# ENHANCEMENT OF NUCLEATE POOL BOILING WITH POLYMERIC ADDITIVES

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Abstract-Heat transfer in the nucleate pool boiling of dilute aqueous polymer solutions was measured and compared with results for pure water. Solutes were hydroxyethyl cellulose (HEC) of three molecular weights, polyacrylamide (PA) of two molecular weights, and acrylamide; solute concentrations ranged from 62 ppm to 500 ppm. Liquids were boiled at atmospheric pressure on a horizontal steam-heated chrome-plated surface. Photographs showed distinct differences in bubble size and dynamics, between polymeric and nonpolymeric liquids.

Heat flux in each polymer solution exceeded that for water, although the monomer acrylamide caused a reduction in heat transfer. Increases were as much as 250 per cent at  $\Delta T \approx 15^{\circ}F$  and 100 per cent at  $\Delta T \approx 60^{\circ}$ F. Results produced by variations of concentration and molecular weight appeared to be correlatable with the solution viscosity. The HEC is a surfactant but PA is not, so surface tension is believed to be only a minor variable. Explanations based on limited polymer solubility and solution viscoelasticity are proposed.

### **NOMENCLATURE**

- area of chromium plate for boiling  $A_{\rm{L}}$  $\lceil ft^2 \rceil$ :
- polymer concentration,  $[g/dl]$ ;
- $\frac{C_{P}}{E}$ heat capacity of liquid  $[But/lb °F]$ ;
- $(h h_{\text{water}})/h_{\text{water}} \times 100$ , efficiency of polymer ;
- $h, h_{\text{max}}$ heat-transfer coefficient *(Q/A* AT) for pool boiling, and its maximum value  $[\text{Btu/hft}^2$  °F];
- heat of vaporization [Btu/lb];  $\Delta H$ .
- k. thermal conductivity of liquid [Btu/hft °F];
- $M_{\odot}$ molecular weight ;
- weight concentration [parts per ppm, million] ;
- rate of heat transfer  $\lceil \text{Btu/h} \rceil$ ; Q,
- $\overline{T}$ temperature  $\lceil \degree F \rceil$ ;
- $(T_{\text{plate}} 212^{\circ})$ , thermal driving force  $\Delta T$ for boiling heat transfer  $\lceil \degree F \rceil$ .

# Greek symbols

 $\mu$ ,  $\mu$ <sub>s</sub>, viscosity of liquid or of solvent alone  $[cP$  or  $lb/ft$  h]:

 $\rho_b$   $\rho_p$ , density of liquid and vapor, respectively  $[1b/\text{ft}^3]$ ;  $\sigma$ , surface tension  $\lceil d\text{ynes/cm} \rceil$ .

#### **INTRODUCTION**

**DILUTE** polymer solutions often exhibit transport properties which are entirely unpredictable by ordinary means and seem to defy the conventional intuition. For example, the friction factors for turbulent pipe flow of liquids containing only 10-100 ppm polymer (certain polymers, that is) are known to be substantially lower than friction factors for the solvent alone [1]. Analogous results have been reported for turbulent-flow heat transfer  $\lceil 2 \rceil$ ; the  $j_{\mathbf{H}}$ -factors are reduced for the polymer solution in even greater proportion than are the friction factors. These phenomena cannot be attributed to viscous effects since the polymer presence makes almost no contribution to the viscosity and the corresponding laminar flow results are unexceptional-usually identical to those for the solvent.

A number of explanations, rationalizations and correlations have been offered, and all involve the existence of viscoelasticity in the solutions. Such a property is expected to be rate sensitive and therefore to manifest itself in all unsteady state motions, of which pipe-flow turbulence is a notable example. This prompts the study of polymer solution behavior in other important turbulent flows, such as the pool boiling discussed here. The fact that pipe flow data has revealed a *reduction* in heat transfer turns out to be a misleading basis upon which to predict pool. boiling results, which show an increase in heat transfer. fn the latter, apparently, the existence of two-phase phenomena provides sufficient opportunity for still other unforeseen mechanisms to come into play.

