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HEAT TRANSFER THROUGH ELECTROLYTIC SOLUTIONS UNDER THE ACTION OF ELECTROLYTIC CURRENTS

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Abstract—Heat transfer rates from an electrically heated thin platinum wire in dilute NaOH and Na_2CO_3 solutions of different concentrations have been measured under the influence of electrolytic currents, using a sensitive Kelvin double bridge. In the low concentration region, the rate of heat transfer is initially found to increase with concentration and then to decrease with further increase in concentration. An explanation of these results on the basis of the behaviour of the thermal boundary layer surrounding the hot wire electrode is suggested. It has been indicated that these results can be employed to improve the performance of boiler systems and electro chemical machining processes.

NOMENCLATURE

A,	heat transfer area [cm^2];
d,	ionic current density, I/A, [mA/cm^2] i.e. cm^2 of the heating wire;
h_0,	heat transfer coefficient in the absence of electrolytic currents, i.e. value of h when electrolytic current is zero [J/s cm^2 degC];
h,	heat transfer coefficient in the presence of electrolytic currents $= q/\Delta\theta_0$ [J/s cm^2 degC];
I,	electrolytic current [mA];
q,	heat flux [J/s cm^2];
$\Delta\theta_w$,	rise in temperature of the wire due to heating [degC];
$\Delta\theta_s$,	rise in temperature of the bulk solution [degC];
$\Delta\theta_0$,	$(\Delta\theta_w - \Delta\theta_s)$ excess of temperature of the wire above that of the surrounding solution [degC].

INTRODUCTION

VARIOUS investigators have studied the effects of additives to liquids in order to obtain increased heat transfer rates. Rhodes and Bridges [1] found that even in the region of film boiling, addition of a small amount of Na_2CO_3 increased the heat transfer coefficient, h, more than ten times with a sudden transition to nucleate boiling regime. Von Stralen *et al.* [2] have observed that addition of certain alcohols and ketones to water greatly increased the critical heat flux (C.H.F.) and the C.H.F. attained a maximum when plotted as a function of additive concentration. Westwater and Dunskus [3] have shown that the increase in the heat flux is caused by the presence of a solute even in trace amounts. Pitts and Leppert [4] studied the boiling patterns in binary mixtures by taking motion pictures and observed that the bubbles in the binary mixtures are considerably smaller than in either components and there appeared to be a minimum bubble size at concentrations between 4 and 7 per cent by weight of methyl-ethyl-ketone in water where maximum C.H.F. occurred. The effect of electrolytic bubbling on enhancing heat transfer rates has also been reported previously by various workers [5–7]. Hence, detailed investigation of the concentration dependence of heat transfer rates in solutions of two additives, NaOH and Na_2CO_3, under the action of electrolytic currents were

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undertaken. These electrolytes were chosen because they are used in feed water treatment to reduce the deposition of scales [8]. They are also found to be better electrolytic cleaning agents [9].

In a preliminary note one of us has reported [10] the variation of heat transfer from an electrically heated thin platinum wire immersed in dilute NaOH solutions of different concentrations. The present paper deals with the results of the investigations on Na_2CO_3 solutions and those of a more detailed study of NaOH solutions.

EXPERIMENTAL PROCEDURE

The experimental set up and procedure used in this work, shown in Fig. 1, is as has previously been reported by one of us [10]. The set up essentially consists of a thin platinum wire (dia: 0·1 mm; length 7·5 cm), stretched horizontally along the axis of a hollow, stainless steel cylinder (internal dia: 3·8 cm; thickness: 0·2 cm; length: 7·8 cm), open at both ends and slotted along its length. This system of the platinum wire and the cylinder is kept immersed in a glass trough (30 × 30 × 25 cm) containing the experimental liquid at room temperature. The wire is heated by a set of storage batteries (0–18 V). A varying potential difference, ranging from 10 to 300 V, is established between the wire and the cylinder with the help of a stabilized power supply unit. The resulting electrolytic current, I, is measured by a milliammeter. A standard low resistance r_1, connected in series with the wire serves to produce a definite temperature rise, $\Delta\theta_w$ in the wire. The temperature of the bulk solution is kept nearly constant by passing a stream of cold water through a copper coil kept in it.

