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Effect of refrigerant oil additive on R134a and R123 boiling heat transfer performance[☆]

M.A. Kedzierski*

National Institute of Standards and Technology, Bldg. 226, Rm B114, Gaithersburg, MD 20899, United States

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Abstract

This paper investigates the effect that an additive had on the boiling performance of an R134a/polyolester lubricant (POE) mixture and an R123/naphthenic mineral oil mixture on a roughened, horizontal flat surface. Both pool boiling heat transfer data and lubricant excess surface density data are given for the R134a/POE (98% mass fraction/2% mass fraction) mixture before and after use of the additive. A spectrofluorometer was used to measure the lubricant excess density that was established by the boiling of the R134a/POE lubricant mixture before and after use of the additive. The measurements obtained from the spectrofluorometer suggest that the additive increases the total mass of lubricant on the boiling surface. The heat transfer data show that the additive caused an average and a maximum enhancement of the R134a/POE heat flux between 5 kW m⁻² and 22 kW m⁻² of approximately 73% and 95%, respectively. Conversely, for nearly the same heat flux range, the additive caused essentially no change in the pool boiling heat flux of an R123/mineral oil mixture. The lubricant excess surface density and interfacial surface tension measurements of this study were used to form the basis of a hypothesis for predicting when additives will enhance or degrade refrigerant/lubricant pool boiling.

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Keywords: Refrigerant; R134a; R123; Boiling; Two-phase mixture; Polyolester; Additive; Heat transfer

R134a et R123: impacts des additifs sur la performance du transfert de chaleur lors de l'ébullition

Mots clés : Frigorigène ; R134a ; R123 ; Ébullition ; Mélange diphasique ; Polyolester ; Additif ; Transfert de chaleur

1. Introduction

The importance of improving the efficiency of existing air-conditioning equipment has been significantly emphasized with the 2003 blackout of the U.S. Northeast. A refrigerant oil additive that improves water chiller efficiency could be a cost-effective and immediate means of reducing

^{*} Only pool boiling heat transfer laboratory tests are presented in this report. Full-scale chiller tests would be required to observe the change in performance for a particular chiller. In addition, heat transfer improvements do not necessarily guarantee improvements and/or changes in chiller performance because of other factors that influence HVAC equipment performance.

^{*} Tel.: +1 301 975 5282; fax: +1 301 975 8973.

E-mail address: mark.kedzierski@nist.gov

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Nomenclature

English symbols		Greek symbols		
A_n	regression constant in Table 1, $n = 0, 1, 2, 3$	β	temperature dependence of fluorescence coeffi-	
а	surface area [m ²]		cient $[K^{-1}]$	
$c_{\rm p}$	specific heat of liquid [kJ K ⁻¹ kg ⁻¹]	δ	thermal boundary layer thickness [m]	
\dot{F}	fluorescence intensity	Г	lubricant excess surface density [kg m ⁻²]	
$F_{\rm c}$	fluorescence intensity from calibration (Eq. (1)	γ	surface free energy $[\text{kg s}^{-2}]$	
	of Ref. [5])	$\Delta T_{\rm s}$	wall superheat $(T_w - T_s)$ [K]	
$F_{\rm m}$	fluorescence intensity measured from boiling	Е	extinction coefficient $[m^2 mol^{-1}]$	
	surface	ρ	mass density of liquid (kg m^{-3})	
$h_{\rm fg}$	latent heat of vaporization of refrigerant	μ	dynamic viscosity [kg m ^{-1} s ^{-1}]	
	$[kJ kg^{-1}]$	σ	surface tension of refrigerant [kg s ⁻²]	
Io	incident intensity [V]			
le	thickness of excess layer [m]	English subscripts		
L_y	length of test surface (Fig. 2) [m]	1	system 1	
$M_{ m L}$	molar mass of lubricant [kg kmol ⁻¹]	2	system 2	
Р	vapor pressure [kPa]	2%	(98/2) refrigerant/lubricant mixture	
$P_{\rm c}$	critical pressure [kPa]	А	additive	
$P_{\rm r}$	reduced pressure $[P/P_c]$	b	bulk	
q''	average wall heat flux [W m ⁻²]	e	excess layer	
Т	temperature [K]	L	lubricant	
$T_{\rm w}$	temperature at roughened surface [K]	m	measured, mixture	
U	expanded uncertainty	q''	heat flux	
ui	standard uncertainty	S	saturated state	
x	mass fraction of lubricant	Tw	wall temperature	
у	test surface coordinate in Fig. 2 [m]	v	vapor	
Ζ	test surface coordinate in Fig. 2 [m]	W	wall or surface	

operating costs and improving the reliability of (by reducing the demand on) a nation's electricity grid. Some manufacturers of oil additives claim as much as a 30% reduction in chiller energy usage. If it were possible to achieve an energy reduction of this magnitude in air-conditioning chillers, millions of dollars a year could be saved in operating costs in the U.S. alone. This would also offer a significant contribution toward satisfying Section 202 of U.S. Executive Order 13123, which requires agency energy use reductions of 35% by the year 2010. In addition, the current version of the "Energy Bill of 2005"¹ encourages all federal agencies to take actions to maximize the efficiency of air-conditioning and refrigeration equipment which may include the use of any additive. Unfortunately, only field data have been used to support oil additive manufacturer claims of system improvement. The lack of controlled experimental data has been one of the greatest obstacles to large-scale applications of refrigerant oil additives.