A number of studies have been made of the effects of solutes on heat transfer in pool boiling, although this is believed to be the first report involving polymers. Aqueous systems containing ordinary solutes, such as sugar and glycerol, have been shown to suffer reduced heat transfer  $[3]$ . Often this is simply a consequence of enhanced viscosity, as is reflected in the correlation proposed by Rohsenow  $[4]$  for the heat-transfer coefficient in nucleate boiling.

$$
h = \text{(const)} \frac{(\Delta T)^2}{C_p^{2/1} \mu^{4/1} (\Delta H)^2} \sqrt{\left(\frac{k g(\rho_l - \rho_v)}{\sigma}\right)}.
$$
\n(1)

This, however, could not explain the lowering of peak heat flux reported for a  $0.016\%$  oleic acid solution [S], since such small amounts of additive have no effect on viscosity.

The role of surface active solutes was explored by Morgan et al. [6]. Working with  $0.1-1.0\%$ aqueous solutions of a commercial surfactant, they found the boiling curves  $(Q/A \text{ vs. } \Delta T)$  were shifted laterally in varying degrees, such that heat transfer at  $\Delta T$ 's below the peak flux was higher than for pure water. The peak fluxes, however, were essentially unchanged in magnitude. Jontz and Myers  $[7]$ , in studying bubble formation in aqueous solutions of surfactants,

also found an increase in heat transfer and similarly concluded that it resulted from the reduced surface tension.

On the other hand, Lowery and Westwater [S] studied the boiling of methanol solutions and noted increased heat transfer despite surface tension being unaffected (although the solutes were substances commonly used as surfactants with water). Again, concentrations were so low  $(0.001 - 0.1\%)$  that no bulk physical properties were apparently affected. In a subsequent work, Dunskus and Westwater [9] examined the boiling of isopropanol with eleven different additives. Concentrations were all about  $0.5\%$ , and the viscosity and surface tension for the solutions matched those of the solvent. Some of the solutions exhibited higher heat flux, which was accompanied by an observed increase in the frequency of bubble release from the heated surface. For chemically similar additives, heat transfer coefficients were greater for the solutes of higher molecular weight; this latter feature was characterized by the investigators in terms of lesser solute volatility. These phenomena were attributed primarily to the property of surface viscosity, which was claimed to reduce coalescence between bubbles.

#### EXPERIMENTAL

*Apparatus* 

The boiler (Fig. 1a) consisted of an 8  $\times$  8  $\times$ 12 in. box, constructed of 304 stainless steel with two Pyrex glass windows. Insulation was provided on all walls, although it could be removed from the windows for photographic purposes. The heating element was a  $\frac{1}{7}$  in. copper plate, 4\$ in. dia. laid ffat in the floor of the boiler and heated from below with saturated steam at controlled pressures (up to 100 psig). Its surface was a 0.005 in. layer of chromium on nickel, electroplated on top of the copper. To prevent spurious heat conduction and boiling on stainless steel surfaces this heater was embedded in a plate of Bakefite which made the contact with the steel. Four thermocouples Iocated in the copper block at various positions disclosed that



FIG. 1. (a) Cross-sectional view of boiler, (b) System.

the temperature distribution was uniform, with- The average molecular weight (believed to in accuracy of the measurement. be a viscosity-average) of PA-10 is reported

ceiling opening to a water-cooled condenser and lo<sup>6</sup>; for PA-20 it is  $2 \times 10^6$ . Concentrations thence to a 400 ml glass receiver vented to the investigated here were 500, 250, 125 and atmosphere (see Fig. lb). A small centrifugal 62.5 ppm (parts per million by weight). pump, whose speed could be controlled by a (2) HEC-L, HEC-M, HEC-H (Natrosol 250L, voltage regulator, was used to empty the receiver Natrosol 250M, Natrosol 250H: Hercules voltage regulator, was used to empty the receiver and recycle the cold condensate through a preheater and back to the boiler. The preheater polymers whose formula is usually produced some superheat but this was

Vapor passed from the boiler via a  $1\frac{1}{2}$  in. by the manufacturer to be approximately

Powder Co.) are hydroxyethyl cellulose

$$
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relieved by venting in the return line, and the temperature of water returned to the boiler was measured at 205-212°F on all occasions.

