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A CRITICAL ANALYSIS OF THE COMPENSATION EFFECT AND ITS APPLICATION TO HEAT EXCHANGER FOULING STUDIES

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ABSTRACT

Occurrences of the compensation effect in published studies on the initial rate of heat exchanger fouling are discussed. When fouling rate experiments are performed on a series of related fluids, it is shown that random errors in the measurements can create an apparent compensation effect. This explains some reported occurrences in the literature. Other reported instances of the compensation effect show a systematic variation in apparent activation energy with fluid flow rate. It is shown that these may be the result of analyzing the temperature dependence of the overall rate of reaction. The conditions under which the compensation effect is expected when flow rate is varied are explored using synthetic data generated by a model for fouling.

INTRODUCTION

Fouling involves the deposition of material from a flowing fluid on to a process surface. The rate of fouling often exhibits a strong dependency on temperature, which in the fouling literature is normally characterised in terms of an activation energy, E_{act}, via the Arrhenius equation.

$$\mathrm{rate} = A\exp\left(-\frac{E_{\mathrm{act}}}{RT}\right) \qquad [1]$$

Here R is the gas constant, A the Arrhenius prefactor and T the absolute temperature. Strictly speaking, E_{act} is an apparent activation energy as the Arrhenius equation relates to a kinetic rate constant. However, its use to describe overall rates is widespread because of its predictive power. Fouling rates are also subject to other factors such as flow rate. These can complicate interpretation of fouling data sets since key parameters such as wall shear stress and surface temperature are influenced by the flow.

Recently researchers such as Bennett *et al.* (2009) and Crittenden *et al.* (2009) have demonstrated that kinetic measurements of initial fouling rate can show a compensation effect in which the logarithm of the prefactor is linearly related to the activation energy E_{act}:

$$\ln A = \alpha + \beta E_{\mathrm{act}} \qquad [2]$$

where α and β are constants. This type of kinetic compensation effect is a widely observed phenomenon in heterogeneous catalysis and other areas of science and has been reviewed by Bond *et al.* (2000) and Liu and Guo (2001). However, there is no general explanation for the compensation effect and there is some controversy over whether it has a mathematical origin or a physical origin.

The compensation effect is related to the so-called isokinetic relationship (Linert and Jameson, 1989; Liu and Guo 2001). The isokinetic relationship is observed when separate lines on an Arrhenius plot intersect at a single point. At this point, specified by the isokinetic temperature, the rates of reaction are the same for a family of reactants. It is straightforward to show that the isokinetic relationship will occur if equation (2) is obeyed exactly. However, when experimental errors are present, small deviations from exact agreement of equation (2) can mean that no isokinetic relationship occurs (Liu and Guo, 2001).

Two different types of compensation effect will be discussed in this paper. In the first case, kinetic measurements are made at various temperatures on a series of related fluids while keeping other parameters (such as flow rate) constant. This type of compensation effect was observed by Bennett *et al.* (2009) for the fouling of four crude oils. For the second type of compensation effect, kinetic measurements are made at various temperatures on a single fluid while varying another parameter that influences fouling rate. This type of compensation effect was observed by Crittenden *et al.* (2009) for the fouling of Maya crude oil while varying fluid flow rate, and also for a model system of styrene polymerization fouling in kerosene. These two types of compensation effect are discussed in turn.

EXPERIMENTS ON A SERIES OF RELATED FLUIDS

Review of published data

Bennett *et al.* (2009) studied the initial rate of liquid-phase fouling for four crude oils with surface temperatures, T_s, ranging from 648-719 K. Figure 1 shows pseudo-Arrhenius plots generated from their data after deleting points described in the paper as suspect. [Footnote: there is an inconsistency for one data point between Table 4 and Figures 11 and 12 of Bennett *et al.* (2009). We have used the data from the Figures in our analysis; identical conclusions are reached if the data in their Table 4 is used]. The straight line fits for the different oils come close to intersecting at a single point, suggesting that an isokinetic relationship may be obeyed. The overall Arrhenius parameters extracted from the straight line fits are plotted on a graph of ln *A* against E_{act} in Figure 2. This type of graph is termed a compensation effect (CE) plot in this paper; it is also commonly known in the catalysis literature as a Constable plot after its first proponent (Constable, 1925).

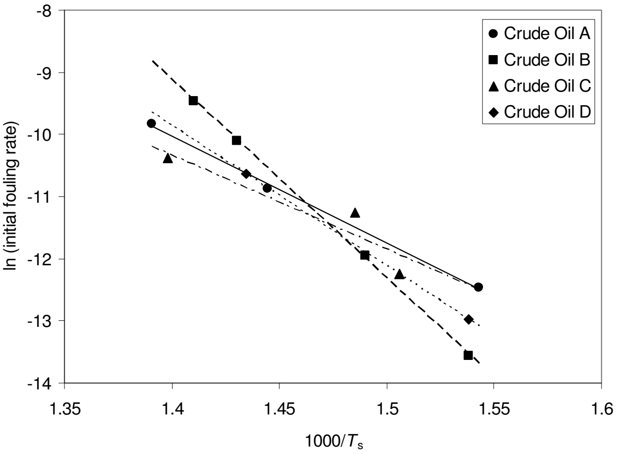

Figure 1 Pseudo-Arrhenius plot of data reported by Bennett *et al.* (2009) showing the initial fouling rates of four crude oils at different surface temperatures. There are four reliable data points for oil B, three for oils A and C, and only two for oil D. The lines were obtained by least squares regression to equation (1).