Several refrigerant oil additives similar to that which was awarded a U.S. Patent in 1990 [17] are available today. Thepremise of the patent claim is that if the additive is sufficiently polar, it will attach to the "highly electron charged" metal surface via Van der Waals forces and displace the oil at the surface. The additive proposed by the patent is a chlorinated α -olefin or paraffin. This study tests a chlorine-free oil additive.^{2,3} Although the additive is not covered by the Wilkins et al.'s [17] patent due to the absence of chlorine, the mechanistic heat transfer claims are similar if not identical to those of the patent.

Recent studies have shown that refrigerant boiling heat transfer is a strong function of lubricant properties [7,10,13]. When a lubricant is added to a refrigerant, anything between an enhancement and a degradation in heat transfer performance is achieved relative to that of the pure refrigerant depending on the lubricant viscosity, miscibility, and concentration. In addition, Kedzierski [9] has shown that if a heat

¹ Energy Policy Act of 2005, "Section 553. Federal Procurement of Energy Efficient Products," subparagraph 2C.

² Certain trade names and company products are mentioned in the text or identified in an illustration in order to adequately specify the experimental procedure and equipment used. In no case does such an identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.

³ http://www.molecular-solutions.com, CAS Number 64742-44-5.

transfer degradation exists due to the use of a lubricant, reducing the lubricant layer will lessen lost performance. Consequently, if the additive behaves as outlined in the patent, it is possible that performance improvements could occur as long as both the additive and the displaced lubricant do not detrimentally affect performance in other ways.

The primary goal of this study was to determine if the pool boiling performance of two refrigerant/lubricant mixtures could be improved with the addition of a liquid additive. The above additive was chosen as the test additive because it has low sulfur content and it does not contain chlorine. The lubricants chosen were a polyolester (POE⁴) for use with R134a and a naphthenic mineral oil (NMO⁵) for use with R123. The viscosities of the POE and of the NMO at 313.15 K were 21.76 μ m² s⁻¹ and approximately 60 μ m² s⁻¹, respectively. The viscosity of the additive at 313.15 K taken from its Material Safety Data Sheet (MSDS) was approximately 32 μ m² s⁻¹. The MSDS also indicated that the additive has a naphthenic petroleum hydrocarbon base.

The secondary goals of the study were to test the additive enhancement mechanism of lubricant displacement. The recently developed measurement technique [9] for measuring the lubricant mass on a boiling surface was used to determine if the additive had displaced lubricant from the surface.

No compatibility tests of the additive with commercial chiller lubricants are provided here. It is essential to understand the compatibility of additives with lubricants and refrigerants given that chiller reliability may depend on it.

2. Apparatus

Fig. 1 shows a schematic of the apparatus that was used to measure the pool boiling data of this study. More specifically, the apparatus was used to measure the liquid saturation temperature (T_s) , the average pool boiling heat flux (q''), the wall temperature (T_w) of the test surface, and the fluorescence intensity from the boiling surface (F). The three principal components of the apparatus were the test chamber, the condenser, and the purger. The internal dimensions of the test chamber were 25.4 mm \times 257 mm \times 1.54 m. The test chamber was charged with approximately 7 kg of refrigerant, giving a liquid height of approximately 80 mm above the test surface. As shown in Fig. 1, the test section was visible through two opposing, flat 150 mm × 200 mm quartz windows. The bottom of the test surface was heated with high velocity (2.5 m s⁻¹) water flow. The vapor produced by liquid boiling on the test surface was condensed by the brine-cooled, shell-and-tube condenser and returned as liquid to the pool by gravity.

Fig. 1 also shows the spectrofluorometer that was used to make the fluorescence measurements and the fluorescence probe perpendicular to the heat transfer surface. The fluorescence probe was a bifurcated optical bundle with 168 fibers spanning from the spectrofluorometer to the test surface. The 168 fibers of the probe were split evenly between the fibers to transmit the incident intensity (I_o) to the test surface and those to receive the fluorescence intensity (F) from the lubricant on the test surface. Further details of the test apparatus can be found in Refs. [6,8].

3. Test surface

Fig. 2 shows the oxygen-free high-conductivity (OFHC) copper flat test plate used in this study. The test plate was machined out of a single piece of OFHC copper by electric discharge machining (EDM). A tub grinder was used to finish the heat transfer surface of the test plate with a crosshatch pattern. Average roughness measurements were used to estimate the range of average cavity radii for the surface to be between 12 μ m and 35 μ m. The relative standard uncertainty of the cavity measurements were approximately $\pm 12\%$. Further information on the surface characterization can be found in Ref. [8].

