Esterification of Ethanol with Sulfuric Acid: A Kinetic Study
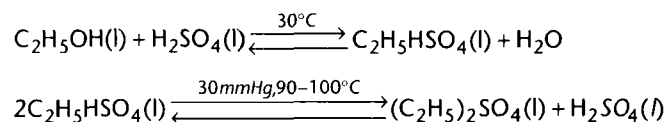
Shammi Theodore and P.S.T. Sai*

Department of Chemical Engineering, Indian Institute of Technology, Madras 600 036, India

Diethyl sulfate (DES) or 'oil of wine' as it was known, is the second member among the homologous series of compounds called dialkyl sulfates. It is mainly used as an alkylating agent. Besides, it is used in a wide variety of applications such as catalysis, detergent preparation, refining of fats, inducing mutations, etc.

There are two routes which are being widely used for the manufacture of DES. They are: absorption of ethylene in concentrated sulfuric acid (Chaudhuri and Sharma, 1991) and action of ethanol with chlorosulfonic acid (Kraft and Lyutina, 1962). One of the principal limitations of the above processes is the difficulty in maintaining extreme operating conditions. In the former process, it is essential that the pressure be kept high (20 to 30 atm) to get a good yield of DES. In contrast, the later process requires a very low temperature (0°C to 5°C) for the esterification step. These conditions deviate widely from the normal pressure and temperature and hence require rigorous control procedures and also careful monitoring. The ethanol-chlorosulfonic acid process produces large amounts of hydrogen chloride which should be recovered as hydrochloric acid. In addition, the cost of the chemicals used in both the processes is very high. Hence, it is essential that a cost effective and alternative process be devised.

Taking into account the factors such as cost, availability and required purity of raw materials, maintenance of operating conditions, complexity of the process, yield of DES and recovery of byproducts, it is found that the ethanol-sulfuric acid process when modified would be a more efficient process than any of the alternate routes. In this process, instead of distilling a mixture of ethanol and sulfuric acid, the process can be carried out in two steps. The first step involves reacting ethanol and sulfuric acid at room temperature to produce ethyl hydrogen sulfate (EHS). The second step is the distillation of EHS, under vacuum, to produce DES. The main advantage of this process is that it requires low cost raw materials and does not require extreme operating conditions. The reactions involved in this process are as follows:

$$C_2H_5OH(l) + H_2SO_4(l) \xrightarrow{\text{30°C}} C_2H_5HSO_4(l) + H_2O$$

$$2C_2H_5HSO_4(l) \xrightarrow{\text{30mmHg,90–100°C}} (C_2H_5)_2SO_4(l) + H_2SO_4(l)$$

Since the distillation of EHS to produce DES is a well established step, as can be seen from the literature information for the other methods of preparation, the esterification reaction between ethanol and sulfuric acid to produce EHS was chosen for the present study.

Experiments were conducted in a stirred batch reactor under isothermal conditions for obtaining kinetics of the esterification reaction between ethanol and sulfuric acid. Reactive adsorption technique was employed to enhance the conversion. Anhydrous sodium sulfate was used as an adsorbing agent to remove the water formed during the reaction. The variables include the mole ratio of ethanol to sulfuric acid, reaction temperature, purity of the reactants, and the amount of adsorbing agent. The reaction was found to be reversible and second order at low mole ratios, and irreversible and first order at high mole ratios. The kinetic parameters of the rate law were estimated. A possible reaction mechanism was proposed and validated with the experimental data. The effect of the mole ratio of reactants, anhydrous sodium sulfate loading, and purity of the reactants on the yield of ethyl hydrogen sulfate was studied, using full-factorial search and optimized conditions were obtained by the method of steepest ascent. More precise optimum conditions were obtained using the Box-Wilson composite method.

Des expériences ont été menées dans un réacteur agité discontinu dans des conditions isothermes afin d'obtenir la cinétique de la réaction d'estérification entre l'éthanol et l'acide sulfurique. On a eu recours à la technique d'adsorption réactive pour accroître la conversion. Du sulfate de sodium anhydre a servi d'agent adsorbant pour retirer l'eau formée pendant la réaction. Les variables comprennent le rapport molaire éthanol-acide sulfurique, la température de réaction, la pureté des réactifs et la quantité d'agent adsorbant. La réaction s'est avérée réversible et de second ordre à de faibles rapports molaires et irréversible et de premier ordre à des rapports molaires élevés. Les paramètres cinétiques de la réaction de premier ordre et de second ordre ont été estimés. Un mécanisme de réaction possible est proposé et validé avec les données expérimentales. L'effet du rapport molaire des réactifs, de la charge de sulfate de sodium anhydre et de la pureté des réactifs sur le rendement en sulfate d'hydrogène d'éthyle a été étudié par un plan factoriel complet, et des conditions optimisées ont été obtenues par la méthode de la descente la plus rapide. Des conditions optimales plus précises ont été obtenues à l'aide de la méthode composite Box-Wilson.

Keywords: esterification, diethyl sulfate, reactive adsorption.

*Author to whom correspondence may be addressed. E-mail address: psts@pallava.iitm.ernet.in

Information regarding kinetics of the reaction leading to the formation of EHS is available only for two cases, namely the presence of equimolar quantities of alcohol and sulfuric acid (Deno and Newmann, 1956) and the presence of excess sulfuric acid (Dunnicliff and Butler, 1921). These two methods suffer from disadvantages since in the former, the yield will be less and in the latter, separation of sulfuric acid is difficult because of its high boiling point and non-availability of a selective solvent. However, since the present study aims at devising a suitable method for the manufacture of DES, alcohol was chosen as the excess reactant because of the ease with which it can be separated from the reaction mixture. The kinetics of the reaction in the presence of an excess of alcohol has not been investigated so far.

This method too has a drawback, namely, the equilibrium limited conversion in the initial reaction leading to the formation of EHS. However, since water is a product of this reaction, the conversion can be enhanced by removing the water formed during the reaction by employing a suitable reactive separation technique. From a review of various reactive separation techniques, namely, reactive distillation, reactive extraction, reactive adsorption, and membrane separation and their applicability to the problem of interest, it was found that, apart from reactive adsorption, the other methods cannot be employed for the current problem.