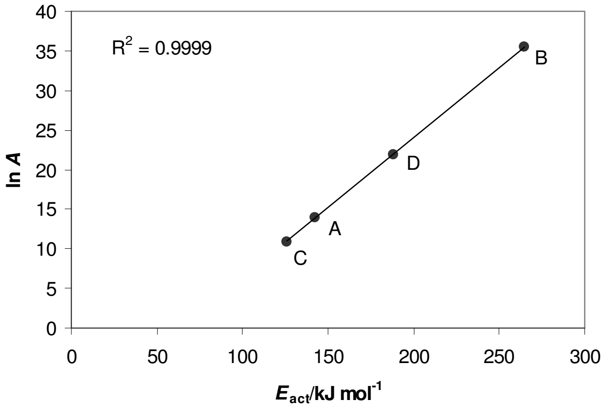

Figure 2 Compensation effect (CE) plot showing the Arrhenius parameters obtained from the data in Fig. 1. The straight line shows the linear regression fit to equation (2).

An excellent straight line fit to the data is apparent – indeed the regression correlation coefficient R^2 exceeds 0.999 – indicating that the compensation effect is obeyed. If the effect has a physical origin, then it has important implications for the modelling of fouling in heat exchangers. However, before this can be concluded, it is important to test the statistical significance of the correlation.

Standard errors for the regression parameters generated by regression algorithms are routinely outputted by curve fitting programs. Those obtained for the Bennett *et al.* data sets are plotted as error bars on Figure 3. The error bars for oil D are undefined because only two reliable data points were obtained with this oil, while the other error bars reflect how close the points in Figure 1 lie to the straight line fit.

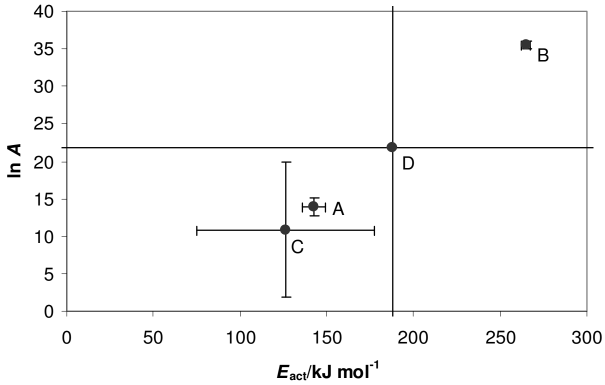

Figure 3 CE plot for the data in Figure 1. The error bars shown are the *standard errors* for the parameters obtained from linear regression. The error bars need to be far larger if 95% confidence intervals for the parameters are desired.

However, standard errors are not always adequate in considering statistical significance, particularly when the number of data points used in the regression is small. It is better to calculate confidence intervals for the fitted parameters. This involves multiplying the magnitude of the standard error by an appropriate *t*-score. For 95% confidence intervals, the error bars in Figure 3 need to be multiplied by a factor of 12.7 when only 3 data points are used in the fit and a factor of 4.3 when 4 data points are used. When that is done, the uncertainties in the E_{act} values become very large. For example, the confidence interval for E_{act} for oil C exceeds 500 kJ mol^{-1}. Given these large uncertainties, it is at first glance surprising that such a good correlation between ln *A* and E_{act} occurs in Figure 2. The explanation lies in the statistical compensation effect that was first described in detail by Krug *et al.* (1976).

The statistical compensation effect

The axiom behind the statistical compensation effect is that parameters ln *A* and E_{act} obtained by linear regression of data on an Arrhenius plot are not independent of each other. One is found from the gradient, while the other is found from the intercept on the *y*-axis. The extent of the correlation between the gradient and intercept can be found by calculating the covariance between them. Rather than using the standard errors evaluated by curve fitting programs to calculate confidence intervals, it is better to calculate a *confidence ellipse* – the region of parameter space in which it is statistically likely that ln *A* and E_{act} lie. This can be calculated from the variance-covariance matrix for the regression parameters (Draper and Smith, 1998).

It turns out that the extent of correlation between the values of ln *A* and E_{act} determined by linear regression of data points on an Arrhenius plot depends only on the range of 1/*T* values used in the kinetic study. More specifically, the correlation coefficient between the intercept and gradient obeys (Krug *et al.*, 1976; Barrie, 2011):

$$\rho^2 = \frac{1/T_{\text{ave}}^2}{1/T_{\text{ave}}^2 + \sigma_{1/T}^2} \qquad [3]$$

where $\sigma_{1/T}^2$ is the variance in $1/T$ values, and T_{ave} is the harmonic mean temperature, defined by:

$$\frac{1}{T_{\text{ave}}} = \frac{1}{n}\sum_{i=1}^{n}\frac{1}{T_i} \qquad [4]$$

Because the range of temperatures at which kinetic measurements are made is inevitably limited, the variance in $1/T$ values is far smaller than the average temperature, and so ρ^2 is close to unity.

