Condensation of Vapors of Immiscible Binary Liquids on Horizontal Copper and Polytetrafluoroethylene-Coated Copper Tubes

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Abstract. Heat transfer data are reported for the condensation of pure organic vapors and their eutectic mixtures with water on both horizontal one inch diameter copper and polytetrafluoroethylene-coated copper tubes at atmospheric pressure.

With the pure vapors heat transfer is reduced by the coating, this reduction being enhanced when condensing cyclohexane, attributable to an absorption effect. For the eutectic mixtures, except for carbon tetrachloride, heat transfer is not reduced by the coating and is substantially increased for the cyclohexane-water system.

An explanation is afforded in terms of buoyancy-surface force interaction.

Zusammenfassung. Es werden Versuchsergebnisse zum Wärmeübergang bei der Kondensation von reinen organischen Dämpfen und ihren eutektischen Mischungen mit Wasser an horizontalen Kupferrohren von 25 mm Durchmesser mitgeteilt, wobei die Rohre blank oder mit Polytetrafluoräthylen beschichtet waren.

Bei reinen Dämpfen verringerte die Beschichtung den Wärmeübergang, besonders bei Cyclohexan infolge Absorptionseffektes. Bei eutektischen Mischungen, außer Tetrachlorkohlenstoff, verringerte die Beschichtung nicht den Wärmeübergang, bei dem System Cyclohexan – Wasser stieg er sogar beträchtlich an. Zur Erklärung wird die Wechselwirkung zwischen Auftriebs- und Oberflächenkräften herangezogen.

Nomenclature

C_p	specific heat based on the weight of water and organic present in the condensate, B.t.u./(lb.) (°F.)
D	outside diameter of the condenser tube, ft.
g	acceleration of gravity, ft./hr.^{2}
h_e	heat transfer coefficient for eutectic mixture, B.t.u./(hr.) (ft.^{2}) (°F.)
h_{Nu}	heat transfer coefficient for filmwise condensation from Nusselt's equation for pure organic vapor condensing on horizontal surfaces, B.t.u./(hr.) (ft.^{2}) (°F.)
h_1	heat transfer coefficient for filmwise condensation from Nusselt's equation for pure water, B.t.u./(hr.) (ft.^{2}) (°F.)
h_2	heat transfer coefficient for filmwise condensation from Nusselt's equation for pure organic, B.t.u./(hr.) (ft.^{2}) (°F.)
H	ratio of eutectic to pure component heat transfer coefficient
K	thermal conductivity based on the weight of water and organic present in the condensate, B.t.u./(hr.) (ft.^{2}) (°F./ft.)
K_{av}	thermal conductivity based on the volume of water and organic present in the condensate, B.t.u./(hr.) (ft.^{2}) (°F./ft.)
K_1	thermal conductivity of water, B.t.u./(hr.) (ft.^{2}) (°F./ft.)
K_2	thermal conductivity of organic, B.t.u./(hr.) (ft.^{2}) (°F./ft.)
M_1	molecular weight of water
M_2	molecular weight of organic
N_{OH_2}	Ohnesorge number of organic, $\{\mu^2/(\rho\,g\,D\,\sigma)\}^{1/2}$
N_{pr_1}	Prandtl number of water
N_{pr_2}	Prandtl number of organic
σ_1	surface tension of water, lb./ft.
σ_2	surface tension of organic, lb./ft.
Q	heat transfer rate, B.t.u./(hr.)
Q_1	heat given up by condensing steam, B.t.u./(hr.)
Q_2	heat given up by condensing organic vapor, B.t.u./(hr.)
v_1	volume fraction of water in condensate
v_2	volume fraction of organic in condensate
$W_{S/L}$	work of adhesion between a liquid and a solid, ergs/cm.^{2}
x_1	weight fraction of water in condensate
x_2	weight fraction of organic in condensate

Greek letters

$\gamma\,L/A$	interfacial free energy between liquid and air
ΔT	difference between the saturation and the inside copper surface temperatures, °F.
ΔT_f	film temperature difference, °F.
$\Delta\rho$	density difference, lb./ft.^{3}
$\Delta\sigma$	surface tension difference, lb./ft.
θ	intrinsic contact angle
λ	latent heat of vaporization based on weight of water and organic in the condensate, B.t.u./(lb.)
λ_1	latent heat of vaporization of water, B.t.u./lb.
λ_2	latent heat of vaporization of organic, B.t.u./lb.
μ	viscosity based on weight of water and organic in condensate, lb./(hr.) (ft.)
μ_1	viscosity of water, lb.(hr.) (ft.)
μ_2	viscosity of organic, lb./(hr.) (ft.)
ρ	density based on weight of water and organic in condensate, lb./ft.^{3}
ρ_1	density of water, lb./ft.^{3}
ρ_2	density of organic, lb./ft.^{3}

The potential use of polytetrafluoroethylene has widened considerably in the last five years. Previously it was recognized as the material useful for seals and connection parts and it had been used to some extent where moving surfaces in contact were involved where it exhibited a low frictional coefficient. It has applications in the chemical, pharmaceutical and food industries, both because of its chemically inert nature and its thermal stability. Up to very recently however, its use was inhibited by the high manufacturing costs. Interest has now arisen because of its dissimilar surface properties to those normally employed in chemical plant. Mizushina et al. [1] and Topper and Baer [2] have shown that there is sometimes an advantage in coating copper tubes with polytetrafluoroethylene when condensing pure vapors since for certain chemicals, the increased thermal resistance of the polytetrafluoroethylene coating is outweighed by the heat transfer produced when the mode of condensation changes from filmwise to dropwise. In the same way Peel and Coggan [3] have developed a transurface contactor for liquid-liquid extraction where the liquids are brought into contact as they flow into films countercurrently over a vertical wetted surfaces of alternating wetting characteristics. There the process is dependent on the phenomenon of preferential wetting on the surfaces of polytetrafluoroethylene and stainless steel, which results in a high throughput capacity and the ability to handle substances which are easily emulsified, or of high viscosity, or contain solids. Davies et al. [4] have shown that the phase separations of primary liquid dispersions can be promoted by mixed packing material made of two dissimilar energy surfaces such as stainless steel and polytetrafluoroethylene and when separating both oil-water and water-oil dispersions, they have shown enhanced coalescence at the junction of the two dissimilar materials. Ponter and Hassanien [5] have shown that higher efficiencies can be obtained using polytetrafluoroethylene packings in distillation columns under certain circumstances and have demonstrated the importance of the interfacial-interstitial properties of such systems.