Liquids to be boiled were characterized with an Ostwald viscometer and a du Nuoy ring tensiometer. Still pictures of boiling phenomena were taken with a Linhof Speed Camera on polaroid film (3000 Speed Type 57); lighting was provided with a Honeywell electronic flash.

## *Materials*

All polymer solutions were prepared by dissolving the powdered solutes in distilled water with gentle stirring over a period of several hours.

(1) PA-10 and PA-20 (Separan NP 10, Separan NP 20; Dow Chemical Co.) are polyacrylamides of differing molecular weight. Their chemical formula is



Their average molecular weights are given by the manufacturer as  $7 \times 10^4$ , 10<sup>5</sup> and 2  $\times$ 10<sup>5</sup> respectively. Concentrations were 250, 125 and 62.5 ppm for HEC-L, and 125 ppm for HEC-M and HEC-M. These polymers are surfactants, as might be inferred from their structure.

(3) Acrylamide (Eastman Organic Chemicals) was employed here for comparison with the polyacrylamides; its molecular weight is 71.1.

### *Procedure*

The heating surface was cleaned routinely before and after each set of three data-points, with a sequence of operations involving application of chrome cleaner and washing with hot tap water and distilled water. Only a soft sponge and absorbent paper tissues contacted the chromium, which remained smooth and completely wettable.

During a typical run, the boiler was loaded with 3000 ml of liquid to bring the free surface to a level 1.9 in. above the heater. Steady state boiling was achieved in 30-40 min after steam entered the heating chamber; this was determined by monitoring both temperature and condensate flow data. Flow rates, if sufficiently high, were measured with a rotameter in the recycle line as condensate level in the receiver was being held constant by adjustment of pump speed. Very small condensate flows were measured batchwise, by collecting a known volume of water in the receiver over a timed interval ; at no time did this deplete the boiler contents by more than 3 per cent.

Polymer solutions were replaced with fresh samples after three runs such as described above. This precaution was taken in order to minimize degradation of the polymer molecules which might have occurred at high temperatures with bubbling agitation over long periods of time. These occasions of sample renewal permitted regular observations of the chromium surface. No visible deposits formed under most test conditions, although boiling of PA-20 at 250 ppm (highest molecular weight polymer and its highest concentration) led to formation of a viscous film on the heating plate; this was transparent and visible only upon draining the boiler.

Surface tension and viscosity measurements of all liquids were made both before and after boiling. Room temperature was maintained at 23°C, so that heat losses from the boiler would be nearly constant in all runs.

## **RESULTS**

## General *observations*

Physical properties of the solutions were affected by their solute content in generally expected fashion (see Table I). Surface tension of water and the acrylamide/polyacrylamide solutions was 71 dyn/cm at 25°C and 65 dyn/cm at 70°C. The HEC solutes were distinctly surface active, however, with  $\sigma = 68$  dyn/cm and about 44 dyn/cm at  $25^\circ$  and  $70^\circ$ C respectively. At lOO"C, an even greater reduction of HEC surface tension would be expected. Concentration effects on surface tension of all solutions were apparently insignificant.

Viscosities increased with increasing concentration and molecular weight, within an homologous series Maximum value observed  $(25^{\circ}C)$  was 3.57 cP (for 250 ppm PA-20), a mere fourfold increase above that for water; viscosity of HEC solutions changed by less than 50 per

Solute	Concentration	Key for	Viscosity, $\mu$ , at 25°C (CP)		Surface tension, $\sigma$ (dyn/cm)	
	(ppm)	Fig. 8	before*	after*	$25^{\circ}$ C	$70^{\circ}$ C
	(water)		0.89	0.89	72	65
acrylamide	500		0.91	0.91	72	64
PA-10	62.5 125 250 500		1-09 1.33 1.76 2.64	$1-03$ 1.19 1.50 $2-05$	71 71 71 71	65 65 65 65
PA-20	62.5 125 250		$2 - 08$ $2-90$ 3.57	1.80 2.49 2.88	71 71 72	65 65 65
<b>HEC-L</b>	62.5 125 250	Δ $\overline{\nabla}$ ⊳	0.92 0.96 1:11	0.92 0.96 $1-10$	68 68 68	45 46 45
HEC-M	125	◯	1.12	1:11	68	44
HEC-H	125		1.32	1.32	67	42