The length of the axes of the confidence ellipse can be derived from the eigenvalues of the variance-covariance matrix. It can be shown that the confidence ellipse will have a very high aspect ratio for all practical kinetic studies so that it approximates a straight line. Furthermore, the orientation of the confidence ellipse on a compensation effect plot can be derived from the eigenvectors of the variance-covariance matrix. It can be shown that the gradient of the major axis of the ellipse is $1/RT_{\text{ave}}$ if the assumptions for linear regression are obeyed (Krug *et al.*, 1976). Similar results are obtained if non-linear regression is used to analyse the experimental data rather than linear regression of data on an Arrhenius plot (Barrie, 2011).

The 95% confidence ellipse obtained for the Arrhenius parameters for the fouling of Bennett *et al.*'s crude oil A is presented in Figure 4. The plot shows that E_{act} has a very wide range of possible values in this case, but that the possible values of ln A vary as the value of E_{act} varies. Any pair of values of ln A and E_{act} that lie within the confidence ellipse give an acceptable fit to the experimental data.

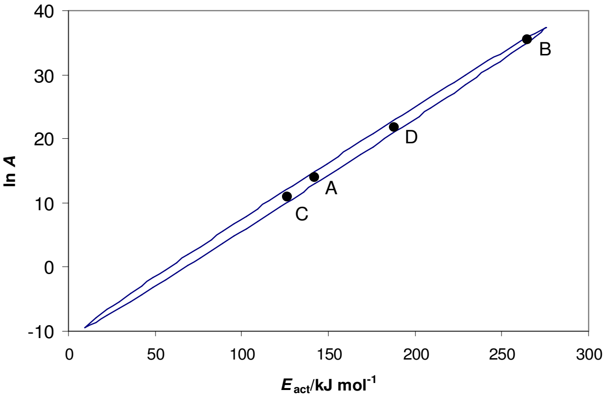

Figure 4 CE plot for the data in Figure 1 showing the 95% confidence ellipse for parameters of crude oil A. The gradient of the major axis of the ellipse is $1/RT_{\text{ave}}$, where T_{ave} is the harmonic mean of the temperatures employed in the kinetic study.

Similar confidence ellipses can be calculated for the other data points in Figure 2 (with the exception of oil D which has undefined uncertainties because only two reliable data points were measured). Because the range of temperatures used in the tests for the different oils was almost the same, the orientation of the 95% confidence ellipse is the same for the other oils. As a result of this, the confidence ellipses for the different oil samples overlap with each other in an approximate straight line.

There is therefore another possible interpretation of the data presented by Bennett *et al.* (2009). Instead of concluding that the samples show an isokinetic relationship and obey the compensation effect, it is possible that the samples have identical (or near identical) Arrhenius parameters ln A_0 and E_0. The experimental kinetic data contain random errors, which cause the Arrhenius parameters determined from the linear regression analysis to be, for each sample, given by

$$E_{\text{act},i} = E_0 + \Delta E_i \qquad [5]$$

where ΔE_i arises from the random errors. The high degree of correlation between ln A and E_{act} values, and the orientation of the confidence ellipse, means that the determined value of ln A will obey:

$$\ln A_i = \ln A_0 + \Delta E_i / RT_{\text{ave}} \qquad [6]$$

Each sample investigated will have a different random error term ΔE_i. Because of this, we expect data points on a compensation effect plot to be distributed on a straight line with gradient $1/RT_{\text{ave}}$ even when the samples have identical values of Arrhenius parameters. This behaviour is sometimes known as the *statistical compensation effect*.

For the data of Bennett *et al.* (2009), the gradient of the compensation effect plot in Figure 2 is $1/RT^*$, where T^* is 681 K. The values of T_{ave} for the kinetic data used to determine the Arrhenius parameters for oils A, B, C and D are 685, 681, 683 and 673 K, respectively. The fact that the gradient in Figure 2 corresponds exactly to that predicted if the statistical compensation effect is occurring indicates that the data of Figure 2 can be explained satisfactorily as arising purely from the influence of random errors in the experimental measurements. Another way of stating this is that it is as likely that the straight lines on the Arrhenius plot in Figure 1 should in fact be identical to each other, as that they are different but intersect at a single point. As such, the compensation effect in this case probably has a mathematical, rather than a physical origin, which means that it is of little value in predictive modelling.

Whenever kinetic experiments are performed on a series of different fluids to determine Arrhenius parameters, errors in the measurements can cause the statistical compensation effect to occur. The effect can be minimized by making measurements at as many different temperatures over as wide a temperature range as possible. However, this is often impossible for practical reasons. Therefore careful error analysis, ideally involving the calculation of confidence ellipses for each data point, is necessary to see whether the observed compensation effect has an underlying physical origin or derives from the random errors in the rate measurements.