A problem encountered in steam distillation, solvent drying and heterogeneous azeotropic extraction, is the prediction of condensation heat transfer rates of vapors forming immiscible liquids. The literature indicates that the correlations presented predict widely varying values of transfer coefficients, allowing little confidence in the design estimate. It is also observed that the methods used rarely involve the interfacial properties of the systems examined. Obviously the relative wetting of the solid surface must be important and could play a dominant role in the heat transfer process.

A plan was proposed therefore to coat a normal heat transfer surface of copper with a thin layer of polytetrafluoroethylene and the prime object was to ascertain whether the increased thermal resistance due to the polytetrafluoroethylene coating would be outweighed by the changes in adhesion by the liquids to the solid surface.

The literature describing the heat transfer which accompanies condensation of vapors upon horizontal surfaces to form binary immiscible liquids has been reviewed recently by Bernhardt et al. [6] and Boyes and Ponter [7]. A summary of the experimental investigations together with the correlations produced are given in Table 1.

Analyses of the surveys clearly demonstrate the empirical nature of the methods developed to determine condensation heat transfer rates up to the time of Stepanek and Standart [8] who actually incorporated the surface tension parameters in a model although finally producing an empirical equation not describing the physical situation involved.

A hypothesis which is now being examined is that since the adhesion of an organic liquid and water to a solid surface would be different, that by changing the tube surface the heat transfer would be influenced since the volume-volume ratio of the immiscible at the wall will change. It is suggested that by using a polytetrafluoroethylene surface where adhesion will be lower, that the increased renewal of the aqueous phase on the solid surface will cause increased heat transfer which might counteract or even outweigh the increased transfer resistance by the polytetrafluoroethylene.

To test the validity of the hypothesis a series of investigations now described, were made using horizontal copper and polytetrafluoroethylene-sprayed copper tubes upon which mixtures of benzene-water, carbon tetrachloride-water, 1,1,2-trichloroethylene-water and cyclohexane-water were condensed. Cyclohexane was included since Boyes and Ponter [9] had shown that an anomalous absorption behavior occurred on a polytetrafluoroethylene surface and it was of particular interest to examine the effect of this on the heat transfer rates.

1. Experimental Procedure

The apparatus shown schematically in Fig. 1 consisted of a single horizontal tube, inside diameter 0.9375 inch and outside diameter 1.125 inch, centered in a mild steel jacket, inside diameter 6 inches and 48 inches long, by stuffing box-type flanges.

The liquids were fed to the boiler via a charging funnel. The boiler was a cylindrical chest 11 inches in diameter and 20 inches long and contained three separate copper heating coils 5/8 inch diameter with equivalent length of 9 feet. Steam was supplied at 5 psig. The resulting vapors entered a 1 inch galvanized pipe to a vapor entrainment separator which comprised a cylindrical container of inside diameter 10 inches and length of 1 foot. Partial insulation of the

Table 1. Summary of experimental investigations together with their correlations

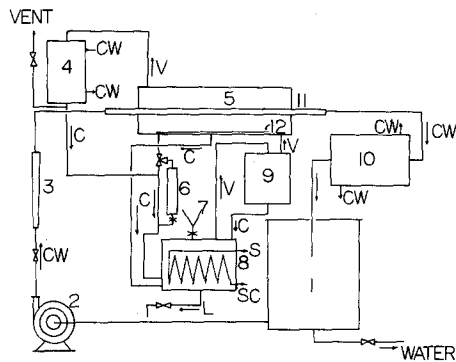| Authors	Liquids condensed with water	Condenser	Size and orientation of tube			Correlations
			Diam (in.)	Length (ft.)	Orientation	
Kirkbride [18]	benzene naphtha	steel	1.313	8.19	horizontal	$h_e = \dfrac{h_2 Q_2 + h_1 Q_1}{Q_2 + Q_1}$
Baker and Mueller [10]	benzene toluene mixed-heptanes trichloro-ethylene	copper (oxidised)	1.314	3.68	horizontal	$h_e \left[\dfrac{\mu_2^2}{k_{av}^3 \rho^2 g}\right]^{0.33} = 1.28 \left(\dfrac{Cp\,\mu_2\,\rho^{0.7}}{k\lambda}\right)^{2.38} \times$ $\times \left(\dfrac{Q_2}{Q_1 + Q_2}\right)^{-3.28}$
Baker and Tsao	benzene toluene chloro-benzene trichloro-ethylene tetrachloro-ethylene	copper (oxidised)	1.0 0.625	3.68 3.68	horizontal horizontal	$\dfrac{h_e}{1 - (0.0167/D)} = 80 + \dfrac{500}{1 + 0.0085\,(\text{vol \% } H_2O)}$ $h_e = \dfrac{366\,[1/D\,(1 - 0.0284/D)]^{0.25}}{1 - 0.0085\,(\text{vol \% } H_2O)} + \dfrac{1.64}{D}$
Patton and Feagon [21]	turpentine	copper (oxidised)	1.315	4	horizontal	$h_e = 3000\,(\Delta T_f)^{-0.5}$
Stépanek and Standart [8]	benzene toluene dichloro-ethylene chloro-benzene	copper	0.393	3.28	horizontal	$h_e = 0.725 \left[\dfrac{R\,k_2^3\,\rho_2^2\,g}{\mu_2\,\Delta T_f D}\right]^{0.25} \cdot K_1\,(1 + K_2\,\Delta T_f)$ $h_e = h_2\,(1 + 0.80\,Z)\,(\Delta T_f)^{0.67\,Z}$
Sykes and Marchello [19]	toluene carbon-tetra-chloride	copper	1.375	2.0	horizontal	$H = \left[\dfrac{1}{H_\infty} + \dfrac{1}{H_{20}\left(1 + \dfrac{x_2\,\lambda_2}{x_1\,\lambda_1}\right)e^{B\Delta T_f}}\right]^{-1}$ $K_1 = \left[1 - 4.38\left(\dfrac{x_1}{x_2}\right)^{0.033}\left(\dfrac{\rho_2}{\rho_1}\right)^{0.62}\left(\dfrac{\Delta\sigma}{\sigma_1}\right)^{3.2}\right]^{1/4}$ $K_2 = 0.0584\left(\dfrac{x_2}{x_1}\right)\left(\dfrac{k_2}{k_1}\right)^{1/2}\left(\dfrac{\rho_1}{\rho_2}\right)^{1.4}\left(\dfrac{\Delta\sigma}{\sigma_1}\right)^{1.6}$ $R = \dfrac{x_1\,\lambda_1 + x_2\,\lambda_2}{x_2}$ $Z = [(\Delta\sigma)\,(\rho_1/\rho_2)]^{1/2}$ $H_\infty = 7.63 - 1.8\,(N_{Pr_2} - N_{Pr_1})$ $H_{20} = \dfrac{17.30 \times 10^{-10}\,N_{Pr_2}}{\left[N_{OH_2}\left(\dfrac{\Delta\sigma}{\sigma_2}\right)^{1/2}\left(\dfrac{\mu_2}{\mu_1}\right)\left(\dfrac{M_1}{M_2}\right)\right]^2}$
Bernhardt et al. [6]						$h_e = h_1\,v_1 + h_2\,v_2$