4. Measurements and uncertainties

The standard uncertainty (u_i) is the positive square root of the estimated variance u_i^2 . The individual standard uncertainties are combined to obtain the expanded uncertainty (U), which is calculated from the law of propagation of uncertainty with a coverage factor. All measurement uncertainties are reported at the 95% confidence level except where specified otherwise. For the sake of brevity, only an outline of the basic measurements and uncertainties is given below. Complete detail on the heat transfer measurement techniques and uncertainties can be found in Refs. [4,8,9,11].

4.1. Heat transfer

All of the copper-constantan thermocouples and the data acquisition system were calibrated against a glass-rod standard platinum resistance thermometer (SPRT) and a reference voltage to a residual standard deviation of 0.005 K. Considering the fluctuations in the saturation temperature during the test and the standard uncertainties in the calibration, the expanded uncertainty of the average saturation temperature was no greater than 0.04 K. Consequently, it is believed that the expanded uncertainty of the temperature measurements was less than 0.1 K.

Twenty 0.5 mm diameter thermocouples were force fitted into the wells on the side of the test plate shown in Fig. 2. The heat flux and the wall temperature were obtained by regressing the measured temperature distribution

⁴ ICI's EMKARATE RL DE 589. (A model polyolester made for NIST. Not a commercial product.)

⁵ This NMO (York-C) is currently not commercially available.



Fig. 1. Schematic of test apparatus.

of the block to the governing two-dimensional conduction equation (Laplace equation). In other words, rather than using the boundary conditions to solve for the interior temperatures, the interior temperatures were used to solve for the boundary conditions following a backward stepwise procedure given in Ref. [12]. Fourier's law and the fitted constants from the Laplace equation were used to calculate the average heat flux (q'') normal to and evaluated at the heat transfer surface based on its projected area. The average wall temperature (T_w) was calculated by integrating the local wall temperature (T). The wall superheat was calculated from T_w and the measured temperature of the saturated liquid (T_s) . Considering this, the relative expanded uncertainty in the heat flux $(U_{q''})$ was greatest at the lowest heat fluxes, approaching 10% of the measurement near 10 kW m^{-2} . In general, the $(U_{q''})$ remained approximately within 3% and 5% for heat fluxes greater than 30 kW m^{-2} . The larger uncertainties in the higher heat flux region are caused by the greater between-run (day-to-day) variations in the measurements, which is a noted characteristic of vigorous boiling [12]. This characteristic may be accentuated by the presence of lubricant [7,9]. The average random error in the wall superheat ($U_{\rm Tw}$) was between 0.02 K and 0.1 K.

4.2. Fluorescence

Kedzierski [6] describes the method for measuring the excess mass of lubricant on the boiling surface per surface area, i.e., the surface excess density (Γ). Because the molar mass of the lubricant is unknown, Γ is defined in this work on a mass basis as:

$$\Gamma = \rho_{\rm e} x_{\rm e} l_{\rm e} - \rho_{\rm b} x_{\rm b} l_{\rm e} \tag{1}$$

where l_e is the thickness of the lubricant excess layer. Precedence for reporting the surface excess density in mass units is given by citing the work of McBain and



Fig. 2. OFHC copper flat test plate with cross-hatched surface and thermocouple coordinate system.

Humphreys [14] in which they experimentally verified the Gibbs adsorption equation by measuring Γ at a liquid–vapor interface.

The equation for calculating the lubricant excess surface density from the measured fluorescence emission intensity (F_m) is [5,7]:

5. Experimental results

5.1. Heat transfer

The heat flux was varied roughly between 100 kW m^{-2} and 5 kW m⁻² to simulate more than most possible operating

$$\Gamma = \rho_{e} x_{e} l_{e} - \rho_{b} x_{b} l_{e} = \frac{\rho_{b} x_{b} \left(\frac{\rho_{L,T_{e}}}{\rho_{L,T_{b}}} - \frac{\rho_{b} x_{b}}{\rho_{L,T_{b}}}\right) \left(\frac{F_{m}}{F_{c}} - 1\right)}{\frac{I_{oe}}{I_{ob}} \left(1 + 1.165 \frac{\varepsilon}{M_{L}} x_{b} \rho_{b} l_{b}\right) \frac{e^{\beta (T_{e} - T_{b})}}{l_{b}} - 1.165 \frac{\varepsilon}{M_{L}} x_{b} \rho_{b} \left(\frac{F_{m}}{F_{c}} - 1\right)}$$
(2)

where the value of ε/M_L was obtained from the fluorescence calibration as 0.0646 m² kg⁻¹, and the fluorescence temperature dependence coefficient (β) of the POE was experimentally determined to be 0.01 K⁻¹ [5]. The β accounts for the difference in temperature between the excess layer and the bulk fluid. The density of the pure lubricant is ρ_L . All of the fluid properties are evaluated at the bulk fluid temperature (T_b) with the exception of ρ_{L,T_c} , which is the pure lubricant density evaluated at the average temperature of the excess layer (T_c).