EXPERIMENTS ON A SINGLE FLUID WHILE VARYING FLOW RATE

Review of published data

A second type of compensation effect occurs when a single fluid is investigated while varying another parameter such as fluid velocity or shear stress, as often performed in fouling studies. This has been observed by Crittenden *et al.* (2009) for the fouling of Maya crude oil while varying fluid flow rate, and also for the model system of styrene polymerization fouling in kerosene. The initial fouling rates reported for the latter system at different mass flow rates are shown in Figure 5. The Arrhenius parameters determined at each value of fluid velocity are shown on the compensation effect plot in Figure 6.

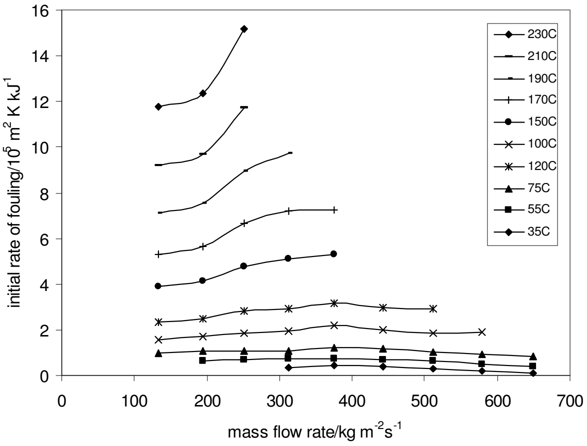

Figure 5 Initial fouling rates reported by Crittenden *et al.* (1987) for chemical reaction fouling of solutions of styrene in kerosene. The legend indicates initial surface temperature. Lines are solely to guide the eye.

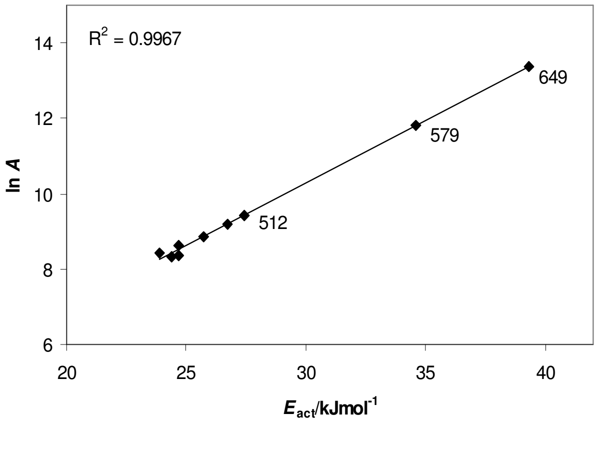

Figure 6 CE plot for styrene fouling data in Figure 5. Each data point derives from initial fouling rate measurements at a particular flow rate. Mass flow rates (in kg m^{-2} s^{-1}) are marked on selected data points. The line shows a straight line fit to the data.

The data in Figure 6 show that the compensation effect is apparent. There is a good linear correlation between the values of ln A and E_{act} obtained at different fluid velocities. However, it is important to establish whether this results from the statistical compensation effect discussed above before making further conclusions. Confidence ellipses can be calculated for each data point, and in this case the statistical compensation effect cannot be completely ruled out as the reason for the apparent compensation. However, no correlation between apparent activation energy and fluid velocity is expected if *random* errors alone are responsible for causing the apparent compensation. It is suggestive that the data points in Figure 6 with highest apparent activation energy were measured at the three fastest fluid velocities. Results reported for the fouling of Maya crude oil also show a clear trend of increasing overall activation energy with fluid velocity (see Figure 7 of Crittenden *et al.*, 2009).

The same trend, of E_{act} increasing with flow rate, was reported for the initial fouling rate of lysozyme solutions by Rose *et al.* (2000). The Arrhenius parameters obtained for this system at different flow rates are plotted in Figure 7. Even though lysozyme is a very different chemical species to styrene and crude oil, a similar compensation effect is observed.

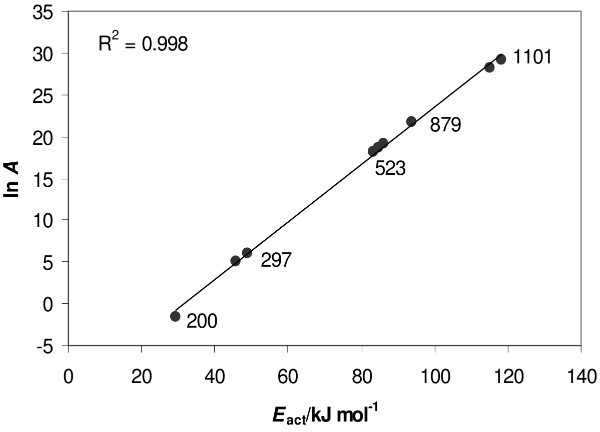

Figure 7 CE plot for fouling of lysozyme solutions using the data reported by Rose *et al.* (2000). Each data point derives from initial fouling rate measurements at a particular fluid velocity. Selected mass flow rates have been marked on the graph (in units of kg m^{-2} s^{-1}). The line is a straight line fit to the data points.