Fig. 1. Schematic flow diagram of equipment.
1. Cooling water reservoir, 2. 'chem-gard Vanton' centrifugal pump, 3. rotameter for measuring cooling water flowrate, 4. secondary condenser, 5. test condenser, 6. calibrated separatory funnel for measuring condensation rate, 7. charging funnel, 8. boiler, 9. vapor entrainment separator, 10. heat exchanger, 11. condenser tube, 12. trough, L liquid, C condensate, V vapor, S steam, CW cooling water, SC steam condensate
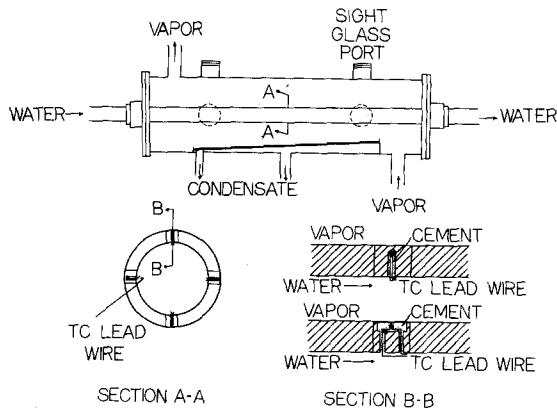

Fig. 2. Test condenser and thermocouple details

separator caused part of the vapors to condense, thus the vapors were in contact with the liquid for the second time.

Vapors from the separator then passed to the test condenser through 1 inch teflon tubing. In the condenser the vapors condensed on the outside of the copper tube. The actual test section was limited to 32 inches and the resulting condensate was allowed to drip into a trough placed directly below the test section. Slight inclination of the trough facilitated easy drainage of the condensate into a calibrated separatory funnel. The latter was used to measure the condensation rate. The excess vapor from the test condenser then entered the secondary or total condenser.

Condensate from the test condenser, the secondary condenser and the vapor entrainment separator was fed back to the boiler, thus very little liquid was lost during the operation. The inerts that may have been present in the system at the start-up were discharged

by allowing the vapors to flow through the vent-line located in the condensate exit-line from the secondary condenser.

Twelve thermocouples (33 gauge, copper-constantan) were imbedded in the condenser tube wall with low expansion cement. The details of thermocouple installation are given in Fig. 2. The wall was polished with emery paper until the surface was smooth and the tube was thoroughly washed with acetone and methanol before placing in the condenser chest. The condenser tube surface was oxidized by using it as a steam condenser. Initially, the steam condensed in a dropwise manner on the polished surface, but changed slowly to a filmwise mode of condensation and after about 30 operating days consistently produced filmwise condensation.

Approximately 4 gallons of organic-water mixture of eutectic composition was placed in the boiler and heated by means of steam flowing through the heating coils which was regulated to prevent an excessive build-up of pressure in the system. Air which may have been present in the apparatus was removed by allowing the vapors to flow out through the vent line for several minutes. Having removed the air the valve in the vent line was closed and the cooling water allowed to flow to the main condenser. The steam flow to the boiler was again adjusted to make certain that there was sufficient vapor flowing through the condenser and that the condenser pressure was about 5–10 mm. Hg above atmospheric pressure. About two hours were allowed after initial start-up to attain steady state and each run took about twenty minutes to perform.

The following measurements were made:

(i) volume and time taken to collect condensate leaving the test condenser;

(ii) cooling water flowrate to the test condenser;

(iii) condenser pressure, barometric pressure and ambient temperature;

(iv) emf output of each thermocouple (copper-constantan as follows:

(a) cooling water inlet and outlet thermocouples;

(b) cooling water thermocouple at the outlet from the heat exchanger;

(c) vapor inlet thermocouple to the test condenser;

(d) six vapor side thermocouples in the test condenser;

(e) twelve condenser surface thermocouples;

(f) vapor inlet thermocouple to the secondary condenser;

(g) condensate thermocouples from the test condenser and the secondary condenser.

The emf output of these thermocouples were measured and recorded with a Hewlett-Packard Data Acquisition System comprising an Integrating Digital Voltmeter, an Input Scanner and a Recorder.

After completing the experimental work with the oxidized copper tube, the tube was removed from the

test condenser and throughly washed with acetone and methanol. It was then coated with polytetrafluoroethy-lene (chemically pure grade) spray supplied by Fisher Scientific Company. The coated tube was cured for 48 hours in an oven maintained at 200 °F. The experimental work was repeated using the polytetrafluoro-ethylene-coated copper tube. The thickness of the coating was obtained by measuring the diameter of the coated tube with a micrometer and an average of 35 measurements gave a value of 0.00135 inch.

Distilled water was used in all of these experiments together with the organic solvents benzene, carbon-tetrachloride, 1, 1, 2-trichloroethylene and cyclohexane. The organic liquids (technical grade) were obtained from Fisher Scientific Company. The physical properties of the organic materials are given by Sykes [11] and Diah [12].

2. Results and Discussions

Plots of condensation heat transfer rates Q, versus the difference between the saturation temperature and the inside copper surface temperature ΔT, for the vapors of the pure systems condensing on the outside of the horizontal copper and polytetrafluoroethylene-coated copper tube are given in Figs. 3–6. In all instances, for a given value of ΔT, the transfer of heat is less when the vapors are condensing on the poly-tetrafluoroethylene-coated tube. This is to be expec-ted if the mode of condensation is the same on both solid surfaces.

