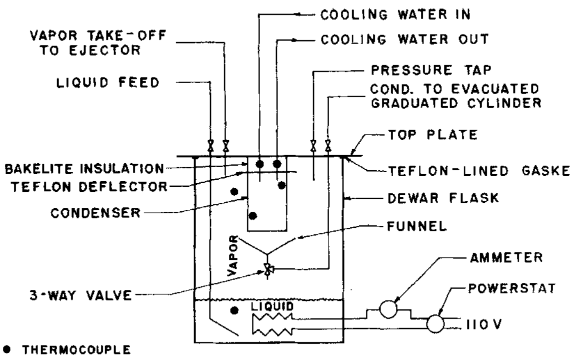

Fig. 1. Schematic of experimental apparatus.

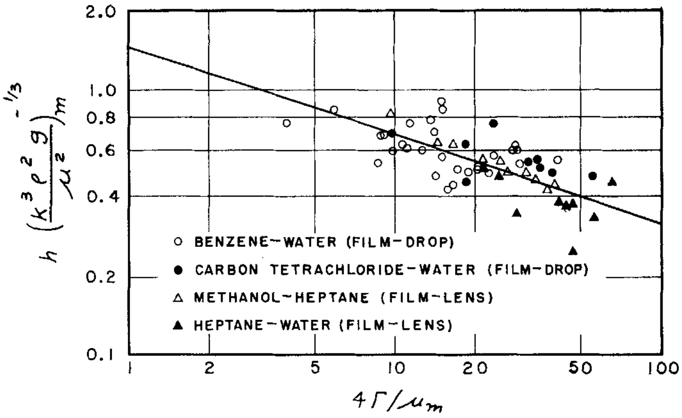

Fig. 2. Correlation of heat transfer coefficients.

ment. These differences depended on both the rate of heat input and the particular system under study. The large differences were noted in the heptane-water system. The heptane-methanol system exhibited very small differences in contrast. The magnitudes are shown for some of the data in Table 1.

During operation the entire condensing surface could be viewed. Notes on the mechanism and other observations were recorded, and photographs were taken of the condensing surface.

Various procedures were followed in studying the surface wetting and condensation mechanisms. Several runs were made in which the two components were introduced simultaneously to allow each component equal opportunity to wet the dry polished brass surface. Other runs were made in which only one component was added at the start. After several hours of operation the second component was added. The authors also made experimental tests lasting over 100 hr. at constant surface temperature and total pressure.

EXPERIMENTAL OBSERVATIONS

During the experiments 120 runs were made on four immiscible systems: benzene-water; *n*-heptane-water, carbon tetrachloride-water, and methanol-*n*-heptane.

The benzene-water system condensed by the film-drop mechanism with coefficients ranging from 265 to 865 B.t.u./hr. sq.ft. °F. Heptane-water condensed by film-drop, film-lens, and channeling mechanisms with coefficients ranging from 162 to 1,800. The carbon tetrachloride-water system condensed by film-drop and channeling mechanisms with coefficients from 293 to 1,810. The methanol-heptane system condensed by a film-lens mechanism with coefficients of 440 to 860.

Differences between vapor compositions and condensate compositions were less than 5% for almost all of the runs. Condensate compositions ranged as follows: benzene-water, 2.4 to 27.7 wt. % water; heptane-water, 0 to 25.8% water; carbon tetrachloride-water, 2.6 to 28.6% water; and methanol-heptane, 62.3 to 66.8% methanol. The condensate compositions were normally within 2% of the calculated eutectic composition.

Channeling mechanisms normally gave higher coefficients than film-drop or film-lens. The channels were very irregular, and frequently wavy strips of liquid would peel off the condenser. At low heat fluxes the film-drop mechanism always occurred. At higher fluxes and particularly at higher surface temperatures channeling occurred in the heptane-water and the carbon tetrachloride-water systems.

The approach to a steady state was somewhat erratic. For example one run was made in which water was introduced and condensed for 2 hr. before the organic phase was admitted. The two-phase coefficient at the beginning was 1,030; after 5 hr., 585; and after 36 hr., 695. The surface was then repolished, cleaned with acetone and dried, and the two components were introduced simultaneously. At the start the coefficient was 322; after 5 hr., 605; after 12 hr., 700; and after 30 hr., 640.