The general trend, that apparent activation energies increase with fluid velocity, means that random errors and the statistical compensation effect *cannot* be responsible. We therefore need to consider another mathematical reason that results in an apparent compensation effect when experiments are performed at different fluid flow rates.

The effect of analyzing overall rate of fouling

The data points in Figures 6 and 7 were obtained by fitting the overall (initial) fouling rate to the Arrhenius equation. Equation (1) can be rewritten to give explicit definitions of apparent Arrhenius parameters at a particular value of fluid velocity *u*.

$$E_{\text{act}} = RT^2\left(\frac{\partial \ln r}{\partial T}\right)_u \qquad [7]$$

$$\ln A = T\left(\frac{\partial \ln r}{\partial T}\right)_u + \ln r \qquad [8]$$

If Arrhenius parameters are obtained at different values of u, then the slope between points on a plot of ln A against E_{act} will be given by:

$$\begin{aligned}\text{slope} &= \left(\frac{\partial \ln A}{\partial u}\right)_T \Big/ \left(\frac{\partial E_{act}}{\partial u}\right)_T \\ &= \left(T\frac{\partial^2 \ln r}{\partial u \partial T} + \left(\frac{\partial \ln r}{\partial u}\right)_T\right) \Big/ \left(RT^2 \frac{\partial^2 \ln r}{\partial u \partial T}\right)\end{aligned} \qquad [9]$$

This gives:

$$\text{slope} = \frac{1}{RT} + \left(\frac{\partial \ln r}{\partial u}\right)_T \Big/ \left(\frac{\partial E_{act}}{\partial u}\right)_T \qquad [10]$$

The slope of the compensation effect plot will depend critically on the relative magnitudes of the first and second terms on the right hand side (RHS) of equation (10). If the second term is negligible, then the slope will be $1/RT$. In all practical kinetic measurements, the range of temperatures investigated is small and so $1/RT$ is approximately constant. Therefore, if the second term is small, equation (10) predicts that the data points on a plot of ln A against E_{act} will fall on a straight line, *i.e.* that the compensation effect will be observed. The gradient in this case will be $1/RT_{ave}$, where T_{ave} is some average of the temperatures used in the kinetic study. In the event that the second term on the RHS of equation (10) is not negligible, then the slope between adjacent points on a compensation effect plot is likely to vary – in that case no compensation effect is expected to occur.

We have analysed the experimental data for styrene fouling shown in Figure 6. In this case a compensation effect is apparent and the gradient of the straight line corresponds to $1/RT^*$, where T^* is 362 K. The temperature range used to obtain the separate data points in Figure 6 differed for each data point – the harmonic mean temperatures for each flow rate range from 327 to 422 K. The observed gradient on the compensation effect plot therefore corresponds to $1/RT_{ave}$.

We have also analysed the experimental data on lysozyme fouling of Rose *et al.* (2000) presented in Figure 7. The gradient of the straight line on the compensation effect plot corresponds to $1/RT^*$ where T^* is 350 K. The experimental wall temperatures used in the study ranged from 332-357 K, with an average of 345 K. Hence the observed gradient of the compensation effect plot corresponds to $1/RT_{ave}$ in this case as well.

It therefore appears that the observed compensation effect in the Arrhenius parameters when fluid velocity is varied is a consequence of the second term on the right-hand side of equation 10 being negligible. The compensation effect provides no particular physical insight in this case – it is simply a mathematical consequence of analyzing the overall rate of a process that varies with parameter u.

Analysis of synthetic data

We now consider the conditions at which the second term on the right-hand side of equation (10) is negligible and those in which it is significant. We have shown above that random errors in the kinetic measurements can cause a compensation effect to occur. In this section, we therefore discuss 'error-free' synthetic data generated by the model for the initial fouling rate developed by Epstein (1994).

Epstein's model has been successfully used to describe several published data sets, including the results reported by Crittenden *et al.* (1987) that are shown in Figure 5. The form of the model for first-order chemical reaction is

$$r = \frac{1}{k_1/u^* + k_2 u^{*2} \exp(E_o / RT_s)} \qquad [11]$$

Here u^* is the friction velocity, T_s the heat transfer surface temperature, and E_o the activation energy of the chemical reaction and adhesion steps. The first term in the denominator relates to mass transfer and dominates when u^* is small: the second relates to reaction and attachment and controls at higher velocities.

It should be noted that Epstein found that Crittenden *et al.*'s data fitted a reaction order of 2.5 rather than the order of 1 used to obtain equation (11). These calculations could be repeated for the 2.5 order, without loss of generality: the first-order case is employed here to illustrate the concepts.