Mizushina et al. [1] have shown that carbon tetra-chloride at atmospheric pressure condenses in a film-wise manner on polytetrafluoroethylene surfaces and Topper and Baer [2] have found that condensation of benzene also occurs in a filmwise manner on this mate-rial. Boyes and Ponter [9] measured the contact angles of benzene and cyclohexane under condensation condi-tions on a polytetrafluoroethylene surface and showed that for benzene a constant contact angle of 32° was obtained, which suggest filmwise condensation, whilst for cyclohexane the contact angle fell from 15° to 0°, depending upon the pressure of the system. They also showed that the contact angles of benzene-cyclohexane mixtures at 760 torr on a polytetrafluoroethylene sur-face fell from 32° to 26° with increasing cyclohexane concentration. Because no adsorption of cyclohexane occurs on a polytetrafluoroethylene surface it was suggested that an absorption process was responsible for the behavior by increasing the solid-vapor inter-facial free energy. No contact angle data are available for the 1, 1, 2-trichloroethylene system on either cop-per or polytetrafluoroethylene surfaces, but its similar-ity in structure with carbon tetrachloride would sug-gest a similar wetting behavior. Boyes [13] also found zero contact angle for benzene, carbon tetrachloride and cyclohexane on clean copper surfaces measured
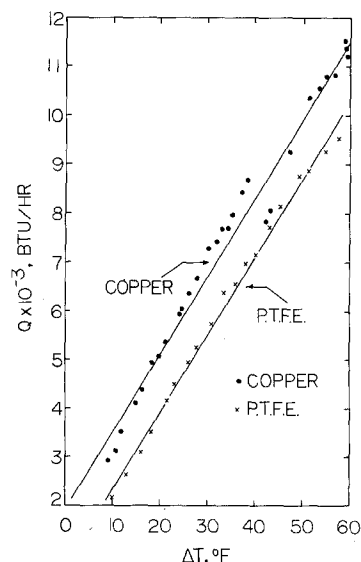

Fig. 3. Heat transfer rate s for pure benzene condensing on copper and polytetrafluoroethylene-coated copper tubes
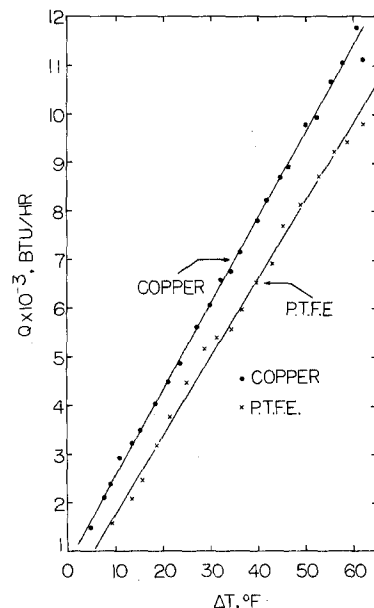

Fig. 4. Heat transfer rates for pure trichloroethylene condens-ing on copper and polytetrafluoroethylene-coated copper tubes

under condensation conditions, proving that these sub-stances condense in a filmwise manner.

For the condensation of the four pure systems on the copper and polytetrafluoroethylene-coated surfaces, the difference in ΔT for a given value of Q should be the same for all liquids if

(a) the mode of condensation on the two surfaces is filmwise and

(b) film breakdown has not occurred on one of the surfaces.

Assuming that the heat transfer through the con-densate liquid film is by conduction alone, the differ-

ence in ΔT values between the two lines for a given transfer rate represents the temperature drop through the polytetrafluoroethylene layer. An inspection of Figs. 3 and 4 shows a similar relation between Q and ΔT for the benzene and trichloroethylene systems. It was previously surmised that because of its closely allied form to carbon tetrachloride, trichloroethylene would condense in a filmwise manner. The above inspection confirms that a film is formed because of its similar behavior to the benzene system which was shown to be filmwise. Using the temperature difference through the polytetrafluoroethylene layer and taking the thermal conductivity of polytetrafluoroethylene to be 0.14 Btu/(hr.) (ft.^{2}) (°F/ft.), the calculated polytetrafluoroethylene thickness on the condenser tube was found to be 0.0015 inch which is in close agreement with the experimentally determined value of 0.00135 inches.

The cyclohexane behavior is different to that of the benzene and trichloroethylene systems in as much as a larger heat transfer resistance is encountered for a given Q. It has been shown that filmwise condensation occurs on both copper and polytetrafluoroethylene surfaces, since the contact angles of cyclohexane on both surfaces are zero. It is suggested that the increased heat transfer resistance is due to an absorption effect. How this occurs is not readily evident, but the cyclohexane molecules absorbed in the polytetrafluoroethylene interstices might exhibit molecular orientation, resulting to some degree in anisotropy in the thermal conduction component required for heat transfer. By assuming that the cyclohexane permeates through the polytetrafluoroethylene layer, the thermal conductivity of the cyclohexane containing polytetrafluoroethylene can be simply calculated, and in fact it can be shown to be less than 0.0653 Btu./(hr.) (ft.^{2}) (°F./ft.) for heat transfer rates of less than 5700 Btu./hr. This value lies below the bulk cyclohexane value of 0.0660 Btu./(hr.) (ft.^{2}) (°F./ft.). For transfer rates greater than 5700 Btu./hr. the thermal conductivity values are greater than the bulk cyclohexane value, but less than that of the polytetrafluoroethylene value. In previous work, Sutherland et al. [14] had suggested that the molecular orientation decreased the thermal conductivity values for octadecane, whilst Ziebland and Patient [15] using more sophisticated measurements found the reverse. At this time therefore, a more definite attempt to attribute the increased heat transfer resistance cannot be made.