Under balanced condition of the bridge, the potential drop across a standard low resistance, r_2, measured by a precision K-potentiometer,

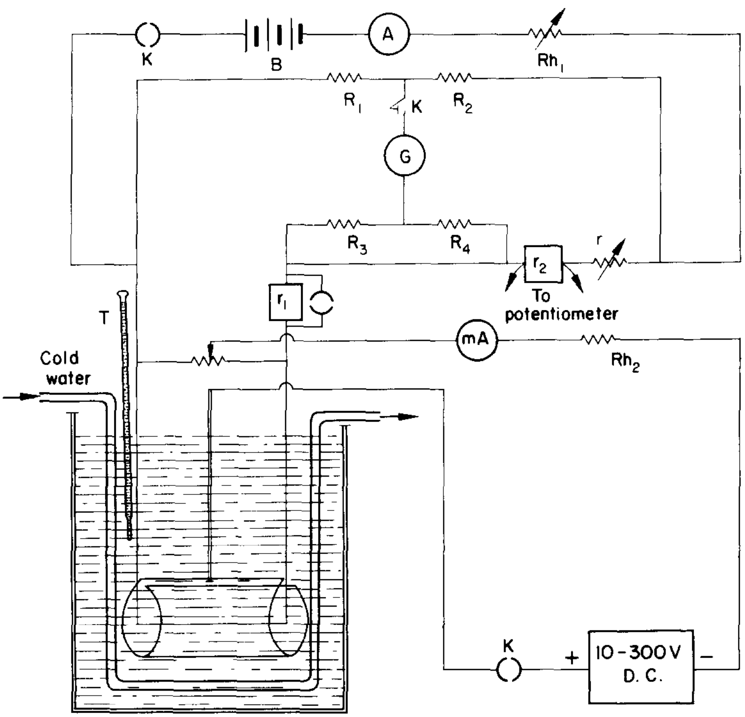

FIG. 1. Experimental arrangement.

serves to know the current flowing through the wire. Measurements of this current and the resistance of the wire are used to determine the heat input to the wire. The connections to the bridge circuit are made with thick copper wires to avoid the heating effects of other bridge resistances. Under equilibrium conditions the heat input equals heat transfer from the wire to the surrounding solution.

To start with, a very small current of the order of 8 mA (which does not heat the platinum wire appreciably) is passed through the bridge circuit and the bridge is balanced by adjusting a variable resistance, r in the balancing arm and the initial resistance of the platinum wire is determined. The standard low resistance, r_1 is then removed and the current through the wire is gradually increased to restore the balance. From the increment in the resistance of the wire, $\Delta\theta_w$ is determined. Thus the platinum wire, apart from being the heating element, also acts as its own sensitive temperature detector.

If now some potential difference is established between the wire and the cylinder, tiny bubbles are found to rise from different points on the wire due to evolution of the gas in the process of electrolysis and the temperature of the wire is slightly reduced. The wire is then brought back to the temperature before the commencement of the electrolytic action by passing a little more current through it from the batteries and the heat exchange between the wire and the surrounding solution is determined.

For low ionic currents, $\Delta\theta_0 \approx \Delta\theta_w$. However in the higher ionic current region a slight increase, $\Delta\theta_s$, in the temperature of the solution in the vicinity of the cylinder takes place and it is

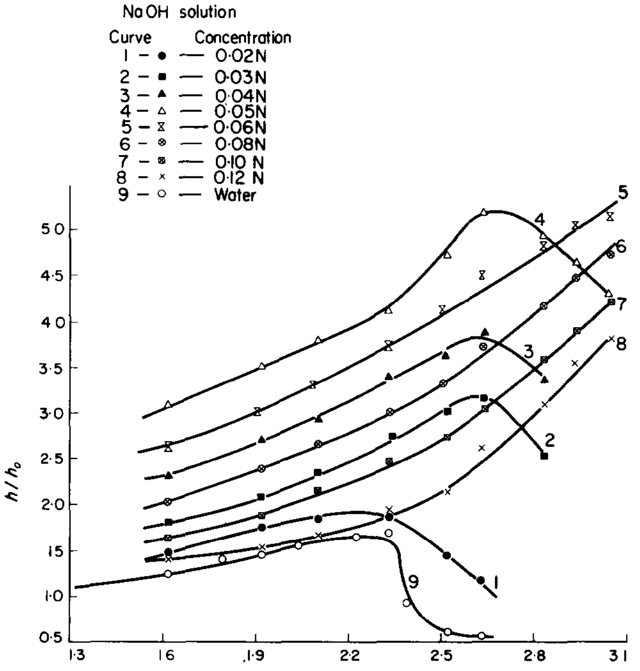

FIG. 2. Variation of h/h_0 with $\log d$ at different concentrations of NaOH solution.