Sets of synthetic data were generated using equation (11) for surface temperatures ranging from 473-573 and flow velocities of 0.1-4.0 m s^{-1} for a 20 mm i.d. tube processing a typical crude oil. E_o was set at 56 kJ mol^{-1}: this is the E_{act} value for the styrene chemical reaction step reported by Crittenden *et al.* (1987) and lies within the range of activation energies for crude oil fouling reported by Yeap *et al.* (2004). Values of k_1 and k_2 were selected to give the change in fouling rate behaviour with velocity exhibited in Figure 5 around $u \sim 1$ m s^{-1}. The absolute fouling rate values are arbitrary and were scaled to match those observed in industry. Temperature affects k_1 and k_2 via the species diffusivity and liquid viscosity, and these effects were included using the analysis presented by Yeap *et al.* (2004, 2006). The selection of results in Figure 8 shows the transition between mass transfer and chemical reaction control apparent in Figure 5. At least 20 temperatures were evaluated at each velocity. The data were fitted to the Arrhenius equation and gave excellent linear fits in each case. The relatively large number of temperature values tested means that the confidence ellipses are small.

Figure 9 shows the compensation plot obtained for a subset of the velocity range studied, between 0.5-2 m s^{-1}. Over this limited velocity range the data appear to exhibit the compensation effect, with a gradient close to $1/RT_{ave}$. A systematic variation with u is evident, as seen in the experimental data sets above. The range of E_{act} values is noticeably smaller than E_o, demonstrating how the velocity effects and influence of temperature on transport properties mask the contribution from chemical reaction.

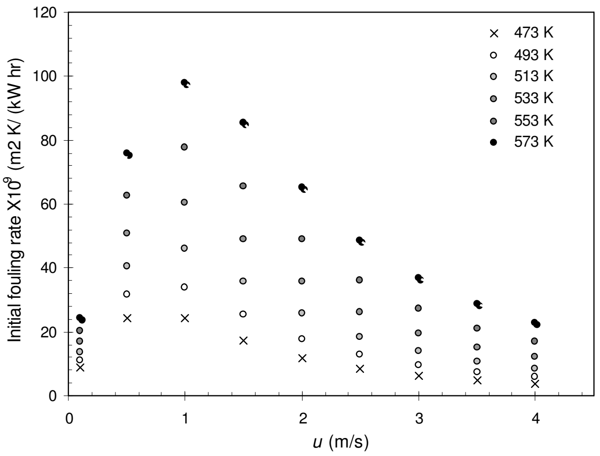

Figure 8 Synthetic fouling rate data generated using the Epstein fouling model for a model crude oil.

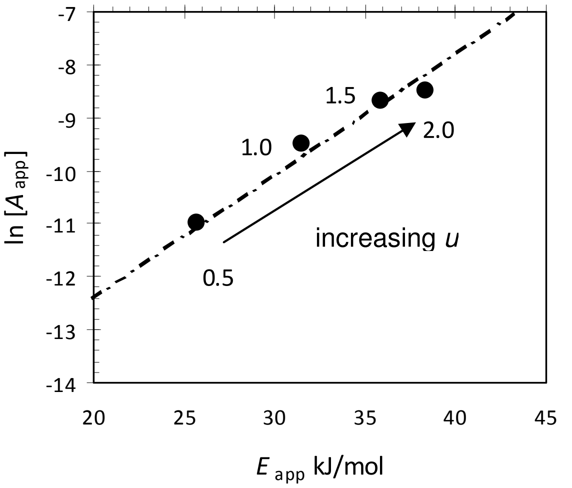

Figure 9 CE plot obtained for synthetic fouling rate data in Figure 8. Data labels show *u* values in m s^{-1}. The gradient of the dashed line is $1/RT_{\text{ave}}$ and is plotted for comparison only.

The similarity between the gradient of the compensation effect plot and $1/RT_{\text{ave}}$ indicates that the second term on the right-hand side of equation (10) is small over this velocity range. The E_{act} value obtained for $u = 0.1$ m s^{-1} deviates from this trend, indicating that the same compensation effect will not be observed at lower velocities. The plot for the full range of velocities studied (Figure 10) shows a significant deviation at higher velocities as well. A systematic trend, of E_{act} increasing with *u* until it reaches a limiting value, is evident. This is expected as the influence of mass transfer becomes less important at higher velocity. Perhaps more surprisingly, a decrease in the value of ln *A* at the highest values of *u* values is evident in Figure 10.

The behaviour at high and low *u* values can be explained by inspection of the model. In the limit of large *u* (and *u**), Epstein's model tends to

$$r \approx \frac{\exp\left(-E_o / RT_s\right)}{k_2 {u^*}^2} \qquad [12]$$

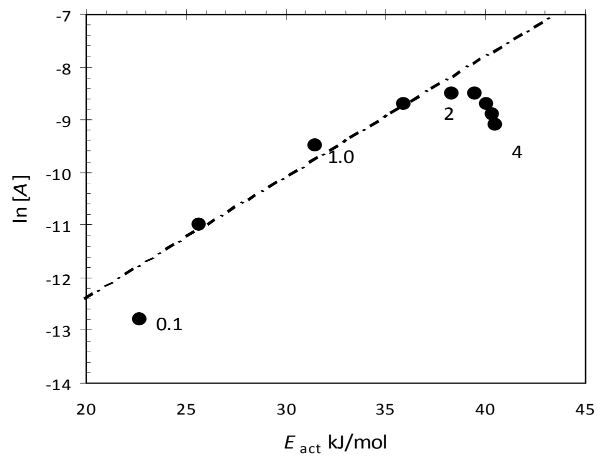

Figure 10. CE plot for all velocities in Figure 8. Data labels show selected *u* values in m s^{-1}. The gradient of the dashed line is $1/RT_{\text{ave}}$.