For pure carbon tetrachloride (Fig. 5) with decreasing Q i. e. decreasing condensation rate, ΔT across the polytetrafluoroethylene approaches zero faster. This implies that the thermal resistance due to the polytetrafluoroethylene coating is outweighed by another mechanism which becomes more predominant as the condensing liquid rate decreases. Mizushina et al. [1] have shown that carbontetrachloride condenses as a
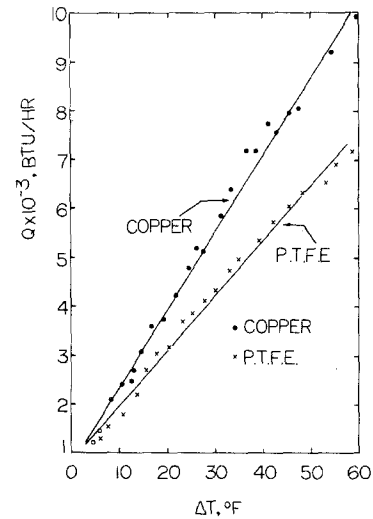

Fig. 5. Heat transfer rates for pure carbon tetrachloride condensing on copper and polytetrafluoroethylene-coated copper tubes
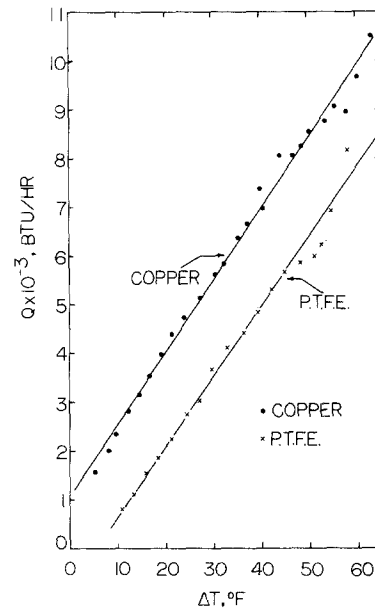

Fig. 6. Heat transfer rates for pure cyclohexane condensing on copper and polytetrafluoroethylene-coated copper tubes

film on a polytetrafluoroethylene surface. Davies et al. [16] measured contact angles of pure carbon tetrachloride at the boiling point and under equilibrium conditions and found that the contact angles varied between 22° to 36° for pressures ranging from 100–760 mm. of Hg. The contact angle of carbon tetrachloride on copper is zero and so it is suggested that the increase in transfer on the polytetrafluoroethylene surface might be due to film breakdown, where although the area for transfer is diminished, the turbulence encountered at the edges of the patches produced would outweigh the area reduction.
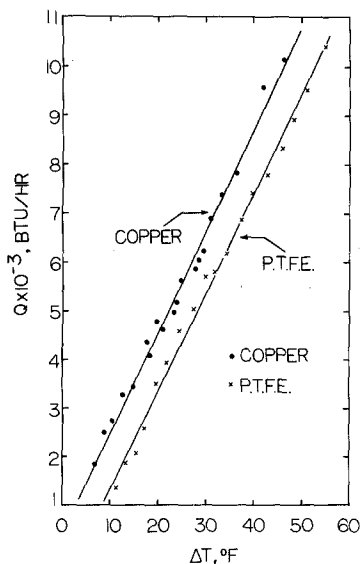
Fig. 7. Heat transfer rates for carbon tetrachloride-water eutectic mixture condensing on copper and polytetrafluoroethylene-coated copper tubes
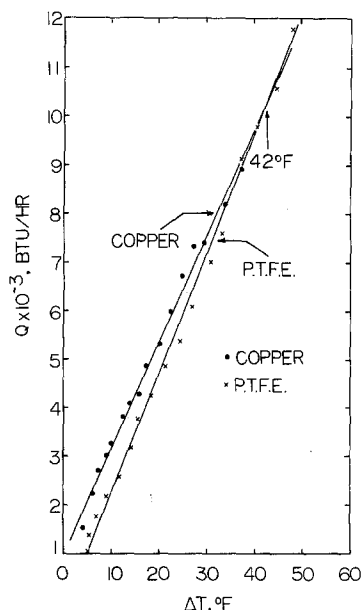

Fig. 9. Heat transfer rates for benzene-water eutectic mixture condensing on copper and polytetrafluoroethylene-coated copper tubes
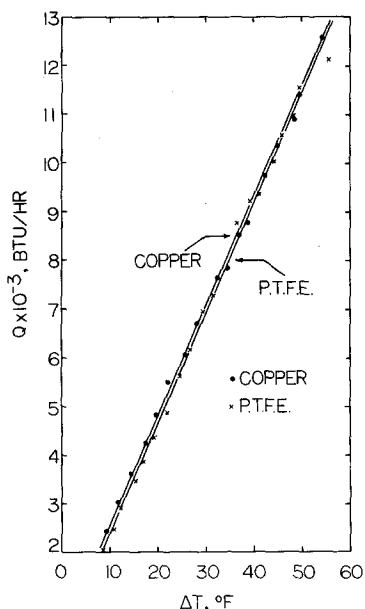

Fig. 8. Heat transfer rates for trichloroethylene-water eutectic mixture condensing on copper and polytetrafluoroethylene-coated copper tubes
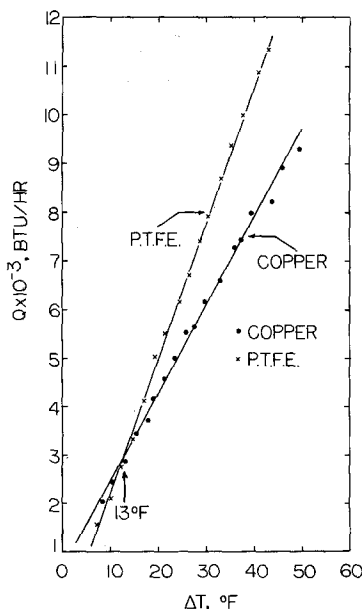

Fig. 10. Heat transfer rates for cyclohexane-water eutectic mixture condensing on copper and polytetrafluoroethylene-coated copper tubes

Condensation heat transfer data for the eutectic systems using the copper and polytetrafluoroethylene-sprayed copper surfaces are presented in Figs. 7—10. A first inspection shows that in some instances the heat transfer rates are improved using the polytetrafluoroethylene-coated surface despite the added heat

transfer resistance incurred. Although a preliminary estimate shows that the increased heat transfer is not large the results are very promising, since the work implies that the condenser tubes having the thermal properties of copper or better can be sprayed without any loss in thermal efficiency. This allows gases con-