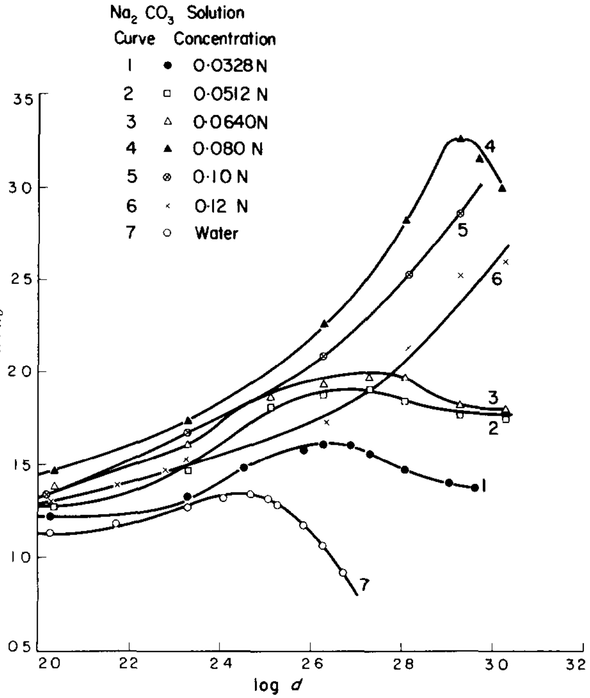

FIG. 3. Variation of h/h_0 with log d at different concentrations of Na_2CO_3 solution.

measured with the help of a sensitive thermometer. Under these circumstances, $\Delta\theta_0$, used in calculating the heat transfer coefficients, has been taken as $\Delta\theta_w - \Delta\theta_s$. The actual value of $\Delta\theta_0$ was 15·4°C for NaOH solutions and 37°C for Na_2CO_3 solutions. Before conducting the experiments, the prepared solutions were boiled to remove dissolved gases and then cooled to room temperature.

RESULTS

Keeping $\Delta\theta_0$ constant, the variation of h/h_0 with d, the ionic current density, for the solution of a fixed concentration was investigated. h/h_0 was calculated in each case instead of merely h, because, although h may vary for different sets of observations, under different surface conditions of the wire, the value of h/h_0 remains sufficiently consistent, the reproducibility being within ±5 per cent. This procedure was repeated for solutions of different concentrations, both for NaOH and Na_2CO_3. The results have been represented graphically in Figs. 2 and 3. These figures include curves for ordinary water under similar conditions for comparison.

It is seen from these figures that in the low ionic current density region the values of h/h_0 for a given value of d first go on increasing up to 0·05 N for NaOH and 0·08 N for Na_2CO_3 and then begin to decrease. It is also seen that the values of $(h/h_0)_{max}$ for 0·05 N NaOH and 0·08 N Na_2CO_3 solutions are about three times greater than the values of $(h/h_0)_{max}$ for water under similar conditions. The nature of the curves for lower concentrations is essentially similar to that obtained for water. For higher concentrations, h/h_0 goes on increasing monotonously with d. The existence of an optimum concentration at which $(h/h_0)_{max}$ reaches its highest value and this ratio being as high as 3·5 or more is of great practical value.

An interesting fact visually observed during these investigations was that the bubbles emerging from the heated wire in the electrolytic solutions were much smaller than those emerging in water under similar conditions, which is in keeping with the observations of Pitts and Leppert [4] and Mixon *et al.* [5].

DISCUSSION

The investigations of various workers who have studied the normal boiling processes [11] point to the formation of a thin thermal boundary of superheated liquid near the heated surface. In the present investigations, as the ambient temperature is much below the boiling point of the liquid the thermal boundary layer surrounding the heated wire is not superheated; yet it is at a much higher temperature (43·4°C for NaOH and 65°C for Na_2CO_3 solutions respectively) than that of the bulk liquid. A tentative mechanism which can qualitatively explain this concentration dependence of the heat transfer coefficient is suggested below.

As the heated platinum wire forms the cathode of an electrolytic cell in the present investigations and the surrounding liquid is an electrolyte, the thermal boundary layer surrounding the wire behaves also as an electro-chemical-multilayer, widely known as the electrical double layer. The effects of this layer on change of electrical conduction with concentration in flowing electrolytes has been discussed by Palit [16]. The constituents of this double layer have also been described in detail by Mohilner [12]. The important point for the present investigations is that a potential gradient develops within this layer on account of the specifically adsorbed anions on the wire and the accummulation of solvated cations on the outer face of the thermal layer. This ion concentration is hundreds of times more than that in the bulk solution as pointed out by Mohilner [12] and hence it makes the potential gradient within the layer very steep. This results in very strong orientation of the water dipoles in the boundary layer, giving rise to electroviscosity [13]. These electro-viscous forces near the wire reduce the size of the gas bubbles emerging from the cathode and prohibit their coalescence as has been observed by Markels and Durfee [17] and Mixon *et al.* [5].