A literature survey regarding the applicability of drying agents indicated that anhydrous sodium sulfate, magnesium sulfate and anhydrous calcium sulfate are applicable. Considering the characteristics of these three drying agents including the activity, action, commercial availability, and water adsorption capacity, it is apparent that anhydrous sodium sulfate has advantages over the other two.

In summary, a critical review of the literature on DES manufacture indicates the need for an alternative route. DES can be manufactured by a process consisting of two reaction steps, the first between ethanol and sulfuric acid, with anhydrous sodium sulfate as the drying agent to produce EHS, and the second comprising of the decomposition of EHS to DES and sulfuric acid. The literature also indicates that there is no published information on the kinetics of the reaction and on the optimization of the parameters that influence DES production. Hence the aim of this communication is to study the effect of mole ratio of the reactants, temperature, purity of the chemicals, and loading of the adsorbing agent on conversion, to elucidate the kinetics of the reaction, to obtain the mechanism of the reaction, and to optimize the process variables for better yield of EHS. A full factorial search was employed to optimize the parameters of the esterification reaction using the path of steepest ascent method. The Box-Wilson composite method was used to obtain precise optimum conditions.

Experimental

Experiments were conducted in a stirred batch reactor (glass, 1000 mL) which consisted of a flat bottomed flask with three necks. A reflux arrangement with a suitable condenser was fixed through the center neck of the flask. A thermometer was placed in one of the side necks using mercury in the thermowell and the other neck was used for collecting the samples. The flask was kept in a bath which was maintained at a constant temperature by circulating cooling water through it. A magnetic stirrer was used for stirring purposes.

Known amounts of ethanol (typically 100 mL) and anhydrous sodium sulfate were placed in the reactor and the calculated amount of sulfuric acid (typically 100 mL) placed in a separate flask. Each was cooled to a temperature of around 5°C to 7°C. The acid was then added to the mixture of ethanol and anhydrous sodium sulfate and the reaction was presumed to commence after half the acid was added to the mixture. Since the reaction is exothermic, the reactants were cooled before they were mixed, in order to limit the temperature rise due to mixing so that isothermal conditions were maintained. The stirring speed was maintained constant throughout the experiment in all experimental runs.

Samples of volume 1 mL were pipetted at different time intervals from the reaction mixture. The reaction was immediately arrested with sodium hydroxide solution of a particular normality depending upon the mole ratio of ethanol and sulfuric acid so that the total sample volume varied from 3 to 5 mL.

The samples were analyzed for ethanol using a gas chromatograph equipped with a flame ionization detector (FID). An integrator was used to record the signal from the chromatograph. The progress of the reaction was followed by monitoring the concentration of unreacted ethanol and the portion that reacted with sulfuric acid was obtained by difference. And finally, the amount of sulfuric acid used for the reaction and hence the conversion, was calculated from the reaction stoichiometery. The sulfuric acid content in the sample could not be determined by titrimetric methods as it gave the total acidity due to both sulfuric acid and EHS. Also separation of sulfuric acid from the sample was difficult as there was no selective solvent for sulfuric acid or EHS extraction.

The variables investigated in the present study with their ranges are presented in Table 1. By mole ratio is meant the mole ratio of ethanol to sulfuric acid.

Results and Discussion

As mentioned earlier, anhydrous sodium sulfate was selected as the adsorbent for the removal of water which forms during the reaction. Since water is being removed continuously during the reaction period by the adsorbing agent, in order to estimate the concentration of reactants and products in the reaction at any instant, the rate of removal of water by the adsorbent is required. Hence a separate set of experiments was conducted to study this aspect.

In order to get an insight into the adsorption process, it was decided to study the rate of adsorption of water in an alcoholic medium. Experiments were conducted by taking a mixture of alcohol and water with alcohol in excess, to mimic the actual conditions employed in the kinetic experiments. The amount of anhydrous sodium sulfate required for adsorbing the entire quantity of water was then added to this mixture. This mixture was stirred and samples at different time intervals were

Table 1. Variables and their ranges.

Variable	Range
Mole ratio	1-12
Temperature, K	291 - 302
Anhydrous sodium sulfate loading	nil-stoichiometric
Purity of sulfuric acid, %	85-97.5

collected and analyzed for their alcohol content. The experiment was conducted twice with a stoichiometric amount of anhydrous sodium sulfate and the average of the values obtained was used for calculation purposes.

It follows from the results that ≈68% (by volume) of the water was adsorbed in 45 minutes. This indicates that the adsorption proceeds at a fast pace and also that there is a substantial amount of adsorption. Although it was not possible to find the rate of adsorption in the actual reaction mixture, these tests indicated that there is enough adsorption to cause an enhancement in conversion and that the adsorption process proceeds at a rapid pace. It was realized that there may be a difference in the adsorption-time profile between where all of the water is present at the start of adsorption and where a reaction has to take place to produce the water available for adsorption. As alternative approaches were not better, this method was used. Another set of experiments was conducted with different amounts of alcohol and water and the rate of adsorption was found to be almost the same as in the previous experiments.

Since anhydrous sodium sulfate adsorbs the water formed during the reaction, the volume of the reaction mixture decreases as the reaction progresses. In order to find the true concentration of the various species present in the reaction mixture, it is necessary to know the volume of the reaction mixture at different times. This can be found only if the rate of adsorption is known. Since the true rate of adsorption of water could not be determined, the above results are used for calculating the concentrations. For this purpose, the rate of adsorption of water, F_D, is plotted against time and subjected to a third degree polynomial fit which is shown in Figure 1. With the values of the coefficients of the polynomial, the equation for the rate of adsorption with time is as follows:

$$F_D = 0.0268 - 6.5091 \times 10^{-4}t + 6.3460 \times 10^{-6}t^2 - 2.0918 \times 10^{-8}t^3 \qquad (1)$$