One type of run was particularly interesting. The surface was thoroughly cleaned with acetone and then dried. A pure organic was then condensed. The organic was removed and the surface dried by evaporation to vacuum. Water was then admitted and the inerts removed by evacuation as heat was added. Steam condensed, but the condensate did not wet the surface. The water droplets would grow and then roll off. In such cases the heat transfer coefficient varied from 40 to 200. Temperature differences of over 100°F. could be

TABLE 1. SELECTED DATA

Benzene-water

Run	T_S	T_E	T_V	T_L	Wt. % H_2O in condensate	q	h
56	139.5	160.0	162.0	180.0	8.8	9,320	455
60	138.1	146.0	148.5	159.0	8.2	3,120	395
61	137.7	150.0	151.5	167.0	8.4	6,200	503
62	138.5	154.5	155.5	172.5	8.6	8,380	523
64	142.5	146.0	152.0	172.0	8.2	2,010	574

Heptane-water

Run	T_S	T_E	T_V	T_L	Wt. % H_2O in condensate	q	h
113	140.3	146.5	146.5	169.0	0	1,195	193
114	141.2	148.5	152.0	172.0	0	1,470	201
115	140.8	146.5	150.0	169.0	0	1,200	210
142	106.6	142.5	154.5	176.0	8.2	7,620	212
154	141.1	160.0	173.0	186.0	8.7	10,223	541
160	139.6	157.0	166.0	192.5	11.0	7,950	456

Carbon tetrachloride-water

Run	T_S	T_E	T_V	T_L	Wt. % H_2O in condensate	q	h
122	110.0	132.0	143.0	144.5	5.6	7,430	338
132	143.9	149.0	157.5	157.5	28.6	6,920	1,360
135	108.7	117.5	118.5	124.5	2.7	3,450	392
136	112.7	125.5	128.0	134.0	25.4	5,460	426

Heptane-methanol

Run	T_S	T_E	T_V	T_L	Wt. % methanol in condensate	q	h
168	110.2	139.5	144.0	144.5	66.8	12,850	440
169	110.4	133.5	137.5	137.5	64.6	10,720	464
170	111.6	126.5	130.0	131.0	63.9	8,420	565
171	111.3	119.6	123.0	124.0	62.3	5,510	665
172	111.8	115.5	119.0	120.0	63.6	3,180	860
173	111.7	113.5	116.5	117.5	64.6	2,470	1,370

maintained between the vapor and the surface. In these cases drop-by-drop condensation occurred, but the coefficients were from ten to fifty times less than would be obtained for film condensation on the same surface when the organics were removed by acetone and subsequent evacuation. A similar phenomenon occurred when the surface was used for the condensation of steam without prior removal of all traces of cutting oil by acetone. In each of these cases the normal procedures for the removal of inerts were followed. Although it is possible that these resulted from the presence of inerts, the authors think that the presence of an adsorbed layer of organic covering the surface may have prevented the condensation of steam because of a lack of nucleating sites. In the heptane-water system operating at low heat fluxes and low water vapor concentrations, heptane condensed but water did not, apparently for related reasons.

Overall accuracy of the heat transfer coefficients is probably within 10%. Temperature measurements are accurate to 0.05 deg. Accuracy of water flow rate determinations is 5%, and pressure determinations are accurate to within 0.1 in. Hg. Total heat transferred, as measured by the cooling water, checked that obtained from electrical power input to within 10% during closed system operation. Condensate compositions were reproducible to within about 1 wt. %.

RESULTS

The heat transfer coefficients for film-drop and film-lens condensation were correlated by the Nusselt equation:

$$h\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = 1.47\left(\frac{4\Gamma}{\mu}\right)^{-1/3} \qquad (2)$$

The viscosity is that of the surface wetting liquid. The density is the average based on weight percent in the condensate, and the thermal conductivity is a volumetric average value. Figure 2 shows data correlated in this manner. The equation represents the data over a range of values of the Reynolds number of 1.0 to 100.0 with a mean deviation of ±10% and a maximum deviation of 30% for all runs of film-drop and film-lens condensation except for the film-drop data in the heptane-water system. Condensate for these runs contained unusually low water content. The coefficient was significantly lower than for pure heptane. Apparently the water acted as a blanket and failed to condense because of a lack of nucleating sites. At higher Reynolds numbers water appeared in the condensate. The coeffcients were significantly higher than those of pure heptane and agreed with Equation (2).