Table 2. Physical and surface properties of the liquids investigated

Liquids	Surface tension (dynes/ cm)	Work of adhesion on Copper (ergs/ cm^2)	Work of adhesion on P.T.F.E. (ergs/ cm^2)	ρ(organic) ρ (water)	Contact angles Copper	P.T.F.E.	% water in eutectic mixture	Remarks
Carbontetrachloride	22.37	44.74	43.18	1.515	0	26	4.1	Heat transfer is higher on a copper surface than on a P.T.F.E. surface for ALL values of ΔT
Trichloroethylene	25.62	51.24	–	1.396	0	not deter- mined	5.4	Heat transfer is higher on a copper surface for ALL values of ΔT
Benzene	23.40	46.80	43.24	0.837	0	32	8.83	Heat transfer is higher on a copper surface for ΔT $<$ 42 °F. Above ΔT = 42 °F, the transfer rates on both surfaces are almost identical
Cyclohexane	16.62	33.24	33.24	0.728	0	0	9.0	Heat transfer for low ΔT ($<$ 13°F) is higher on the copper surface. Above ΔT = 13 °F, the heat transfer on copper surface fall below that on P.T.F.E.
Water	66.18	86.63	49.05	1	72	105	–	

taining corrosive impurities such as sulfur dioxide and hydrogen sulfide, encountered in the petroleum industry for example, to be processed.

To analyse the results it is necessary to estimate the adhesion of the two liquids, i. e. organic and water, to the solid surface. Dupré [17] has shown that the work of adhesion, $W_{S/L}$, of a liquid to a solid is given by

$$W_{S/L} = \gamma_{L/A} (\cos \theta + 1) .$$

Whether a droplet residing on a surface and surrounded by the other liquid, remains there or is removed by the density differences will depend upon the relative values of the surface and buoyancy forces. The actual value of the buoyancy effect cannot be deduced since this requires a knowledge of the size and the shape of the droplets. By considering that the droplets are small however, and that they form hemispheres on the surface, it is simple to demonstrate that for the systems having higher densities than the aqueous phase the buoyancy effects will outweigh the surface forces very considerably. Table 2 presents values of the work of adhesion for water and organic materials on copper and polytetrafluoroethylene surfaces together with the density ratios and the eutectic compositions. From these data it is possible to interpret the experimental values of the heat transfer rates given in Figs. 7–10 by comparing the relative adhesions of the organics and water on the two surfaces.

For the carbon tetrachloride-water system condensing on a polytetrafluoroethylene surface the heat transfer rates are found to be always lower than on a copper surface. From Table 2, the density of carbon tetrachloride is higher than that of water and therefore the water droplets will tend to reside at the liquid-vapor interface. Bernhardt et al. [6] have observed that in addition to these small mobile droplets at the liquid-vapor interface which move with the organic liquid film, there are large standing drops in contact with the metal wall. The growth of these standing drops is by coalescence with the neighboring droplets of water and also by further condensation of vapors. When the standing drops have grown sufficiently large, they roll down the condenser surface under the influence of gravity and will tend to accelerate portions of the organic liquid film in their path. The area of the condenser surface stripped clean of the condensate by the moving "standing" drops would be immediately covered by further condensation of the mixed vapors and/or by spreading of the organic film surrounding the bare areas. The presence of the drop forming phase will result in the agitation of the wall-wetting phase, causing local thinning and rippling of the organic liquid film. Because of the lower work of adhesion of water, this action of the standing water drops is repeated more frequently on the polytetrafluoroethylene surface and hence an improved transfer rate would be expected to result during the condensation of vapors of immiscible liquids on the polytetra-

fluoroethylene surface. From Fig. 7 it can be seen that the major resistance to heat transfer is due to the polytetrafluoroethylene coating. The resistance offered by the polytetrafluoroethylene layer on the copper tube will in this case always outweigh any effect of the changes in the surface behavior.

Similar behavior is noted for the trichloroethylene-water mixture, Fig. 8. The difference in ΔT between the two lines is considerably smaller than for carbon tetrachloride-water mixture indicating that the surface behavior caused by the standing drops is much greater than that encountered in the previous case and is suffi-ciently large to outweigh the resistance due to the polytetrafluoroethylene layer. The improved condi-tions may be due to a greater number of large stand-ing drops (since the amount of dropforming phase in the eutectic mixture is greater) in contact with the condenser surface, causing thinning and rippling of lar-ger portions of the organic liquid film. Judging from the closeness of the two lines in Fig. 8 if the polytetra-fluoroethylene thickness on the copper condenser tube is reduced, higher heat transfer rates can be expected on this surface in spite of its low thermal conductivity.

In the case of the benzene-water eutectic system, owing to the lower organic phase density a large pro-portion of the drop-forming phase will be in contact with the solid surface of the condenser tube. As pointed out by Bernhardt et al. [6] there will be some small mobile drops at the organic liquid film surface. Because of the lower work of adhesion of the aqueous phase on polytetrafluoroethylene, the renewal of the large standing drops will be expected to be greater and hence give an increased heat transfer rate. However from Fig. 9 it can be seen that the heat transfer is higher on the copper surface for temperature difference of upto about 42 °F. Above 42 °F the transfer rates on both surfaces are nearly identical in the range con-sidered, the former suggesting that the thermal resis-tance due to the polytetrafluoroethylene coating is controlling and the latter indicating that the surface behavior is sufficient to counteract the thermal resis-tance of the polytetrafluoroethylene on the tube.

For the cyclohexane-water system Fig. 10 clearly demonstrates the increased heat transfer for all values of temperature differences over 13 °F. From the pre-vious liquid system, benzene-water, it was observed that at high heat transfer values the advantage lay in using the polytetrafluoroethylene-coated surfaces. From Table 2 it is seen that the cyclohexane has the lowest density of the systems investigated and that the water droplets will come in contact with the solid sur-face. Once again, as in the case of the benzene-water system, the surface interaction outweighs the thermal resistance due to the polytetrafluoroethylene coating. Fig. 10 clearly shows that even at low temperature differences the results for the polytetrafluoroethylene and copper surfaces are similar. At higher values of
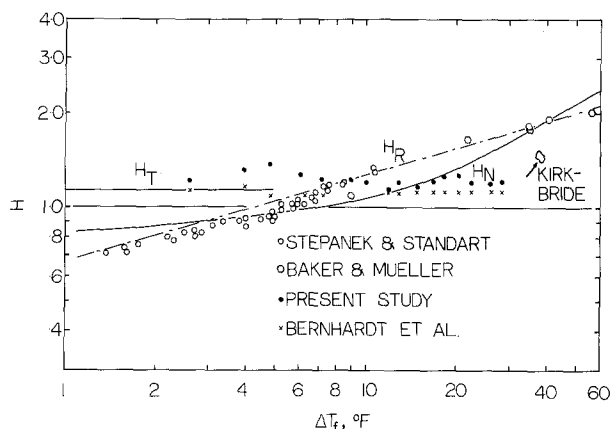

Fig. 11. Benzene-water eutectic heat transfer coefficients

Q the effect is marked and obviously highly advantage-ous in industry when cyclohexane-water mixtures are condensed. The reason for this higher transfer is ob-scure but the water momentarily in contact with the solid surface must in some way reduce the higher resistance caused by the absorption of the cyclohexane.