The various steps involved in the evaluation of the true concentrations of the various species in the reaction mixture is outlined in the appendix.
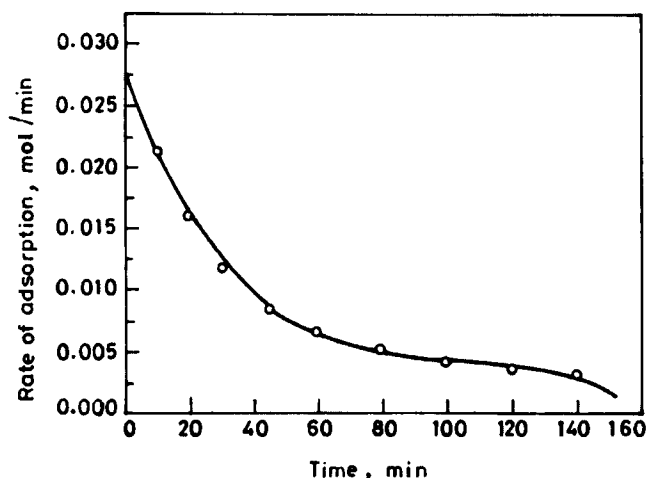
Effect of Operating Variables
Effect of Mole Ratio
Experiments were conducted at different mole ratios, covering a wide range (1.1 to 12) at a constant temperature of 302 K, with and without the addition of anhydrous sodium sulfate which was added in stoichiometric amounts for this study. Stoichiometric amount is the amount of anhydrous sulfate that is required for adsorbing the water that would be formed due to the complete conversion of sulfuric acid taking into consideration the fact that each mole of anhydrous sodium sulfate adsorbs ten moles of water. The experimental data showing the variation of fractional conversion with mole ratio is shown in Figure 2. The results indicate that in the presence of anhydrous sulfate, the conversion increases from ≈63% at a mole ratio of 1.1 to ≈97% at a mole ratio of 8 after which there is no further change in conversion. In the absence of anhydrous sodium sulfate, the maximum conversion obtained is ≈83%, again at a mole ratio of 8.

Effect of Temperature
Experimental data showing the variation of concentration of the various species with time in the presence of stoichiometric amounts of anhydrous sodium sulfate is shown, typically at a mole ratio of 1.1 and temperature of 302 K, in Figure 3. The variation of fractional conversion of sulfuric acid with time at the same mole ratio and at different temperatures is also depicted in Figure 4. It can be inferred from Figure 4 that at a mole ratio of 1.1, there is a marginal increase in conversion, as the temperature increases. A marginal decrease in equilibrium conversion with increase in temperature is also noticed. This is the case with exothermic reversible reactions. But at a mole ratio of 6, there is an increase in fractional conversion with temperature, the change being more from 294 K to 302 K when compared to that from 291 to 294 K. Further, there is little or no change in equilibrium conversion with temperature for a mole ratio of 6. This can occur only if the reaction is
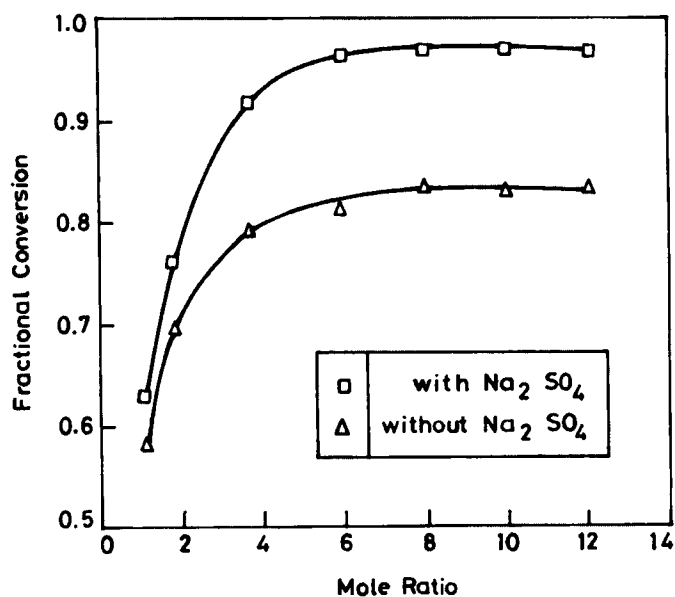

Figure 1. Polynomial fit for the rate of adsorption as a function of time.

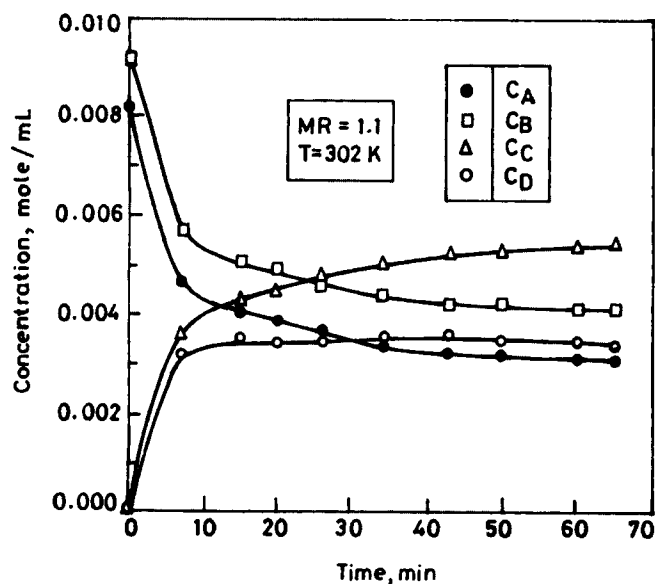Figure 2. Variation of fractional conversion with mole ratio.

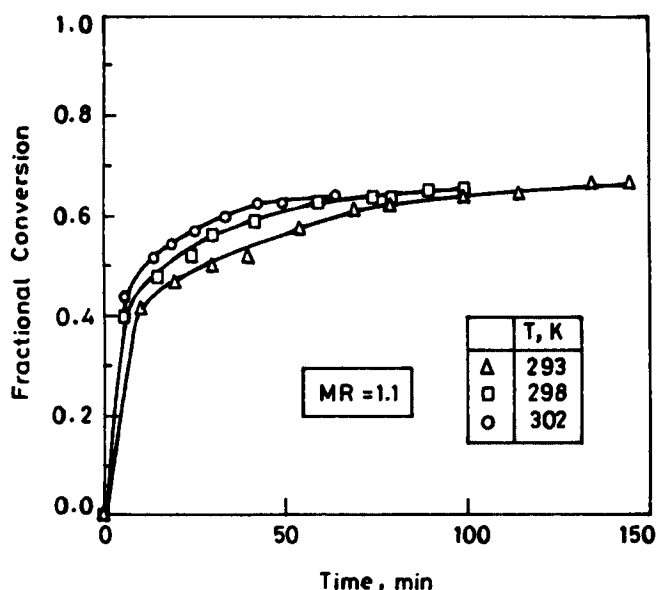**Figure 3.** Variation of concentration of various species with time in the presence of anhydrous sodium sulfate.