Table 1. Physical properties of test liquids

\* Measurements were made (a) before any heating had occurred, and (b) after steadystate boiling had been completed.

cent. Data on the HEC-L solutions could be plotted as  $(\mu - \mu_s)/c\mu_s$  vs. c and extrapolated to zero concentration to obtain the intrinsic viscosity  $[10]$ ; this value, used in conjunction with established correlations [11], permitted an independent determination of molecular weight  $(7.3 \times 10^4)$  which agreed with that of the manufacturer (7  $\times$  10<sup>4</sup>). Similar analysis for other polymers was deemed inappropriate, since the  $\mu(M)$  correlations were established for lower ranges of molecular weight,

Solutions of HEC exhibited very stable viscosities, which were generally unaflected by the boiling process. PA solutions, however, suffered noticeable reductions in viscosity. The possibility that this might be due to thermal degradation or solvation effects was discounted when it was found that ordinary heating to 205°F for various periods of time produced by itself no changes. It is therefore presumed that PA viscosity losses during boiling were caused by mechanical degradation of the polymer chains under the influence of the vigorous agitation of boiling. The HEC molecule was apparently strong enough to resist this.

Viscosities of PA-20 solutions were anomalous in another way. Plots of  $(\mu - \mu_s)/c \mu_s$ vs.  $c$  exhibited a negative slope, unlike all other data encountered here. Such behavior is characteristic of polyelectrolytes  $[10]$ , although the PA-20 samples supplied for this work were understood to be nonionic. It is notable also that only for a PA-20 solution was a viscous deposit observed on the heating plate after boiling.

The phenomenon of foaming, often observed during boiling in the presence of surfactant, was found with all HEC solutions but in none of the others. Foam height (at a given  $\Delta T$ ) increased with polymer concentration and molecular weight, becoming so severe with the 250 ppm solution of HEC-H that  $\Delta T \approx 65$ °F could not be exceeded without foam escaping the boiler and reaching the condenser,

Substantial differences in boiling dynamics and bubble formation were observed in comparing the various classes of liquids. This was true for both the steady and the transient states, and the corresponding photographic evidence is extremely revealing. Photographs are available elsewhere  $\lceil 12 \rceil$  of the build-up to steady boiling and the subsequent decay after shutdown;  $certain$  observations are summarized in Table 2 where three liquid systems are compared.

Steady-state boiling is shown for these three systems in Fig. 2. For water (Fig, Za), bubble action is seen to be extremely chaotic, with extensive coalescence during rise. Interestingly,

	Time (min)	Water	$250$ ppm HEC-L in water	$250$ ppm PA-10 in water
<b>Bubble</b>	3	large	small, uniform	large
size	7	larger	some larger	intermediate
	$\infty$	very large, coalesced	small, uniform. little coalescence	mostly small, little coalescence
Surface	3	little	complete	intermediate
coverage		incomplete	complete	complete
<b>Bubble</b>	3	none	some	some
release		some	more	nearly steady
Rise pattern	œ	chaotic but generally conical	very ordered. conical	intermediate order. tightly conical

Table 2. Ouglitative observations  $(\Delta T = 27.5^{\circ}C)$ 



FIG. 2. Vigorous full boiling,  $\Delta T = 27.5^{\circ}F$  and  $t \approx 15$  min. (a) Water. (b) 250 ppm of HEC-L in water. (c) 250 ppm of PA-10 in water.

the same behavior was exhibited by solutions of the monomer acrylamide; visual comparisons of boiling in a 500 ppm acrylamide solution with boiling in water revealed no discernable differences [12]. However, marked differences occurred for all the polymer solutions. For both HEC (Fig. 2b) and PA (Fig. 2c) systems, bubble sizes were distinctly smaller and more uniform. Little coalescence seemed to occur. The rising bubbles produced a well-defined conical region, which was most "pointed" in PA liquids.