It is useful to compare the measured eutectic data with those reported by previous workers. The available heat transfer results for condensing mixtures of ben-zene-water, trichloroethylene-water and carbon tetra-chloride-water on horizontal copper surfaces are given in Figs. 11–13 together with the predictions of Sykes and Marchell's [19] models and the Bernhardt et al. [6]. In these figures the eutectic heat transfer data are expressed as the ratio of the eutectic to pure organic liquid heat transfer coefficients and ΔT_f is the differ-ence between the saturation and the condenser surface temperatures.

The most often used system is benzene-water which has been investigated by Kirkbride [18], Baker and Mueller [10] and Stépanek and Standart [8]. It is ob-served that the experimental data of Stépanek and Standart at low ΔT_f values lie well below those ob-tained in this investigation and in fact the heat transfer data presented by them often lie below the values expected for the organic component alone. Objections to the veracity of these results have been raised by Sykes and Marchello, and Bernhardt et al. when it was observed that the condenser contained no vent for the removal of inerts so allowing an additional gas phase resistance to be present under experimental conditions. The authors concur with this view. An examination of Fig. 11 shows that the results of the present work lie close to those predicted by the laminar two film model of Sykes and Marchello. This is considered to be for-tuitous since the density and surface properties of this system suggest that two discrete immiscible layers would not in fact form. Sykes and Marchello them-selves pointed out that the analytical model cannot adequately handle the experimental data. The data
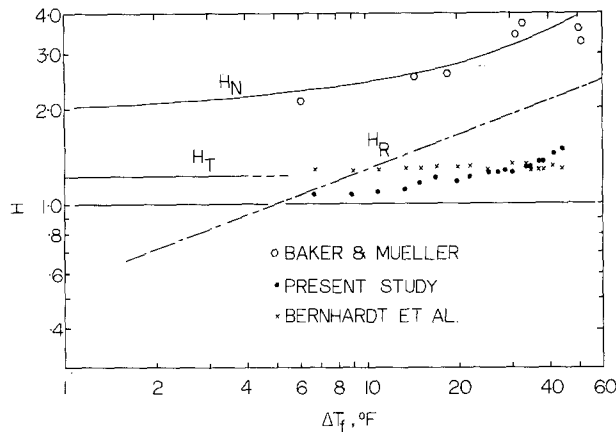
Fig. 12. Trichloroethylene-water eutectic heat transfer coefficients

Fig. 13. Carbon tetrachloride-water eutectic heat transfer coefficients

of Baker and Mueller were measured at high film temperature differences ΔT_f, and it is rather difficult to make a pronouncement when comparing them with those measured in this investigation. It was noted however that for other system (toluene-water) investigated by them and Sykes [11] that their results were consistently higher.

The available heat transfer data using the trichloroethylene-water eutectic mixture on horizontal surfaces are presented in Fig. 12. Baker and Mueller [10] experimentally determined the heat transfer data whilst Bernhardt et al. [6] used their equation to predict the transfer coefficients. The heat transfer coefficient predictions by the models of Sykes and Marchello [19] are also presented in this figure. Again it has been noted that the values reported by Baker and Mueller are considerably higher than those of the present study. In this early work no consideration seems to have been given to the preparation of the condenser tube surface. In our investigation described it was noted that the initial preparation of the surface was important. This was accomplished by condensing steam on the condenser tube until filmwise condensation resulted since initially the steam condensed in a dropwise manner, indicating a non-uniform surface. It is suggested that the seemingly different heat transfer results were due to an ill-prepared surface which exhibited different wetting characteristics and might have resulted in film breakdown and pseudo-dropwise condensation. Bernhardt et al. correlation gives heat transfer values in remarkably close agreement with the present work, whilst the Nucleation Model of Sykes and Marchello predicts values as high as 200%.

For the carbon tetrachloride-water mixture the only experimental data available were those reported by Sykes (1968). These are included with the present results along with the correlations presented by Sykes and Marchello [19] and Bernhardt et al. [6] in Fig. 13.
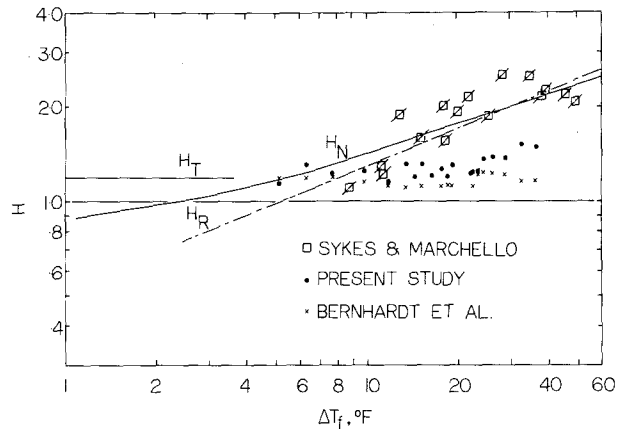
At low ΔT_f both experimental data are in good agreement and again the correlation of Bernhardt et al. closely predicts the heat transfer rates. The Nucleation model proposed by Sykes and Marchello predicts considerably higher values, of the order of 35 to 200%.

No other experimental data for the cyclohexane-water system are reported in the literature. Bernhardt et al. correlation for this system predicts the heat transfer coefficients within + 20% of the experimental data presented by the authors.

The heat transfer coefficients predicted from Bernhardt et al. equation and the experimental results of this study for the four eutectic mixtures are presented in Figs. 14 and 15. The comparisons made so far have been for eutectic mixtures condensing on copper surfaces.