Figure 4. Variation of fractional conversion with time in the presence of anhydrous sodium sulfate.

alcohol is considered as the pure component or vice-versa. In the present study, the purity of sulfuric acid was varied from 97.5% to 85% keeping the purity of alcohol at 100% with anhydrous sodium sulfate as adsorbing agent in stoichiometric amounts.

It is observed that the decrease in conversion with decrease in purity is more pronounced when the purity levels are more than 90%. Since the conversion is only ≈73% when the purity is 90%, it is desirable to have high purity for commercial purposes. The optimum purity can be determined by optimizing the various variables involved in the reaction.

From the results, it is also evident that at a mole ratio of 8 and with 97.5% pure sulfuric acid, the conversion obtained is 97%. By reducing the purity, both the initial concentration of sulfuric acid and the amount of water initially present do change. The decrease in conversion observed when the purity is reduced could be because of the lower initial concentration of sulfuric acid and also the presence of water which promotes the reverse reaction. However, the reduction in conversion due to a small change in initial concentration of sulfuric acid is less, as is evident from the discussion on the effect of mole ratio. Hence it can be concluded that the reduction in conversion is mainly due to the water initially present and the reversible nature of the reaction. Since the drying agent was taken in stoichiometric amounts only (taking into account only the water formed due to the reaction and not the water initially taken) in all these experiments, the water present could not be adsorbed by the adsorbing agent and hence behaved like a reversible reaction. This is in contrast with the earlier observation made during the study of the effect of mole ratio where it was observed as an irreversible reaction.

Effect of Anhydrous Sodium Sulfate Loading

In order to study the effect of anhydrous sodium sulfate loading on conversion, experiments were conducted at mole ratios of 1.1 and 6, at a temperature of 302 K. For a mole ratio of 1.1, the variation of conversion at different loadings is given in Table 2. It follows from Table 2 that the change in conversion was significant (≈4%) when the amount of sodium sulfate was varied from nil to the stoichiometric requirement. When 50% excess of the stiochiometric requirement was added, there was a further increase in conversion (1.15%) and when 100% excess amount was added, the conversion was 64.1%. Thus, the effect of anhydrous sodium sulfate was less pronounced when the amount of anhydrous sodium sulfate was increased

irreversible. These results indicate that the reaction is reversible exothermic at low mole ratios and becomes irreversible at high mole ratios.

Effect of Purity

Even though water is one of the products of the reaction, the water present initially will affect the conversion since this is a reversible reaction at low mole ratios. Hence it was decided to study the effect of purity of the reactants on conversion. Also, since the present study is of commercial importance, this aspect is required. Changing the purity of any one of the reactants alters the amount of water initially present in the reaction mixture. Hence the purity can be taken as that of sulfuric acid if

Table 2. Effect of anhydrous sodium sulfate loading on conversion. $MR = 1.1$; $T = 302$ K; $t = 60$ min.

Sl. No.	Loading of anhydrous sodium sulfate	Conversion, %	
		$MR = 1.1$	$MR = 6$
1	Nil	58.20	81.10
2	Stoichiometric	62.25	96.50
3	50% excess	63.40	96.29*
4	100% excess	64.10	96.55*

*Corresponding to a reaction time of 55 minutes.

beyond the stoichiometric requirement and it showed a decreasing trend in the change in conversion. The conversion values presented in the Table 2 correspond to a time of 1 h, after which there was no change in conversion.

Similar studies were carried out at a mole ratio of 6. These results, presented in Table 2, indicate that an increase in conversion of ≈15% between nil and stoichiometric amount of anhydrous sodium sulfate. When the amount of anhydrous sodium sulfate is increased beyond stoichiometric requirement, there is no change in conversion. Only the time required to reach the final conversion is different, the time required being less when excess amount of anhydrous sodium sulfate is added. Hence the effect of sodium sulfate is more pronounced at high mole ratios. On comparison of these results with those of the effect of purity, it can be concluded that a change in purity has more effect on conversion than a change in the amount of drying agent.

Kinetics of the Reaction

The experimental program for obtaining the kinetics of the reaction consisted of runs at different mole ratios and temperatures but with pure reactants and anhydrous sodium sulfate in stoichiometric amounts. Concentration versus time data at different mole ratios and at different temperatures were subjected to both the integral and differential methods of analysis for deriving a suitable rate law. The rate laws considered are: irreversible and first order with respect to sulfuric acid, irreversible and first order with respect to both ethanol and sulfuric acid, reversible and second order (first order with respect to each component) in both forward and reverse directions and reversible and first order (with respect to sulfuric acid in the forward direction and water in the reverse direction).

Integral Method of Analysis

Plots of $-\ln(1 - X_A)$ versus time and $\ln \{(M - X_A)/M(1 - X_A)\}$ versus time at a mole ratio of 1.1 and at different temperatures indicate that the data do not follow a linear fit through the origin. From these plots, it is clear that both irreversible first and second order kinetics are not valid at a mole ratio of 1.1. Hence as a test for reversible kinetics, the reversible second order form of rate law is tested. For this form of rate law, the relation between conversion and time is as follows:

$$\ln\left(\frac{\{(p/r)+1\}}{\{(p/s)+1\}}\right) = k_1 t \quad (2)$$

From the plots of the function on the left hand side of Equation (2) versus time, shown typically at a temperature of 302 K in Figure 5, it follows that the data fall on a reasonably straight line through the origin. The goodness of this fit is further verified by the differential method of analysis. Hence, the other rate form namely reversible first order is not attempted.

Since the data at a mole ratio of 1.1 give a good fit for reversible second order kinetics, the data at a mole ratio of 6 are also subjected to an integral plot of the same rate law. From the plots of the function on the left hand side of Equation (2) versus time, shown typically at a temperature of 294 K in Figure 6, it follows that the data do not give a straight line fit through the origin and this is further confirmed by the differential method which is discussed later. In order to test whether the data follow

reversible first order kinetics, plots of $-\ln(1 - X_A/X_{Ae})$ versus time are made and the data points give a poor fit for the assumed rate law.