Input for Eq. (2) is as follows. The fluorescent intensity from the calibration (F_c) is obtained from Eq. (1) of Ref. [5] evaluated at the charged bulk lubricant concentration of test fluid in the boiling apparatus. The l_b is the distance between the probe and the heat transfer surface and $l_b \gg l_e$. The ratio of the absorption of the incident excitation in the bulk to that in the excess layer (I_{oe}/I_{ob}) was 0.985 for the R134a/POE (98/2) mixture. conditions for R134a and R123 chillers. All pool boiling tests were taken at 277.6 K saturated conditions. The data were recorded consecutively starting at the largest heat flux and descending in intervals of approximately 4 kW m^{-2} . The descending heat flux procedure minimized the possibility of any hysteresis effects on the data, which would have made the data sensitive to the initial operating conditions. Kedzierski [4] provides the measured heat flux and wall superheat for all the data of this study and the number of test days and data points for each fluid.

The mixtures were prepared by charging the test chamber (see Fig. 1) with pure refrigerant (either R134a or R123) to a known mass. Next, a measured mass of lubricant (POE with R134a and NMO with R123) was injected with a syringe through a port in the test chamber. The refrigerant/ lubricant solution was mixed by flushing pure refrigerant through the same port where the lubricant was injected. After the tests with the refrigerant/lubricant mixture were completed, the additive was added to the existing test chamber charge in the same manner as for the lubricant. The additive was added to the refrigerant/lubricant (98/2) mixture as roughly 10% of the existing mass of lubricant in the system giving an R134a/POE/additive (97.8/2/0.2) mixture and an R123/NMO/additive (97.8/2/0.2) mixture. All compositions were determined from the masses of the charged components and are given on a mass fraction percent basis. The maximum uncertainty of the composition measurement is approximately 0.02%, e.g. the range of a 2.0% composition is between 1.98% and 2.02%.

Fig. 3 is a plot of the measured heat flux (q'') versus the measured wall superheat $(T_w - T_s)$ for the R134a/POE (98/2) mixture at a saturation temperature of 277.6 K. The open circles represent 16 days of boiling measurements made over a period of approximately four weeks. The solid lines shown in Fig. 3 are cubic best-fit regressions or estimated means of the data. Three of the 144 measurements were removed before fitting because they were identified as "outliers" based on having both high influence and high-leverage [2]. Table 1 gives the constants for the cubic regression of the superheat versus the heat flux for all of the fluids tested here. The residual standard deviation of the regressions representing the proximity of the data to the mean - range between 0.14 K and 0.39 K. The dashed lines to either side of the mean represent the lower and upper 95% simultaneous (multiple-use) confidence intervals for the mean. From the confidence intervals, the expanded uncertainty of the estimated mean wall superheat was 0.15 K and 0.26 K for superheats less than and greater than 7 K, respectively.

Fig. 4 plots the measured heat flux (q'') versus the measured wall superheat $(T_w - T_s)$ at a saturation temperature of 277.6 K for the R134a/POE/additive (97.8/2/0.2) mixture. The mean of the R134a/POE (98/2) mixture is plotted as a coarsely dashed line. Comparison of the two boiling curves shows that they intersect at a superheat of approximately 8 K. For mean superheats less than 8 K, the R134a/POE/additive



Fig. 3. R134a/POE (98/2) boiling curve for plain surface.

(97.8/2/0.2) mixture exhibits an enhancement in the heat flux as compared to the R134a/POE (98/2) mixture. In contrast, the R134a/POE (98/2) mixture heat flux is greater than that of the R134a/POE/additive (97.8/2/0.2) mixture for superheats greater than 8 K. Apparently, the additive enhances the site density and, in turn, the heat transfer at superheats less than 8 K. For superheats greater than 8 K, the degradation exhibited by the R134a/POE/additive (97.8/2/ 0.2) mixture is likely to have resulted from the decrease in bubble size as compared to the two-component mixture (see Ref. [10]).

Fig. 5 is a plot of the measured heat flux (q'') versus the measured wall superheat $(T_w - T_s)$ for the R123/NMO (98/2) mixture at a saturation temperature of 277.6 K. The closed circles represent nine days of boiling measurements made over a period of approximately six months. The average expanded uncertainty of the estimated mean wall superheat averaged over all heat fluxes was 0.14 K.

Fig. 6 is a plot of the measured heat flux (q'') versus the measured wall superheat $(T_w - T_s)$ for the R123/NMO/ additive (97.8/2/0.2) mixture at a saturation temperature of 277.6 K. The closed squares represent 17 days of boiling measurements made over a period of approximately four weeks. The expanded uncertainty of the estimated mean wall superheat for the entire range of measured superheats was 0.13 K. The mean of the R123/NMO (98/2) mixture heat transfer measurements is provided as a coarsely dashed line for comparison.