During build-up, it was particularly noticeable that bubbles formed on the plate in HEC solutions were very much smaller than in water, and the plate was more quickly covered with them. This difference can probably be attributed in large measure to the surfactant properties of HEC. It is known that reduced surface tension results in a decrease of energy required to create a bubble, and thus in more bubbles and smaller ones [13]. The PA systems were at first intermediate in appearance. The number of bubbles was less than for HEC solutions but more than for water (due, perhaps, to the polymer behaving as an activator of bubble initiator sites) and bubble sizes were about the same as in water (probably because PA does not influence surface tension). However, the PA liquids were the first to achieve continuous nucleate boiling.

## *Heat transfer*

A boiling curve for distilled water is shown in Fig. 3. It was entirely reproducible and was frequently repeated between polymer tests, to verify that the heating surface had not changed its characteristics. The lower portion of the curve, for  $\Delta T \leq 20^{\circ}$ F, shows a rather unexpected dip ; such behavior was noted also with the polymer solutions. This corresponds to a very low boil-up rate, for which partial condensation on the boiler walls and ceiling (thereby reducing the apparent Q) may have been a significant fraction of the vapor formed. From the intermediate region of the curve it is found that  $Q \sim (\Delta T)^{2.15}$ . The exponent 2.15



**FIG.** 3. Boiling curve for distilled water.

is less than the 3-O implied by equation (1) and seen in the data of many workers. This may reflect the presence of some surface contamination (slopes as low as unity have been reported [4]) or a great degree of smoothness [14]. A peak heat flux was not obtained here or in any of these experiments; the greatest heat flux achieved with water was  $2.1 \times 10^5$  Btu/hft<sup>2</sup>.

The boiling curves for solutions are shown in Figs. 4-7. Polymeric systems invariably gave higher heat flux than did water, and the manomer acrylamide led to lower heat flux. Various features of these results are discussed below.

(1) *Effect of concentration*. As seen in Fig. 4, the general effect of increasing the concentration of polymeric additives is to increase the heat transfer. This is violated only in the case of HEC-L (Fig. 4a) at high  $\Delta T$ , where the 250 ppm solution becomes less effective than those of lesser concentration. A similar cross-over of the 125 ppm line over the 62.5 ppm line appears imminent.

These observations are consistent with those of several other workers [7,9,10] ; in such cases



FIG. 4. Effect of polymer concentration on the boiling curve.<br>(a) HEC-L solute. (b) PA-10 solute. (c) PA-20 solute.

it appears that the boiling curves have been shifted to the left by increasing amounts of additive. In the polymeric case, however, vastly smaller concentrations are being employed. Furthermore, for PA-10 (Fig. 4b) there is no sign of any bending over of the curves at high  $\Delta T$ . The implication here is that the peak heat fluxes-if they could have been obtainedwould be higher than for water, and that the PA solute *raises* the whole curve rather than shifting it laterally.

(2) *Surjizctant effects.* According to equation (1) and other correlations, heat transfer should be increased somewhat by a reduction in surface tension. Such an increase does occur for solutions of HEC, which has surfactant properties, but it also occurs for solutions of polyacrylamide, which has none. In addition, the constancy of surface tension with polymer concentration-whereas the boiling curves are separated-suggests that surface tension *per se* is not the dominant factor in this phenomenon. The





FIG. 5. Surfactant effects illustrated by comparison of solutions of HEC-H ( $\sigma_{70} = 42$  dyn/cm) and PA-10 ( $\sigma_{70} =$ 65 dyn/cm =  $\sigma_{\text{water}}$ ) Polymer concentration = 125 ppm and solution viscosity  $\approx$  1.32 cP.

FIG. 6. Molecular weight effects. (a) HEC of three grades, 125 ppm (b) PA of two grades at 250 ppm and monomer acrylamide at 500 ppm

surface tension reduction in HEC solutions does play an expected role in causing substantial foam formation, which in itself might bc contributing to the cross-over of curves in Fig. 4a.