Since both the reversible forms of rate law do not fit the data well, the irreversible form of rate expression is tested. Irreversible first order plots for a mole ratio of 6 similar to those presented earlier is shown in Figure 7. The data do fall on a reasonably good straight line fit through the origin. Hence, another rate law form is not tested.

Differential Method of Analysis

The rate laws which were confirmed earlier by the integral method of analysis are subjected to differential method of analysis. At a mole ratio of 1.1, a reversible second order
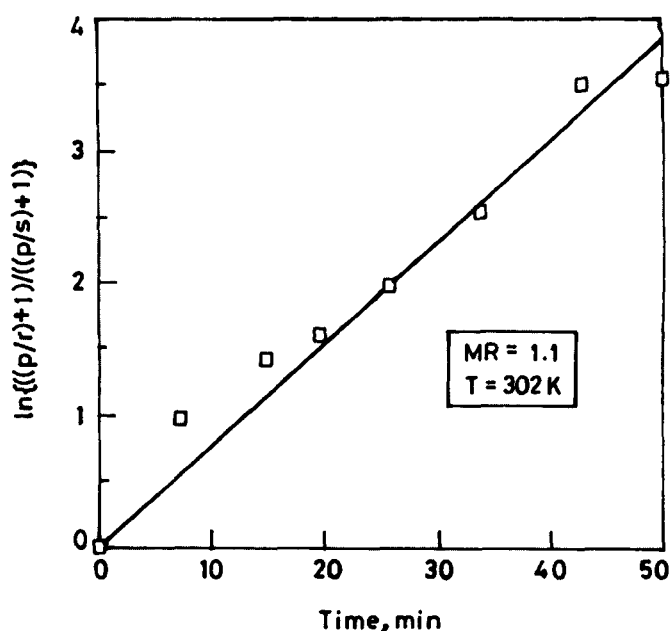

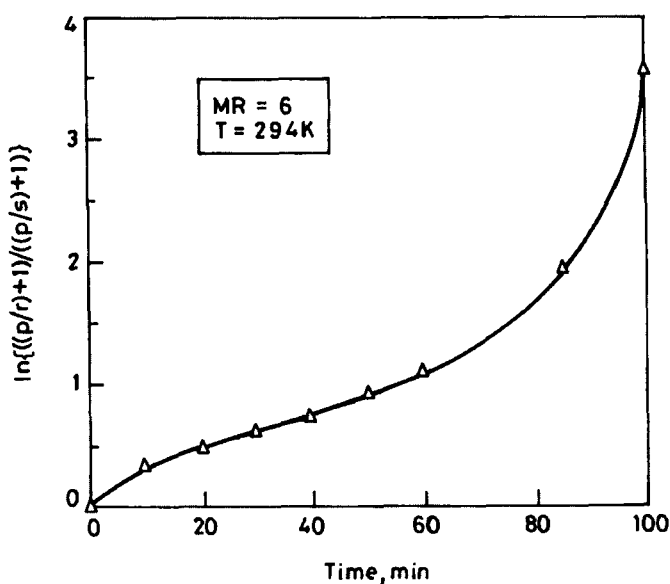Figure 5. Test for reversible second order kinetics by integral method.

Figure 6. Test for reversible second order kinetics by integral method.
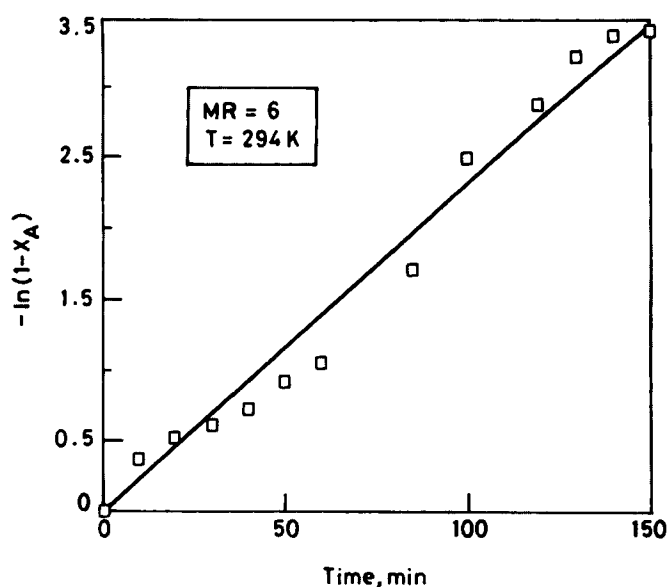
58

Figure 7. Test for irreversible first order kinetics by integral method.

Table 3. Slopes of the reversible second order kinetics fit by differential method.

Mole ratio	Temperature, K	reversible second order	Slope reversible first order	irreversible first order
1.1	302	1.1423		
1.1	298	1.1250		
1.1	293	1.1260		
6.0	302	0.6408	0.6408	0.8497
6.0	294	0.6688	0.6208	0.8747
6.0	291	0.7153	0.4572	0.8192

reaction was found to fit the experimental data by the integral method of analysis. For this type of reversible second order reaction, the differential method gives the following relation between rate of reaction and concentration:

$$\ln(-r_A) = \ln k_1 + \ln(C_A\, C_B - C_C\, C_D/K) \qquad (3)$$

For this kinetics to be valid, a plot of $\ln(-r_A)$ versus $\ln(C_A C_B - C_C C_D/K)$ should give a straight line fit with a slope of unity. The above mentioned plots for a mole ratio of 1.1 and at different temperatures are shown, typically at a temperature of 298 K, in Figure 8. The slopes obtained from these fits are shown in Table 3. These slopes are close to unity and indicate the goodness of the fit of the data to this form of rate law.
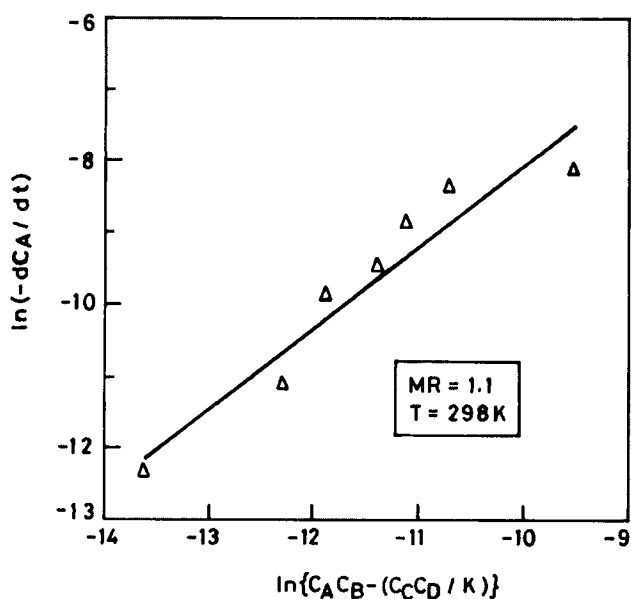
Similar graphs are plotted for a mole ratio of 6 and the analysis of these figures and Table 3 indicate that the data do not give a slope of unity even though the fit appears to be good and hence this kinetics is not valid at a high mole ratios. The slopes obtained from these plots are also shown in Table 3.