A more detailed comparison of the refrigerant/lubricant and the refrigerant/lubricant/additive heat transfer performances for the R134a and the R123 mixtures is given in Fig. 7. Fig. 7 plots the ratio of the R134a/POE/additive (97.8/2/0.2) heat flux to the R134a/POE (98/2) heat flux $(q_m'/q_{2\%}'')$ versus the R134a/POE (98/2) mixture heat flux $(q_{2\%}'')$ at the same wall superheat. Likewise, the R123/ NMO/additive (97.8/2/0.2) heat flux to the R123/NMO (98/2) heat flux $(q''_m/q''_{2\%})$ versus the R123/NMO (98/2) mixture heat flux $(q_{2\%}'')$ at the same wall superheat is also plotted. A heat transfer enhancement exists where the heat flux ratio is greater than 1.0 and the 95% simultaneous confidence intervals (depicted by the shaded regions) do not include the value 1.0. Fig. 7 shows that R134a/POE/ additive (97.8/2/0.2) mixture exhibits an enhancement over the R134a/POE (98/2) mixture for heat fluxes between $5\ kW\ m^{-2}$ and $30\ kW\ m^{-2}.$ The maximum heat flux ratio was 1.95 ± 0.02 at 13 kW m^{-2} . The heat transfer data show that the additive caused an average and a maximum enhancement of the R134a/POE (98/2) mixture heat flux between 5 kW m⁻² and 22 kW m⁻² of approximately 73% and 95%, respectively. Fig. 7 also shows that the R123/ NMO/additive (97.8/2/0.2) mixture exhibits a heat transfer degradation for all heat fluxes between approximately 22 kW m^{-2} and 78 kW m⁻². The additive caused essentially no change in the heat transfer performance in the R123/ NMO (98/2) mixture from approximately 8 kW m^{-2} to 22 kW m^{-2} given that the average heat flux ratio in that

Table 1
Estimated parameters for cubic boiling curve fits for plain copper surface

Fluid	A_0	A_1	A_2	A_3
R134a/POE (98/2)				
$3 \text{ K} \le \Delta T_{s} \le 7 \text{ K}$	-1.76162	1.53377×10^{-3}	$-1.01205 imes 10^{-7}$	2.41953×10^{-12}
$7 \text{ K} \le \Delta T_{s} \le 11 \text{ K}$	6.91642	$1.57640 imes 10^{-5}$	$1.97728 imes 10^{-10}$	$-5.36523 imes 10^{-16}$
R134aa/POE/additive (97.8/2/0).2)			
$3 \text{ K} \le \Delta T_{s} \le 7 \text{ K}$	1.45977	$5.25209 imes 10^{-4}$	$-2.10525 imes 10^{-8}$	3.15524×10^{-13}
$7 \text{ K} \le \Delta T_{s} \le 12 \text{ K}$	3.16112	$1.60861 imes 10^{-4}$	$-1.52139 imes 10^{-9}$	7.03271×10^{-15}
R123/NMO (98/2)				
$3.5 \text{ K} \le \Delta T_{s} \le 22.5 \text{ K}$	-0.26241	$9.35500 imes 10^{-4}$	$-1.39311 imes 10^{-8}$	$7.11354 imes 10^{-14}$
R123/NMO/additive (97.8/2/0.	2)			
$6.5 \mathrm{K} \le \Delta T_{\mathrm{s}} \le 22.5 \mathrm{K}$	-0.84726	$9.83088 imes 10^{-4}$	-1.43136×10^{-8}	$6.99224 imes 10^{-14}$

 $\Delta T_s = A_0 + A_1 q'' + A_2 q''^2 + A_3 q''^3$, ΔT_s in Kelvin and q'' in W m⁻².

region was approximately 1.0. The minimum heat flux ratio for this mixture was 0.73 ± 0.05 at approximately 73 kW m⁻². The average heat flux ratio for the R123/ NMO/additive (97.8/2/0.2) mixture from approximately 10 kW m⁻² to 80 kW m⁻² was 0.88.

5.2. Excess surface density

The primary purpose of the excess surface density measurements presented here was to test the enhancing mechanism proposed in a 1990 U.S. Patent [17], which claims that certain refrigerant oil additives displace chiller lubricants from the heat transfer surface.⁶ One way to accomplish this would be to develop a new fluorescence calibration, F_{c} , for the R134a/POE/additive mixture composition that exists at the wall. As Fig. 8 shows, determination of the wall composition is problematic because it depends on the physical chemistry of the surfaces. Do the lubricant and the additive form a well-mixed⁷ excess layer on the wall as shown in system 1? Or does an additive monolayer form between the wall and the lubricant/additive excess layer as claimed in the patent and shown in system 2? With these questions in mind, a method is required to measure the excess surface density that relies neither on the knowledge of its composition at the wall nor its surface chemistry.