In certain ways, the surfactant character of HEC leads to predictable results. The heat transfer coefficients calculated from Fig. 4a have maximum values  $h_{\text{max}}$  which agree with the correlations

$$
(h_1/h_2)_{\text{max}} = (\sigma_2/\sigma_1)^a \tag{4}
$$

where  $a = 0.62$  [15] or 0.65 [7]. These correlations fail, of course, to predict  $h_{\text{max}}$  for the PA solutions; for PA-10 it appears that  $h_{\text{max}}$ increases monotonically with concentration, even though surface tension is unaffected. One indication of the influence of surface tension on the entire boiling curve is the comparison in Fig 5 between HEC and PA for conditions of equal concentration (125 ppm) and equal viscosity ( $\sim$ 1.32 cP at 25°C before boiling); it is noted that  $\sigma_{\text{HFC}} = 42$  dyn/cm and  $\sigma_{\text{PA}} = 65$ dyn/cm at 70°C.



FIG. 7. Boiling curves for all HEC solutions, shown to **correlate in terms of viscosity.** 

 $(3)$  Molecular weight effects. It has been claimed by others [ll] that higher solute molecular weights---among low-M homologs--lead to greater heat transfer. This is borne out by the HEC solutions, as demonstrated in Fig. 6a ; surface tensions are nearly the same for these three liquids, and concentrations are identical.

Results for the acrylamide systems appear anomalous, at least superficially. According to Fig. 6b, the monomer acrylamide reduces the heat transfer below that in pure water. When the molecular weight reaches polymeric magnitude, as with PA-lo, heat transfer increases as might be predicted from the HEC results. Further molecular weight increase, to that of PA-20, results in an unexpected reduction in heat transfer. (Other anomalies in PA-20 behavior have already been mentioned.) Although the latter is surprising, it seems nonetheless true that some *polymeric* character is absolutely essential to achieve improved heat transfer when nonsurfactant molecular structures are involved.

(4) Viscosity effects. According to equation  $(1)$ , the viscosity  $\mu$  is the most influential liquid property in determining nucleate boiling performance. The prediction of reduced heat transfer with increased viscosity is qualitatively in accord with the behavior of acrylamide (nonpolymer) solution, although not accurate quantitatively ; it underestimates the effect, 10 per cent as opposed to the actual 30 per cent reduction.

Such correlations are of no utility whatever when trace amounts of polymeric solutes are the means by which viscosity is enhanced. Indeed, the HEC data show exactly the reverse tendency. HEC results discussed above in terms of molecular weight and concentration effects can be unified rather well if viscosity alone is used as a correlating parameter (see Fig. 7). This functional dependence is represented in explicit fashion in Fig. 8 for both HEC and PA solutions, with  $\Delta T = 30^{\circ}$ F. The HEC and PA-10 curves suggest that the intrinsic effect of a *polymeric* additive is to improve the heat transfer. A polymer which is also a surfactant seems to be

more effective in this regard, at least at this low  $\Delta T$ ; at high  $\Delta T$  the non-surfactant PA-10 is more effective. For both these systems, it is expected that a point of diminishing returns would be reached as viscosity increased even further. This might be the interpretation of the PA-20 data, which suggest—according to Fig. S-that at viscosities beyond about 3 CP a polyacrylamide solution (of any molecular weight or concentration) will provide poorer heat transfer than water. This latter generalization should be regarded as speculation until more data are available, especially in view of the other PA-20 anomalies and the observed deposits which would probably act simply as another heat transfer resistance. It can be added, however, that one highly viscous PA solution was prepared and found to be incapable of true nucleate boiling at all ; this fluid was far beyond the point of diminishing returns indicated in Fig, 8.

#### **DISCUSSION**

Although the data in this study are somewhat limited, it has been possible to examine the influence of (a) polymeric solute in general (PA as opposed to acrylamide); (b) surfactant character superimposed on polymeric character (HEC contrasted with PA); and (c) variations in the parameters of concentration and molecular weight (and, through them, the viscosity). The conclusions may be summarized as follows :