The reduction in the size of the emerging bubbles will result in increasing the rate of bubble frequency which in turn will lead to enhanced heat transfer rates.

However this beneficial effect on the heat transfer rate increases only up to a certain optimum concentration of the solution. As the concentration of the solution increases, the concentration of the solvated ions at the outer face of the thermal layer also increases and when this layer of solvated ions is fully formed, any further increase in the concentration of the solution will not lead to an increase in the charge density at the outer face of the thermal layer but only increases the viscosity of the bulk solution. The emerging bubbles will therefore not decrease in size any further. However, the increase in the viscosity in the bulk solution will offer a higher resistance to the motion of the bubbles. The heat transfer rate will therefore decrease. The bulk concentration needed for this purpose is not very high because the concentration of the positive ions at the outer face of the thermal layer is hundreds of times greater than that in the bulk as pointed our earlier.

The main results of the present investigation: (1) enhancement of heat transfer rate by electrolytic bubbles and (2) a further increase in heat transfer rate in solutions of the cleaning agents NaOH and Na_2CO_3 of optimum concentrations are of great practical utility and can be employed to improve the performance of boiler systems. Recently electrolytic solutions in conjunction with applied electric fields, have been employed in electro-chemical-machining (E.C.M.) processes [15]. It is felt that the use of electrolytes of optimum concentrations may help to improve the efficiency of the E.C.M. processes also.

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TRANSFERT THERMIQUE AU TRAVERS DE SOLUTIONS ÉLECTROLYTIQUES SOUS L'ACTION DE COURANTS ÉLECTROLYTIQUES

Résumé—A l'aide d'un pont double sensible de Kelvin, on a mesuré les flux thermiques pour un fil mince de platine chauffé électriquement dans des solutions de NaOH et Na_2CO_3 dilués à différentes concentrations et soumis à l'action de courants électrolytiques. On a trouvé, dans la région de faible concentration, que le flux thermique croît initialement avec la concentration puis diminue lorsque la concentration continue à croître. On propose une explication de ces résultats sur la base du comportement de la couche limite thermique qui entoure le fil chaud. On indique que ces résultats peuvent être employés pour améliorer les performances des systèmes bouilleurs et les processus électro-chimiques industriels.

WÄRMETRANSPORT DURCH ELEKTROLYTISCHE LÖSUNGEN BEI STROMFLUSS DURCH DEN ELEKTROLYTEN

Zusammenfassung—Es wurden Wärmeübergangsmessungen an einem elektrisch beheizten, dünnen Platindraht in verdünnten NaOH- und Na_2CO_3-Lösungen verschiedener Konzentrationen unter dem Einfluss von elektrolytischen Strömen untersucht, wobei eine empfindliche Kelvin-Doppelbrücke benutzt wurde. In Gebieten niederer Konzentrationen wurde zunächst ein Ansteigen des Wärmeübergangs mit der Konzentration beobachtet und bei weiterer Zunahme der Konzentration wieder eine Abnahme des Wärmeübergangs. Es wird eine Erklärung dieser Ergebnisse durch das Verhalten der thermischen Grenzschicht um die beheizte Draht-Elektrode gegeben. Es wird gezeigt, dass diese Ergebnisse angewandt werden können, um die Wirksamkeit von Boilern und elektrochemischen Prozessen zu verbessern.

ПЕРЕНОС ТЕПЛА ЧЕРЕЗ ЭЛЕКТРОЛИТИЧЕСКИЕ РАСТВОРЫ ПОД ДЕЙСТВИЕМ ЭЛЕКТРОЛИТНЫХ ТЕЧЕНИЙ

Аннотация—С помощью двойного мостика Кельвина измерялось изменение скорости переноса тепла от электрически нагретой тонкой платиновой проволочки в жидких растворах NaOH и Na_2CO_3 различных концентраций под влиянием электролитических течений. Найдено, что в области низкой концентрации, скорость вначале переноса тепла увеличивается с увеличением концентрации, а затем уменьшается с дальнейшим увеличением концентрации. Предложено объяснение этих результатов на основе поведения термического пограничного слоя, окружающего электрод из нагретой проволоки. Указано, что эти результаты можно использовать для улучшения кпд бойлеров и процессов электрохимической обработки.