For this case, the apparent Arrhenius parameters become

$$E_{\text{act}} \approx E_0 - RT^2 \frac{d\ln(k_2 {u^*}^2)}{dT} \qquad [13]$$

$$\ln A \approx -\ln\left(k_2 {u^*}^2\right) - T\frac{d\ln(k_2 {u^*}^2)}{dT} \qquad [14]$$

Equation 13 explains why the apparent E_{act} value tends to a limit at high fluid velocities. The difference between this limit and the value of E_0 (56 kJ mol^{-1}) depends on the temperature dependence in k_2 and u^*. Activation energies for the individual transport properties contained within these parameters were found to lie in the range 22-25 kJ mol^{-1}. The slope of the compensation effect plot at high velocities for points obtained at differing values of u^* is predicted to be

$$\text{slope} = \frac{1}{RT} + \frac{1}{RT^2}\frac{2}{u^*}\frac{1}{\left(\dfrac{d^2\ln(k_2 {u^*}^2)}{du^* dT}\right)} \qquad [15]$$

It is clear from the results shown in Figure 10 that the second term on the right-hand side of this equation can become large and negative for the conditions employed in the simulation.

At low velocities, equation (11) tends to

$$r \approx \frac{u^*}{k_1} \qquad [16]$$

and the slope of the compensation effect plot at differing values of u^* is predicted to be

$$\text{slope} = \frac{1}{RT} + \frac{1}{RT^2}\frac{1}{u^*}\frac{1}{\left(\dfrac{d^2\ln(u^*/k_1)}{du^* dT}\right)} \qquad [17]$$

It is clear from the results in Figure 10 that the second term on the right-hand side of this equation becomes significant at low velocities for the conditions in the simulation.

Although Epstein's model appears to give a good description of the trend shown by Crittenden *et al.* data in Figure 6, the experimental data do not exhibit the decreasing trend in ln A values evident at the highest velocities in Figure 10. One of the reasons for this is the limited number of experimental data points collected at high flow rates, resulting in large uncertainties in the resulting parameters. It is nevertheless noticeable that the largest E_{act} values in both cases lie around 40 kJ mol^{-1}. Another reason is that the lowest temperatures used in our simulations corresponded to the highest temperatures in Crittenden's experimental study. Ongoing work includes analysis of simulation data sets obtained at lower temperatures.

The analysis of synthetically generated data shows that the apparent Arrhenius parameters for fouling obeying Epstein's model will be strongly related to fluid velocity. They also demonstrate that, in the absence of random errors, we should only expect to observe a compensation effect over a restricted parameter range when measuring fouling rates for heat exchangers. Over certain velocity regimes, the gradient on the compensation effect plot will correspond to $1/RT_{ave}$. However, in the general case, the slope can deviate greatly from this value. The deviation depends on the temperature dependence of the transport properties of the fluid at high flow rates, and on mass transport effects at low flow rates.

OTHER EXPERIMENTAL DATA SETS

We have analysed several of the data sets in the heat exchanger fouling literature where the compensation effect has been observed. There is insufficient space to report all the results – the following represent some interesting cases.

Whey protein solutions

Rose *et al.* (2000) reported a set of fouling data obtained for aqueous solutions of 1 wt% whey protein concentrate at pH 6 in addition to the lysozyme solutions discussed above. The compensation effect plot (Figure 11) shows a strongly linear trend, with the 95% confidence ellipses overlapping strongly. A straight line could be plotted through the data with a gradient given by $1/RT_{ave}$, where T_{ave} = 359.5 K but has been omitted for clarity.

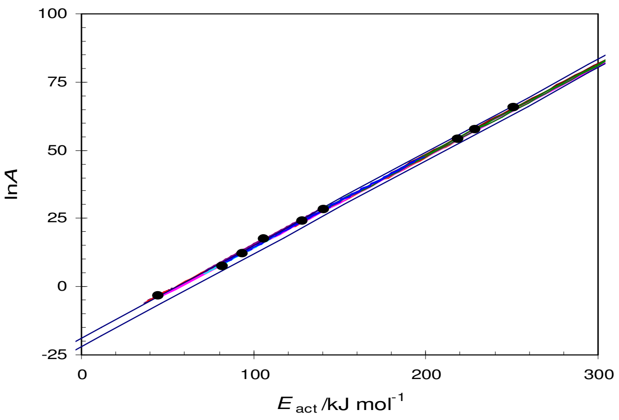

Figure 11 CE plot for whey protein solutions reported by Rose *et al.* (2000) with 95% confidence ellipses plotted for each data point.