- $\overline{ }$ 1. Trace amounts of polymers dissolved in water lead to substantial increases in nucleate boiling heat flux.
- Surfactant polymers such as HEC seem to be<br> more effective in this regard than nonsurface-active polymers (for moderate  $\Delta T$ ) at equal viscosities or mass concentrations. But, like low molecular weight surfactants, their *h*<sub>max</sub> and probably peak heat flux are not significantly improved. Foaming can be a serious problem.
- $\overline{ }$ ' PA leads to significantly improved *h* over the entire  $\Delta T$  range studied here. The data suggest that peak heat fluxes would be considerably higher than for water, and  $h_{\text{max}}$  is distinctly increased. This is presumably typical of nonsurfactant polymers. No foaming occurs.
- For all solutes, the enhancement of heat



FIG. 8. Percentage effectiveness of HEC and PA salutes as a function of their solution viscosities. Points are taken from smoothed curves, at  $\Delta T = 30$ °F, and symbols are identified in Table 1.

transfer seems ultimately limited by the effect of viscosity. For polymers composed of certain chemical groups, an optimum solution viscosity-influenced by concentration and molecular weight-can be selected.

It is important to question the mechanism by which these phenomena occur. No perfectly satisfactory answers are available at this point, although speculation is again possible. It seems significant that the polymer solution boiling was always accompanied by hydrodynamic patterns quite different than for water; bubbles were smaller, released faster and rose in a more orderly fashion, with reduced coalescence. These observations resemble some of those reported by other workers [9] for certain low molecular weight solutes which were not surfactants. It is also recognized that a reduced surface tension in general results in smaller bubbles [14], and indeed the HEC-L solutions studied here were characterized by having the smallest bubble sizes and highest rate of formation. It was apparent, however, that PA-10 solutions produced the greatest frequency of bubble release from the heating plate. All these observations are surely directly related to the increased heat transfer, yet do not tell why it occurred for polymers in particular.

We propose a synthesis of several mechanisms. First, the greater number of bubbles is probably due to the fact that polymers are notoriously less soluble than small molecules [10] and therefore prefer to aggregate or adsorb on surfaces when solubility is further reduced at high temperatures. This, in turn could lead to a large number of new potential nucleation sites and thus more bubbles. Reduced bubble size (if considering non-surfactant effects) is very likely a consequence of increased liquid viscosity, which would retard bubble growth rates. This tendency would be further enhanced by elastic stresses in the liquid, a phenomenon unique to polymeric systems. In addition, evaporation of the water into a bubble serves to concentrate the solute locally, and the viscous and elastic liquid

properties (which retard bubble growth) are known to be extremely sensitive to slight changes in polymer concentration.

Other possible factors are even more difficult to interpret. As suggested elsewhere [9], the surface viscosity may well be an important parameter, but it seems rarely to be measured (this might also prove difficult to do near boiling temperatures). The surface viscosity, like the shear viscosity  $\mu$ , is also likely to be a very sensitive function of polymer concentration. This combination of changing interfacial concentration plus reduced interfacial polymer solubility during boiling could make the surface viscosity a highly significant factor. At the very least, it is expected to reduce the bubble coalescence which occurs so extensively in pure water.

Finally, it is distinctly possible that bubble dynamics and gross convection are altered by the viscoeleastic nature of the liquid. The existence of fluid viscoelasticity is known to give rise to unusual secondary flows and, as discussed in the Introduction, to produce anomalous drag and heat transfer reduction in turbulent pipe flow. Indeed, among the secondary reasons for choosing HEC and PA for this study was their ability to act as drag reducers and thus be particularly interesting candidates.

Although complete explanations of such phenomena are still lacking, these preliminary results should encourage more extensive investigation of complex but familiar engineering processes involving liquids which might operate more effectively with the addition of polymer solutes.

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#### RENFORCEMENT DE L'ÉBULLITION NUCLÉÉE EN RÉSERVOIR AVEC DES ADDITIFS DE POLYMÈRES

Résumé—Le transport de chaleur dans l'ébullition nucléée en réservoir de solutions aqueuses diluées de polymères a été mesuré et comparé avec les résultats pour l'eau pure. Les solutés étaient de l'hydroxyéthylcellulose (HEC) avec trois poids moléculaires, du polyacrylamide (PA) avec deux poids moléculaires, et de l'acrylamide; les concentrations de soluté allaient de 62 à 500 ppm. Les liquides étaient en ébullition à pression atmosphérique sur une surface chromée horizontale chauffée par la vapeur d'eau. Les photographies montraient des différences distinctes, dans la taille et la dynamique des bulles, entre les liquides avec et sans polymères.