The equation relating rate of reaction with concentration for a reversible first order rate law is as follows:

$$\ln(-r_A) = \ln(k_1) + \ln(C_A - C_D/K) \qquad (4)$$

Since sulfuric acid and water are the limiting reactants for the forward and reverse reactions respectively, the forward and reverse rate laws are assumed to be independent on these two components only. Plots of $\ln(-r_A)$ versus $\ln(C_A - C_D/K)$ for a mole ratio of 6 is shown, typically at a temperatures of 291 K, in Figure 9. These plots clearly show the ineptness of the data for this type of kinetics. The slopes obtained from these plots are presented in Table 3.

Although the integral method showed that the irreversible first order form of rate law is valid at high mole ratios, the aptness can be made much clearer by employing the differential
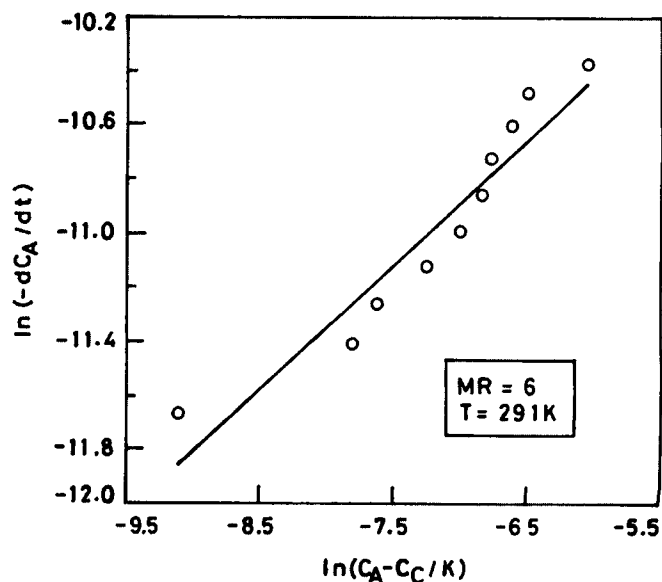

Figure 8. Test for reversible second order kinetics by differential method.

Figure 9. Test for reversible first order kinetics by differential method.

method of analysis. For this purpose, plots of $\ln(-r_A)$ versus $\ln(C_A)$ are made at a mole ratio of 6 and at different temperatures. These are shown typically in Figure 10. The slopes obtained from these plots are presented in Table 3. It can be inferred from these figures and Table 3 that the data do give a good fit as seen from the values of the slopes.

The values of the parameter in these rate laws, namely, the reaction rate constants, obtained under various experimental conditions are presented in Table 4. The frequency factor and activation energy, are evaluated from an Arrhenious plot. The values of activation energy and frequency factor, presented in Table 5, are in the range normally encountered in liquid–liquid reactions.
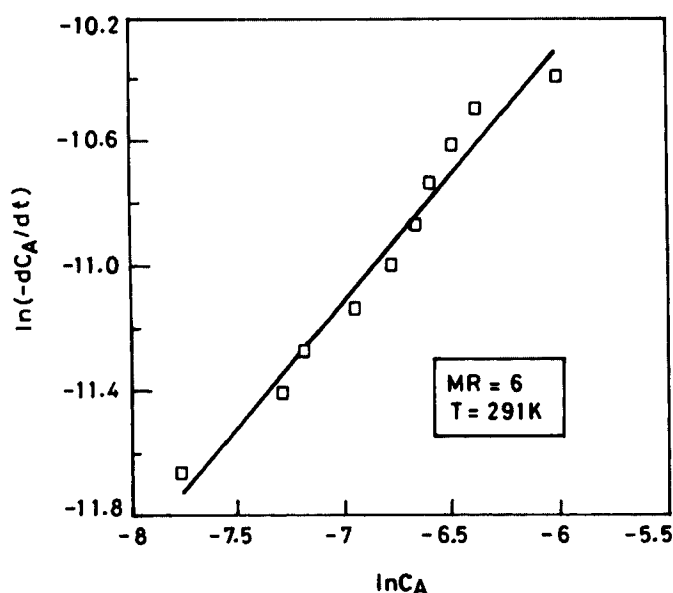

Figure 10. Test for irreversible first order kinetics by differential method.

Table 4. Reaction rate constant values under various experimental conditions.

Mole ratio	Temperature, K	$k_1 \times 10^{-4}$ s⁻¹·(mol/m³)	$k_2 \times 10^{-4}$ s⁻¹·(mol/m³)	$k \times 10^{-5}$ s⁻¹
1.1	302	13.63	9.60	–
1.1	298	9.06	5.53	–
1.1	293	5.97	2.97	–
6.0	302	–	–	26.70
6.0	294	–	–	6.50
6.0	291	–	–	7.67

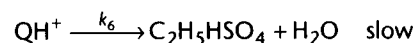**Table 5.** Values of activation energy and frequency factor.
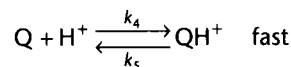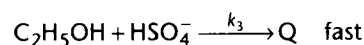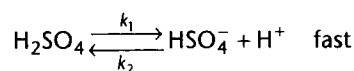
Mole ratio	Temperature range, K	E_a, (kJ/mol) (forward reaction)	E_a, (kJ/mol) (reverse reaction)	A (forward reaction)	A (reverse reaction)
1.1	293–302	70.0	95.9	5.68×10^{18}	3.52×10^{23}
6.0	291–302	91.8	–	1.83×10^{20}	–

Reaction Mechanism

Experimental observations indicate an irreversible trend when the mole ratio is high. However, at low mole ratios, the reaction follows a reversible trend and the rate equations agree with the stoichiometry. This indicates that the reaction is elementary at low mole ratios and non-elementary at high mole ratios. Hence, the multiplicity of mechanisms at different mole ratios exist. Since the reaction is non-elementary only at high mole ratios, it is necessary to determine the mechanism only at these mole ratios.