It would not be necessary to know the surface chemistry and/or the composition, if the additive and the lubricant had the same fluorescence and adsorption characteristics. In fact, measurements of the POE and the additive in two separate cuvettes showed that the fluorescence intensity of the additive for the same excitation and emission wavelengths was approximately half that of the POE. Given that the additive is approximately 2% of the mass of the lubricant, and that the thickness of a monolayer is approximately four orders of magnitude thinner than the thickness of the entire excess layer, it is expected that both system 1 and system 2 will exhibit nearly 98% of the mass in the excess layer as lubricant. Consequently, any difference in the fluorescence characteristics of the additive should have a relatively small effect on the fluorescence intensity of the excess layer given its relative fluorescence with the lubricant. Following this reasoning, the original R134a/POE calibration was used for the R134a/POE/additive mixture. The resulting excess surface density measurement underestimates the true mass of lubricant and additive on the wall because the fluorescence intensity of the additive is overestimated by using the R134a/POE calibration.

Lubricant excess surface density measurements were made for the R134a/POE/additive (97.8/2/0.2) and the R134a/POE (98/2) mixtures according to the measurement technique outlined in Ref. [5] and above. Fluorescence measurements were made between 50 kW m⁻² and 15 kW m⁻² to limit the time required to quench the boiling below the



Fig. 4. R134a/POE/additive (97.8/2/0.2) boiling curve for plain surface.

⁶ The manufacturer of the additive used in this study makes the same mechanistic claims even though the additive is not covered by this patent because it does not contain chlorine.

⁷ The additive was observed to be soluble in the lubricant at the test temperature.



Fig. 5. R123/NMO (98/2) boiling curve for plain surface.

fluorescence probe. The reported excess surface density measurements were obtained by extrapolating the measured Γ to just before quenching.

Fig. 9 shows the lubricant excess surface density measurements, as calculated with Eq. (2), for the two R134a/ POE mixtures versus the following excess property group that was developed in Ref. [5]:

$$\frac{(\rho_{\rm L} - \rho_{\rm b} x_{\rm b}) x_{\rm b}^{1.8} T_{\rm s} \sigma P_{\rm r}}{(1 - x_{\rm b}) \rho_{\rm L} h_{\rm fg}(T_{\rm w} - T_{\rm s})}$$
(3)

where the properties of the refrigerant are the reduced pressure (P_r) , the latent heat of vaporization (h_{fg}) and the liquid-vapor surface tension (σ) .

The measured Γ for the R134a/POE (98/2) mixture are shown as open circles and were taken from Ref. [5]. The measured Γ for the R134a/POE/additive (97.8/2/0.2) mixture (closed squares) are on average significantly greater than the measured Γ for the R134a/POE (98/2) mixture. This suggests that the additive contributes to the mass of lubricant that



Fig. 6. R123/NMO/additive (97.8/2/0.2) boiling curve for plain surface.



Fig. 7. R134a/POE/additive (97.8/2/0.2) and R123/NMO/additive (97.8/2/0.2) mixture heat fluxes relative to that of the refrigerant/lubricant (98/2) mixture for a plain surface compared at the same ΔT_{s} .

is on the wall rather than reducing the lubricant mass as the patent claims. The average lubricant excess surface density for the R134a/POE/additive (97.8/2/0.2) mixture was 0.96 ± 0.23 kg m⁻² at the 95% confidence level. This is approximately 81% greater than the average Γ for the mixture without the additive, which was 0.53 ± 0.06 kg m⁻². Considering that the confidence intervals do not coincide, the two means differ at the 95% confidence level. Even though the present excess measurements have shown that the additive has caused an increased excess layer, it has validated neither system 1 nor system 2 shown in Fig. 8.

Given that the excess surface density measurement is valid for either system 1 or system 2, this measurement has not disproved either system. A different means must be used to validate one of the systems. If we assume that system 2 evolves from system 1, the evolution can occur spontaneously only if the change from system 1 to system 2 results in a reduction of system surface energy [16]. The requirement for system 2 to exist can be expressed in terms of surface energies by applying the analysis of spreading coefficients given by Rosen [16]:

$$a\gamma_{\rm m_2b} + a\gamma_{\rm Am_2} + a\gamma_{\rm wA} < a\gamma_{\rm wm_1} + a\gamma_{\rm m_1b} \tag{4}$$

Here *a* is the surface area, γ_{m_2b} is the interfacial free (surface) energy per unit area at the lubricant/additive mixture 2–bulk refrigerant/lubricant/additive mixture interface. Similarly, γ_{Am_2} , γ_{wA} , γ_{wm_1} , and γ_{m_1b} are the surface energies of the additive–lubricant/additive mixture 2, the wall–additive, the wall–lubricant/additive mixture 1, and the lubricant/additive mixture 1–bulk refrigerant/lubricant/additive interfaces, respectively. Subscripts 1 and 2 on the lubricant–additive mixture represent slightly different compositions of the two excess layers to account for some loss of additive to the monolayer in system 2.