Le flux de chaleur dans chaque solution de polymères dépassait celui pour l'eau, bien que le monomère acrylamide provoquait une réduction du transport de chaleur. Les augmentations allaient jusqu'à 250 pour cent pour  $T = 9.45^{\circ}$ C et à 100 pour cent pour  $T = 15.55^{\circ}$ C. Les résultats produits par des variations de concentration et de poids moléculaire semblent se corréler avec la viscosité de la solution. La HEC est un agent de surface mais le PA ne l'est pas, de telle façon qu'on croit que la tension superficielle est seulement une variable mineure. Des explications basées sur la solubilité limitée du polymère et la viscoélasticité de la solution sont proposées.

#### ERHÖHUNG DES BLASENSIEDENS BEI BREIER KONVEKTION MIT POLYMEREN ZUSÄTZEN

Zusammenfassung-Der Wärmeübergang beim Blasensieden von verdünnten, wässrigen, polymeren Lösungen wurde gemessen und mit den Ergebnissen für reines Wasser verglichen. Gelöste Stoffe waren Hydroxyäthylzellulose (HÄZ) dreimolar, Polyacrylamid (PA) zweimolar, und Acrylamid: die Lösungskonzentration reichte von 62 bis 500 ppm. Die Flüssigkeiten wurden bei Atmosphärendruck an einer horizontalen, dampfbeheizten, chromplattierten Oberfläche zum Sieden gebracht. Photographien zeigten besondere Unterschiede in Blasengrösse und Dynamik, zwischen polymeren und nichtpolymeren Flüssigkeiten.

Der Wärmefluss in jeder polymeren Lösung übertraf den für Wasser, obwohl die momomeren Acrylamide eine Minderung des Wärmeüberganges hervorriefen. Die Antiege betrugen 250 Prozent bei  $T = -9.5$ °C und 100 Prozent bei  $T = 15.5$ °C. Die Ergebnisse, die zustande kamen durch Variation von Konzentration und Molekulargewicht, lassen sich anscheinend in Beziehung setzen zu der Viskosität der Lösung. Die HÄZ wirkt benetzend, aber PA nicht, so wird die Oberflächenspannung als untergeordnete Einflussgrösse angesehen. Erklärungen, basierend auf einer begrenzten Polymer-Löslichkeit und der Viskoelastizität der Lösung werden vorgeschlagen.

#### ИНТЕНСИФИКАЦИЯ ПУЗЫРЬКОВОГО КИПЕНИЯ В ОТКРЫТОМ ОББЕМЕ С ПОМОЩЬЮ ПОЛИМЕРНЫХ ДОБАВОК

Аннотация-Измерялся перенос тепла при нузырьковом кипении в открытом объёме жидких водных полимерных растворов, и проводилось сравнение с результатами для чистой воды. В качестве растворов использовались оксиэтилцеллюлоза с тремя молекулярными весами, полиакриламид с двумя молекулярными весами и акриламид. Концентрация растворов составляла 62 ppm до 500 ppm. Жидкости доводились до кипения при атмосферном давлении на горизонтальной нагреваемой паром и покрытой хромом поверхности. На фотографиях видна четкая разница между размерами пузырьков и их динамикой для полимерных и неполимерных жидкостей.

Тепловой поток в каждом полимерном растворе превышал тепловой поток для воды, хотя мономер акриламид вызывал снижение переноса тепла. Увеличение теплового потока составляло 250% при  $T = 15^{\circ}F$  и 100% ирп  $T = 60^{\circ}F$ . Оказалось, что результаты, полученные при изменении концентрации и молекулярного веса, коррелируются с вязкостью раствора. Оксиэтилцеллюлоза является поверхностноактивным веществом, в то время как полиакриламид не является таковым, поэтому сделан вывод, что поверхностное натяжение играет незначительную роль. Предложены объяснения, базирующиеся на ограниченной растворимости полимеров и вязкоупругих свойствах раствора.