For this case, the data show no particular trend of apparent E_{act} value as the velocity increases. However, the uncertainties in the measured parameters are quite large, as demonstrated by the 95% confidence ellipses. It therefore appears that this data set is dominated by the statistical compensation effect. The effect of random errors in the measurements outweighs the expected effect that E_{act} increases with velocity.

Crude oil fouling

Panchal *et al.* (1997) reported crude oil fouling rate data obtained in various pilot and process plant tests, which exhibit the compensation effect. Some of these are reproduced in Figure 12 along with a subset of 95% confidence ellipses.

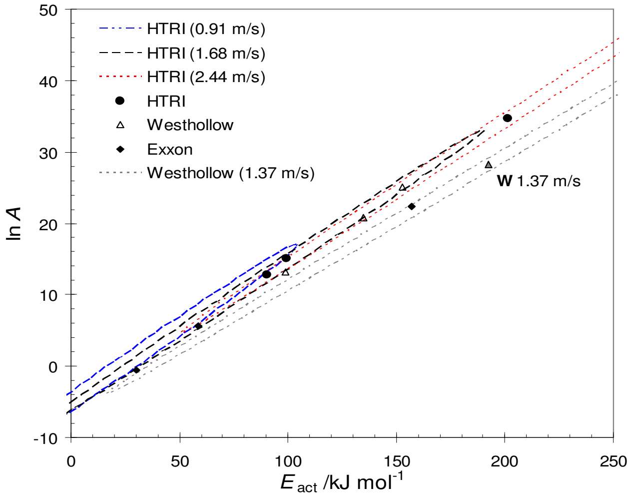

Figure 12 Selected CE plots for crude oil fouling tests reported by Panchal *et al.* (1997)

The data lie close together, with a large degree of overlap between the confidence ellipses, although there is a suggestion of E_{act} increasing with u for the HTRI data set. The confidence ellipses for many of the data sets are large owing to the small number of temperature data points. For each crude oil, the gradient on the compensation effect plot is found to equal $1/RT_{ave}$ where T_{ave} represents the average temperature used for the measurements on that particular oil. The statistical compensation effect therefore explains the trends shown in Figure 12.

CONCLUSIONS

This paper has discussed mathematical reasons that account for the observation of the compensation effect (CE) in heat exchanger fouling data.

The first reason is the statistical compensation effect. Random errors in the kinetic measurements can cause an apparent compensation effect. The gradient on a CE plot is expected to be close to $1/RT_{ave}$ where T_{ave} is an average of the temperatures used – it will be the harmonic mean if the same experimental temperatures were used to determine each data point on the plot. The statistical compensation effect can account for apparent compensation when fouling rate measurements are made on a series of different crude oils at otherwise identical conditions.

When fouling rate experiments are conducted on a single fluid at different flow rates, then the statistical compensation effect remains a possibility. If it occurs, then no correlation between apparent activation energy and fluid velocity is expected. However, in experimental studies, the apparent activation energy is often found to increase with fluid velocity. In this case, another mathematical reason can cause the compensation effect. It may be due to analyzing the overall rate of fouling by the Arrhenius equation, rather than an intrinsic rate constant, under conditions in which the second term on the right-hand side of equation 10 is negligible. In this case, the gradient on a CE plot is expected to be close to $1/RT_{\text{ave}}$, where T_{ave} is an average of the temperatures used, as was also the case for the statistical compensation effect.

Apparent Arrhenius parameters have also been obtained as velocity is varied using synthetic, 'error-free' data generated from Epstein's model for initial fouling rates. These show that the gradient on the CE plot may be $1/RT_{\text{ave}}$ over a restricted velocity range. However, in the general case, the combined effects of chemical reaction and mass transport can cause large deviations of the gradient from this value. If experiments are conducted over a wide velocity range, the model predicts that no compensation effect is expected to occur, though there remains the possibility of random errors causing the statistical compensation effect to be observed experimentally.

The results in this paper lead us to propose the following guideline. If a kinetic compensation effect is observed, then the gradient of a compensation effect plot should be measured. If it is found to be close to $1/RT_{\text{ave}}$, where T_{ave} is an average of the temperatures used, then a mathematical reason for the observed compensation effect should be suspected. In that case, the observed compensation effect does not have an underlying physical basis and so has limited modelling capability.

NOMENCLATURE

Roman

A	Arrhenius prefactor, m^2 K J^{-1}
E_{act}	activation energy, J mol^{-1}
k_1	parameter in equation (11), W m^{-1} K^{-1}
k_2	parameter in equation (11), W K^{-1} s^{-1}
n	number of data points, -
R	gas constant, J $mol^{-1}K^{-1}$
r	rate, m^2 K J^{-1}
T	temperature, K
T_{ave}	average temperature, K
T_{s}	surface temperature, K
u	mean flow velocity, m s^{-1}
u^*	friction velocity, m s^{-1}

Greek

α	constant in equation (2), -
β	constant in equation (2), mol J^{-1}
ρ^2	correlation coefficient
σ^2	variance

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