Fig. 8. Two possible surface energy systems for the R134a/POE/additive mixture.

By assuming that the additive monolayer does not significantly deplete the lubricant/additive excess layer of additive, γ_{m_1b} and γ_{m_2b} are approximately equal for the two systems. Many of the additive and the lubricant/additive mixture fluid properties are similar because they are essentially both lubricants. Consequently, the surface energy between the additive and the lubricant/additive mixture is expected to be small and can be neglected. Using the two above approximations Eq. (4) reduces to:

$$\gamma_{\rm wA} < \gamma_{\rm wm_l} \cong \gamma_{\rm wL} \tag{5}$$

Eq. (5) is a necessary condition for the additive monolayer to exist at the surface. Note that γ_{wL} and γ_{wm_1} are nearly equivalent because the lubricant/additive mixture 1 is well mixed (by definition of the system) and at least 98% lubricant by mass. An estimate of the relative magnitudes of the surface energies in Eq. (5) can be obtained from surface tension measurements and an analysis of drops on copper plates exposed to air. For lubricant drops exposed to air, Young's equation [1] represents the equilibrium surface force balance on a droplet as:



Fig. 9. Lubricant excess surface density for R134a mixtures.

$$\gamma_{\rm wv} = \gamma_{\rm Lv} \cos \theta + \gamma_{\rm wL} \tag{6a}$$

where the subscript "v" for vapor is used to represent the air above the droplet.

Likewise, Young's equation for additive drops exposed to air is:

$$\gamma_{\rm wv} = \gamma_{\rm Av} \cos \theta + \gamma_{\rm wA} \tag{6b}$$

where the contact angle, θ , is the angle between the droplet liquid–vapor interface and the substrate measured at the wall. For equilibrium, $\cos \theta$ is approximately 1.

Capillary rise measurements show that $\gamma_{Lv} \cong 0.026 \text{ N m}^{-1}$ and $\gamma_{Av} \cong 0.03 \text{ N m}^{-1}$ [4]. Eliminating γ_{wv} between Eqs. (6a) and (6b) and substituting the values for the measured liquid– vapor surface tensions yields:

$$\gamma_{\rm wL} - \gamma_{\rm wA} = \gamma_{\rm Av} - \gamma_{\rm Lv} = 0.004 \text{ N} \text{m}^{-1}$$

$$\tag{7}$$

Eq. (7) suggests that requirement for a pure additive monolayer to exist at the surface as given by Eq. (5) is satisfied. In other words, the preceding analysis, which is based on physical chemistry and indirect measurements, suggests that the forces are sufficient for the additive to spontaneously form a monolayer⁸ and act as a barrier between the wall and the lubricant/additive similar to what was outlined in the patent [17].

5.3. Heat transfer enhancement

As shown by Kedzierski [10], the viscosity, miscibility and concentration of the lubricant strongly influence refrigerant/lubricant pool boiling. The lubricant closest to the wall essentially controls the boiling. Consequently, if an additive (or added lubricant) is to have an impact on a given refrigerant/ lubricant system, there would be a greater likelihood for influence, if the additive can exist as a monolayer on the surface (system 2 in Fig. 8). If the additive is well mixed in the excess layer as in system 1 in Fig. 8, it will have minimal influence

⁸ For the lubricants and additives examined in this study.

on the heat transfer if it is only 2% by mass of the lubricant (recommended charge) that is next to the wall in the excess layer. For this reason, it is believed that the additive enhances R134a/POE pool boiling because it exists as a monolayer on the surface and its viscosity is greater than the lubricant. Kedzierski [10] has shown that lubricants with larger viscosities tend to have larger boiling heat transfer coefficients because the thermal boundary layer (δ) is thicker:⁹

$$\frac{\delta_1}{\delta_2} = \sqrt{\frac{\mu_1 c_{\mathsf{P}_2}}{\mu_2 c_{\mathsf{P}_1}}} \tag{8}$$

In general, the specific heat (c_p) does not differ much from lubricant to lubricant despite a large variation in viscosity. Consequently, Eq. (8) shows that the thermal boundary layer is a strong function of viscosity providing for a larger active site density for thicker boundary layers [3], which improves the boiling heat transfer.¹⁰

The viscosity of the additive is approximately 45% greater than that of the POE lubricant. As a result, an enhancement of the pool boiling may be expected if the additive exists as a monolayer on the surface. On the other hand, the additive viscosity is approximately half that of the NMO. This would suggest that a significant degradation should have occurred as a result. However, the NMO and the additive are both naphthenic base. For this reason it is likely that the additive remains well mixed in the excess layer with the NMO and has a minimal influence on the pooling properties because it is only 2% by mass of the lubricant. As a result, little change from the pre-additive heat transfer performance was observed for the R123/lubricant/additive mixture for heat fluxes where the R134a mixture exhibited a significant enhancement.