Assumptions

The assumptions are based partly on experimental information and partly on accumulated knowledge about characteristics of the different species involved in the reaction. The various assumptions involved are: 1) the alcohol forms a complex Q with a component of the acid; 2) a small proportion of the complex gets protonated; and 3) the rate determining step is a irreversible, unimolecular decomposition of the protonated complex to form the ester since experimental observation indicate an irreversible first order reaction. From the above stated assumptions, the following steps are postulated:

$$H_2SO_4 \xrightleftharpoons[k_2]{k_1} HSO_4^- + H^+ \quad \text{fast}$$

$$C_2H_5OH + HSO_4^- \xrightarrow{k_3} Q \quad \text{fast}$$

$$Q + H^+ \xrightleftharpoons[k_5]{k_4} QH^+ \quad \text{fast}$$

$$QH^+ \xrightarrow{k_6} C_2H_5HSO_4 + H_2O \quad \text{slow}$$

Considering the slowest step among the above as the rate determining one, the rate equation takes the form

$$r_{EHS} = k_6 [QH^+] \tag{5}$$

Employing pseudo-steady state approximation, the concentration of the intermediate [QH⁺] is expressed in terms of ROH and HSO_4^-. Applying pseudo-steady state approximation for all the intermediates:

$$[QH^+] = (k_3/k_6) [C_2H_5OH] [HSO_4^-] \tag{6}$$

$$[HSO_4^-] = k_1 [H_2SO_4] / (k_2 [H^+] + k_3 [C_2H_5OH]) \tag{7}$$

$$\therefore r_{EHS} = k_a \frac{[C_2H_5OH][H_2SO_4]}{[H^+] + k_b[C_2H_5OH]} \tag{8}$$

where $k_a = k_1 \cdot k_3/k_2$ and $k_b = k_3/k_2$.

Since at high mole ratios, $[C_2H_5OH] \gg [H^+]$, the above equation gets simplified to the following form:

$$r_{EHS} = k [H_2SO_4] \tag{9}$$

which is the final form of the rate equation where $k = k_a / k_b$. This rate equation is the same as the one obtained from the analysis of the rate data by both integral and differential methods. Hence, the assumed mechanism is consistent with the experimental observations.

Optimization

Factorial Design

Of the variables that influence the yield of EHS, three variables viz., mole ratio of ethanol to sulfuric acid, amount of anhydrous sodium sulfate and purity of the reactants were optimized using full-factorial search (Akhnazarova and Kafarov, 1982). The fourth variable viz. temperature was fixed at 302 K and the time at which samples were collected was fixed at 1 h. A two-level factorial experiment was carried out and the complete design matrix is shown in Table 6.

A linear regression equation containing two and three factor interaction coefficients is considered for the purpose of relating the responses, and the regression equation with the values for the various coefficients takes the following form:

$$y = 62.84 + 11.69\ x_1 + 2.33\ x_2 + 12.32\ x_3 + 1.22\ x_1\ x_2 + 1.45\ x_2\ x_3 + 3.88\ x_1\ x_3 + 0.97\ x_1\ x_2\ x_3 \quad (10)$$

The significance of the coefficients was determined using t-test, where the necessary critical values for 90% probability are also given in Table 6, from Akhnazarova and Kafarov (1982). Thus, the coefficients b_{12}, b_{23} and b_{123} are insignificant and the regression equation after the deletion of the insignificant coefficients takes the following form:

$$y_p = 62.84 + 11.69\ x_1 + 2.33\ x_2 + 12.32\ x_3 + 3.88\ x_{13} \quad (11)$$

In order to examine the statistical significance of the above equation, Fisher's test is applied. The experimental F value is less than the tabulated value (9.1 for 95% probability) and the estimated regression equation fitted the experimental data adequately.

The method of steepest ascent is employed for obtaining the optimum conditions and the various combinations of the factors are presented in Table 7. It can be seen from the table that the conversion increased to a maximum of 97.06% corresponding to experiment 18. The values corresponding to this experiment are the optimum values and are: mole ratio, 7.37; anhydrous sodium sulfate loading, 0.584 (stoichiometric); and purity, 95.85%.

Table 6. 2^3 full-factorial design.

| Run No. | Mole ratio | Sodium sulfate loading | % purity | Coded factors | | | |
				x_1	x_2	x_3	y, %
1	1	0	80	−1	−1	−1	42.08
2	1	0	97	−1	−1	1	58.00
3	1	stoichiometric	80	−1	1	−1	43.33
4	1	stoichiometric	97	−1	1	1	61.20
5	8	0	80	1	−1	−1	57.21
6	8	0	97	1	−1	1	84.77
7	8	stoichiometric	80	1	1	−1	59.46
8	8	stoichiometric	97	1	1	1	96.70
9	4.5	stoichiometric/2	88.5	0	0	0	59.04
10	4.5	stoichiometric/2	88.5	0	0	0	61.20
11	4.5	stoichiometric/2	88.5	0	0	0	61.60

Critical values: $t_{0.9}$ (2) = 3.18 ; $F_{0.1}$ (4,8) = 9.1.
Statistics for the coefficient: $s_y^2 = 1.896$; $s_{bi}^2 = 0.237$; $t \cdot s_{bi} = 1.548$.
Statistics for the model: $S_R^2 = 11.9$; $F_{exp} = 6.27$.

Table 7. Calculation of path of steepest ascent and subsequent trials.