Under those conditions in which channeling occurred, the condensate flow pattern was very erratic. The heat transfer coefficient can be satisfactorily correlated by assuming that each component condenses independently of the other. Thus the two-component coefficient can be obtained by weighting the pure component coefficients in accordance with the amount of heat transferred by each. Thus

$$h = \frac{a\,\lambda_A\,h_A + b\,\lambda_B\,h_B}{a\,\lambda_A\,b\,\lambda_B} \qquad (3)$$

The experimental data closely paralleled those values as calculated by Equation (3); however the average values calculated were 20% greater than the experimental values. Hence the value calculated by Equation (3) should be multiplied by 0.8. See Figure 3 for this relation.

Although it is not possible to unerringly predict the mechanism of two-phase condensation, the spreading coefficient is certainly indicative. Harkins and Feldman list the following data at 20°C.:

Substance	S_{BA} (organic on water)	S_{AB} (water on organic)
Benzene	8.9	− 79.1
Heptane	1.8	− 90.2
Carbon tetrachloride	1.06	−104.9

The magnitude of the negative coefficient for the water on the organic indicates that in no case will a film of water form. The positive values of the organic on water do indicate the possibility of the organic filming over water. From the experimental observations it was noted that benzene-water condensed by the film-drop mechanism in all cases except two runs at very high Reynolds numbers. In the case of the heptane and carbon tetrachloride, film-drop and film-lens condensation occurred up to Reynolds numbers as high as 50. The tendency for channeling increased markedly as the temperature of the surface increased.

Comparisons of data from other investigations have been attempted. Only Baker and Hazelton (*1*) have fully described the condensation mechanism observed in their work. Their data, together with that of Tobias and Stoppel (3), are in the range of Reynolds numbers of 100 to 1,000, which is beyond the range of most of this work. However the agreement with results predicted by applications of Equations (2) or (3) is good.

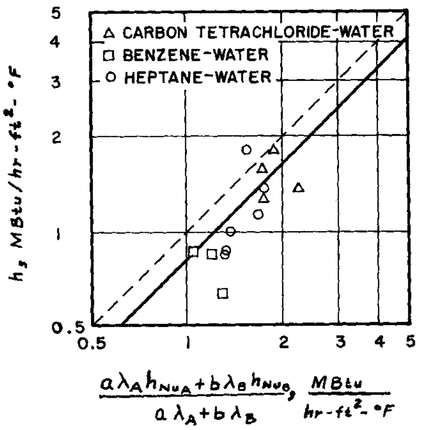

Fig. 3. Heat transfer coefficients for systems condensing by channeling.

CONCLUSIONS

1. The difference in the eutectic temperature and the condenser surface temperature can be taken as the effective temperature drop across the liquid film. Heat transfer coefficients evaluated on this driving force are consistent.
2. By grouping heat transfer relations in accordance with the condensing mechanism of the immiscible components, correlations based on modifications of the Nusselt equation adequately represent the experimental data.
3. The spreading coefficient is indicative of the type of mechanism of the condensation of two immiscible liquids. Experimental quantitative description of the mechanism can be made.

NOTATION

A = component, usually water
a = weight per cent of component A in condensate
B = component, usually organic
b = weight per cent of component B in condensate
g = acceleration of gravity, 4.17×10^8 ft./hr.²
h = heat transfer coefficient, B.t.u./(hr.)(sq.ft.)(°F.)
k = thermal conductivity, B.t.u./(hr.)(ft.)(°F.)
S_{AB} = spreading coefficient for liquid A on liquid B, dynes/cm.
T_E = eutectic temperature, at which the sum of the pure component vapor pressures equals the total system pressure, °F.
T_S = temperature of the surface, °F.
T_V = temperature of the vapor, °F.
T_L = temperature of the liquid, °F.

Greek Letters

γ = surface tension, dynes/cm.
γ_{AB} = interfacial tension, dynes/cm.
Γ = mass flow rate of condensate, lb./hr.-ft.
μ = viscosity, lb./ft.-hr.
ρ = liquid density, lb./cu.ft.
λ = latent heat, B.t.u./lb.

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