A hypothesis for predicting when an oil additive can potentially enhance the pool boiling of refrigerant/lubricant mixtures can be formed from the above analysis. Three requirements must be satisfied before an additive can potentially enhance refrigerant/lubricant heat transfer. First, the additive and the base lubricant must be "chemically dissimilar." Second, the liquid—vapor surface tension of the additive must be greater than that of the lubricant. Third, the liquid viscosity of the additive must be greater than that of the base lubricant. The first two requirements are necessary for the additive to form a monolayer at the wall. These requirements ensure that the Van der Waals forces that create the monolayer are of sufficient strength to overcome the molecular forces between the additive and the lubricant molecules in the bulk of the liquid. Consequently, the propensity for the monolayer to form is proportional to the difference between the additive and lubricant surface tensions if they are chemically dissimilar. Likewise, the strength of the attractive forces between the bulk lubricant and the bulk additive molecules is related to how well the fluids mix. "Chemically dissimilar" fluids will not "mix as well" as ones that are "chemically similar." Thus, ensuring that the additive and the lubricant are "chemically different", e.g., let one be a naphthenic oil and the other be a polyolester lubricant, can encourage the formation of a monolayer.

6. Future research

Lubricants for air-conditioning and refrigeration applications tend to have viscosities between $32 \,\mu \,m^2 \,s^{-1}$ and 220 µ m² s⁻¹ at 313.15 K [15]. In addition, POEs are typically very polar which would suggest that both a polar additive and a POE would have the propensity to form a monolayer at the surface [15]. These considerations suggest that several variables should be investigated to test the hypothesis that has been proposed in preceding sections. First, the proposed effect of the relative viscosity of the lubricant and the additive needs to be further investigated with boiling heat transfer measurements with additives that have viscosities that are greater and less than lubricant viscosities that typically exist for real applications. Second, the effect of additive liquid-vapor surface tension should also be investigated. Will further increases in additive surface tension improve heat transfer or is large surface tension relative to the lubricant only important in establishing the monolayer? Third, the effect of lubricant miscibility and additive miscibility with the refrigerant should be investigated. Fourth, it should be determined how the thermal boundary layer interacts with the excess layer and its properties. Fifth, the effect of the lubricant type and its polarity should be investigated. These are just a few of the possible future research directions that may be pursued to improve the usefulness of this type of research for the refrigeration and air-conditioning industry.

7. Conclusions

The effect of an additive on the boiling performance of an R134a/polyolester lubricant (POE) mixture and an R123/ naphthenic mineral oil lubricant mixture on a roughened, horizontal flat surface was investigated. The pool boiling heat transfer data show that the additive caused an average and a maximum enhancement of the R134a/POE heat flux between 5 kW m⁻² and 22 kW m⁻² of approximately 73% and 95%, respectively. For nearly the same heat flux range, the additive caused little change in the pool boiling heat flux of an R123/naphthenic mineral oil mixture. In addition, a maximum degradation of the heat flux for the R123/ naphthenic mineral oil mixture caused by the addition of the additive was observed to be approximately 27% at a heat flux of 73 kW m⁻².

⁹ This equation was misprinted in Ref. [10] but both equations give the same trend with respect to viscosity.

¹⁰ The thermal boundary layer may be thicker than the monolayer. However, the largest temperature gradients exist at the wall. Consequently, the fluid properties of the monolayer are expected to significantly affect the thickness of the thermal boundary layer given that the potential for the thermal boundary layer is provided by wall heat transfer.

Excess surface density measurements were used to test the enhancing mechanism proposed in a 1990 U.S. Patent, which claims that certain refrigerant oil additives displace chiller lubricants from the heat transfer surface. The measurements showed that the accumulated mass on the heat transfer surface for the R134a/POE mixture with the additive was greater than that without the additive, which contradicts the patent claims. However, surface tension measurements and other surface chemistry analysis were done to support the opinion that the additive can form a monolayer between the wall and the lubricant/additive excess layer if the lubricant and additive are sufficiently dissimilar chemically. An enhancement mechanism was proposed based on previous studies with heat transfer enhancing lubricants. It may be the case that the additive replaces less viscous lubricant at the immediate wall (monolayer), which in turn is responsible for the heat transfer enhancement. It was also hypothesized that a monolayer will not form if the additive and the refrigerant oil are too chemically similar, e.g., both naphthenic based as for the additive/R123 mixture. For this case, the additive will have little influence on the refrigerant/lubricant pool boiling because it remains well mixed in the excess layer with the lubricant and is typically only 2% by mass fraction of the lubricant charge.

Only pool boiling heat transfer laboratory tests are presented in this report. Full-scale chiller tests would be required to observe the change in performance for a particular chiller. In addition, heat transfer improvements do not necessarily guarantee improvements and/or changes in chiller performance because of other factors that influence HVAC equipment performance.

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