No previous data have been reported for the condensation of vapors of eutectic mixtures on low energy surfaces such as polytetrafluoroethylene but the use of
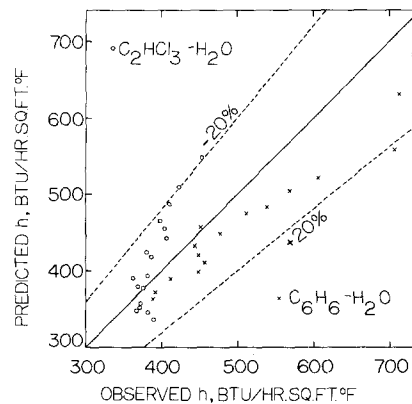

Fig. 14. Bernhardt et al. Correlation for data of present study for benzene and trichloroethylene water eutectics on copper tube
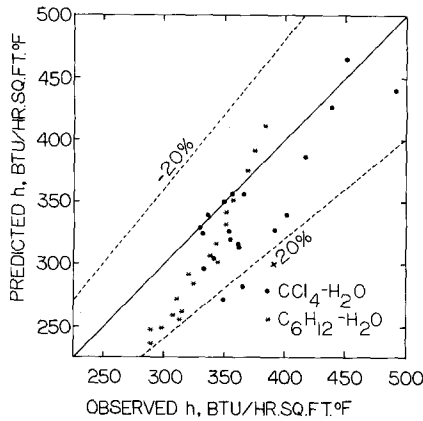
Fig. 15. Bernhardt et al. Correlation for data of present study for carbon tetrachloride and cyclohexane-water eutectics on copper tube
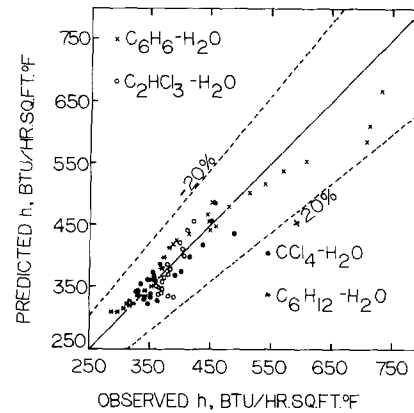

Fig. 17. Correlation by Eq. (1) using data of present study for carbon tetrachloride, benzene, trichloroethylene and cyclohexane-water eutectics on copper tube
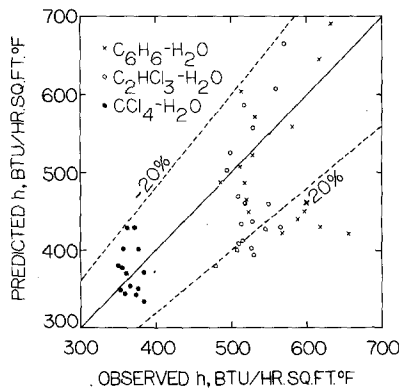

Fig. 16. Bernhardt et al. Correlation for data of present study for benzene, carbon tetrachloride and trichloroethylene-water eutectics on polytetrafluoroethylene-coated copper tube
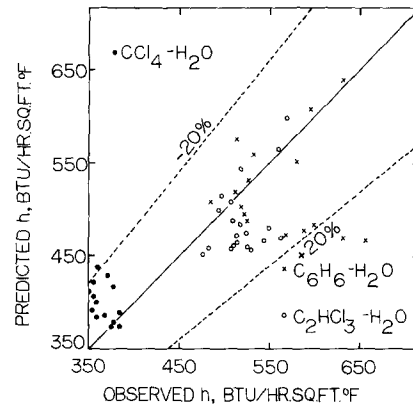

Fig. 18. Correlation by Eq. (2) using data of present study for benzene, carbon tetrachloride and trichloroethylene-water eutectics on polytetrafluoroethylene-coated copper tube

Bernhardt et al. equation gives good agreement with the experimental results (Fig. 16) in spite of the increased thermal resistance resulting from the low thermal conductivity polytetrafluoroethylene coating. As expected the cyclohexane water system gave poor agreement.

The heat transfer data for all the eutectic mixtures using the horizontal copper tube can be correlated by the following empirical Eq. (12)

$$h_e = \frac{h_{Nu}}{1 - 1.99 \times 10^4 \left[\dfrac{\Delta \sigma^3 \Delta \rho}{\mu^4 g}\right]^{-0.413} \left[\dfrac{\lambda \mu}{K \Delta T_f}\right]^{-0.286}}$$

to within ± 20% as shown in Fig. 17, whilst for the condensation of vapors of immiscible liquids, excepting cyclohexane-water mixture, on the polytetrafluoroethylene-coated copper tube, the results were correlated to within ± 20% in most case by

$$h_e = \frac{h_{Nu}}{1 - 0.047 \left[\dfrac{\Delta \sigma^3 \Delta \rho}{\mu^4 g}\right]^{0.143} \left[\dfrac{\mu \lambda}{K \Delta T_f}\right]^{-0.359}} \qquad (2)$$

(1) , as illustrated in Fig. 18.

3. Conclusions

It has been demonstrated that increased condensation heat transfer results when condensing certain eutectic mixtures on a polytetrafluoroethylene-coated copper tube. The results have highly important industrial implications since many eutectic mixtures in the petroleum industry are contaminated with corrosive materials, such as sulfur dioxide and hydrogen sulfide. The problem of corrosion associated with these gases when using copper surfaces can be overcome by coating the condenser tube with very thin layers of polytetrafluoroethylene.

In the case of the cyclohexane-water eutectic mixture, considerably higher heat transfer rates are observed which suggest that it would be advantageous to study the basic physical chemistry of the absorption of molecules into the plastic pores. This could lead to the development of different materials giving enhanced heat transfer rates.

The heat transfer rates with polytetrafluoroethylene-coated copper tube can be further improved by reducing the thickness of the coated material.

The experimental results have raised an additional doubt as to the reliability of the data of Stépanek and Standart [8] and Baker and Mueller [10] and highlights two important aspects of experimental technique, namely an adequate arrangement must be provided for purging any non-condensables from the system and an homogeneous surface be attained before reliable experimental data can be obtained.

Insight into the interaction between buoyancy effects produced by density differences and the surface forces has been shown, but this study reveals that a fundamental study of the dropsize distribution of the aqueous phase and the residence times of such drops on the solid surface have to be made before a quantitative model describing the condensation of vapors of binary immiscible liquids can be adequately established.

The Bernhardt et al. [6] equation has been shown to be the most successful to date in spite of its simplicity to predict condensation transfer rates using binary immiscible systems.

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