	Mole ratio	sodium sulfate loading	% purity	y, %	Run No.
a) Base level	4.50	0.50	88.50		
b) Unit	3.50	0.50	8.50		
c) Estimated slope (from regression equation)	11.69	2.33	12.32		
d) (b) × (c)	40.92	1.17	104.7		
e) Change of level per 0.01 change of (d)	0.410	0.012	1.050		
f) Possible trails as per steepest ascent path	4.91	0.512	89.55	−	12
	5.32	0.524	90.60	75.60	13
	5.73	0.536	91.65	−	14
	6.14	0.548	92.70	83.40	15
	6.55	0.560	93.75	93.40	16
	6.96	0.572	94.80	96.44	17
	7.37	0.584	95.85	97.06	18
	7.78	0.596	96.90	96.63	19

Box-Wilson Composite Design

The optimum conditions obtained by the method of steepest ascent are close to the extremum. Hence in order to complement the previous results and to obtain the optimum conditions more accurately, the Box-Wilson composite design was chosen for optimization process (Akhnazarova and Kafarov, 1982). This design employs second order non-linear polynomials and the second order response surfaces lend themselves to systematization. The later property means that the extremum point can be detected with ease.

The star points in the present study are ($\pm\alpha$, 0, 0), (0, $\pm\alpha$, 0) and (0, 0, $\pm\alpha$) and the value of in the present case is 1.353. With the values on N and , the design matrix as shown in Table 8 was composed and the experiments were conducted accordingly. The responses were noted and are given in the last column of Table 8. To obtain an orthogonal matrix, the x_j^2 columns are linearly converted by:

$$x_j' = x_j^2 - (1/N) \Sigma x_{ji}^2 \qquad (12)$$

The values of the x_j' s thus obtained are given in Table 8. Since the design matrix is orthogonal, all the regression coefficients are determined independently and the responses are then fitted to a nonlinear model as follows:

$$y = 57.47 + 16.24x_1 + 3.12x_2 + 13.53x_3 + 1.22x_1x_2 + 1.45x_2x_3 + 3.88x_1x_3 - 5.63x_1^2 + 2.7x_2^2 + 10.34x_3^2 \qquad (13)$$

The significance of the regression coefficients are then tested by the t-test like earlier. For the t-test, the significance level chosen was 0.05 and the corresponding critical value is 3.18. The coefficients b_{12} and b_{23} are found to be insignificant. The nonlinear model after the elimination of the insignificant terms from the regression equation is as follows:

$$y = 57.47 + 16.24x_1 + 3.12x_2 + 13.53x_3 + 3.88x_1x_3 - 5.63x_1^2 + 2.7x_2^2 + 10.34x_3^2 \qquad (14)$$

The estimated second-order regression equation is analyzed to determine the coordinates of the optimum. The usual procedure in this case is to transform the second-order polynomial derived from the experimental data into a standard canonical equation:

$$\hat{y} - y_s = \lambda_{11}X_1^2 + \lambda_{22}X_2^2 + \lambda_{33}X_3^2 \qquad (15)$$

In order to reduce Equation (14) to the form of Equation (15), the regression equation is simplified by eliminating one of the variables. This is done by considering the variable, namely, anhydrous sodium sulfate loading, and its value at the optimum conditions (0.584) was taken from the previous results obtained in the method of steepest ascent. The simplified equation takes the following form:

$$y = 59.79 + 16.24 \ x_1 + 13.53 \ x_3 + 3.88 \ x_1 \ x_3 - 5.63 \ x_1^2 + 10.34 \ x_3^2 \qquad (16)$$

To transform this equation into canonical form, the coordinates of the response surface center are first calculated as follows:

$$\frac{\partial y}{\partial x_1} = 0 \quad \Rightarrow x_{1s} = 1.1429$$

$$\frac{\partial y}{\partial x_3} = 0 \quad \Rightarrow x_{3s} = 0.8689 \qquad (17)$$

The characteristic polynomial is given by:

$$P_k (\lambda) = \lambda^2 - 4.71 \ \lambda - 61.98 = 0 \qquad (18)$$

The roots of the polynomial are $\lambda_1 = 10.5723$ and $\lambda_2 = -5.8623$. The canonical form of the equation is:

$$\hat{y} - 63.19 = 10.57 X_1^2 - 5.86 X_3^2 \qquad (19)$$

Table 8. The Box-Wilson composite design matrix.

x_0	x_1	x_2	x_3	x_1'	x_2'	x_3'	y, %
1	-1	-1	-1	0.3141	0.3141	0.3141	42.08
1	-1	-1	1	0.3141	0.3141	0.3141	58.00
1	-1	1	-1	0.3141	0.3141	0.3141	43.33
1	-1	1	1	0.3141	0.3141	0.3141	61.20
1	1	-1	-1	0.3141	0.3141	0.3141	57.21
1	1	-1	1	0.3141	0.3141	0.3141	84.77
1	1	1	-1	0.3141	0.3141	0.3141	59.46
1	1	1	1	0.3141	0.3141	0.3141	96.70
1	1.353	0	0	1.1447	-0.6859	-0.6859	70.80
1	-1.353	0	0	1.1447	-0.6859	-0.6859	00.00
1	0	1.353	0	-0.6859	1.1447	-0.6859	57.20
1	0	-1.353	0	-0.6859	1.1447	-0.6859	44.10
1	0	0	1.353	-0.6859	-0.6859	1.1447	86.50
1	0	0	-1.353	-0.6859	-0.6859	1.1447	42.78
1	0	0	0	-0.6859	-0.6859	-0.6859	59.04
1	0	0	0	-0.6859	-0.6859	-0.6859	61.20
1	0	0	0	-0.6859	-0.6859	-0.6859	62.60

Now the response surface is a hyperbolic paraboloid (Figure 11). On passing planes of constant value, y = constant through the response surface, hyperbolas (Figure 12) are obtained. The linear transformation is given by:

$$X_1 = 0.119x_1 + 0.993x_3 \text{ and} X_2 = -0.993x_1 + 0.119x_3 \qquad (20)$$

Starting at the minimax point and moving along the axis X_1 (the canonical form coefficient is positive), X_3 being equated to zero, the maximum conversion is obtained:

$$X_1 = \sqrt{\frac{y - 63.19}{10.57}}, \qquad X_3 = 0 \qquad (21)$$

As the quantity "y" increases, one checks to see that the condition $x_1 = x_3 \leq 1.35$ is satisfied. Thus the maximum conversion obtained is 97.1% corresponding to $x_1 = 1.36$ and $x_3 = 0.9096$. The maximum conversion obtained by this method is the same as that obtained by the full-factorial search.
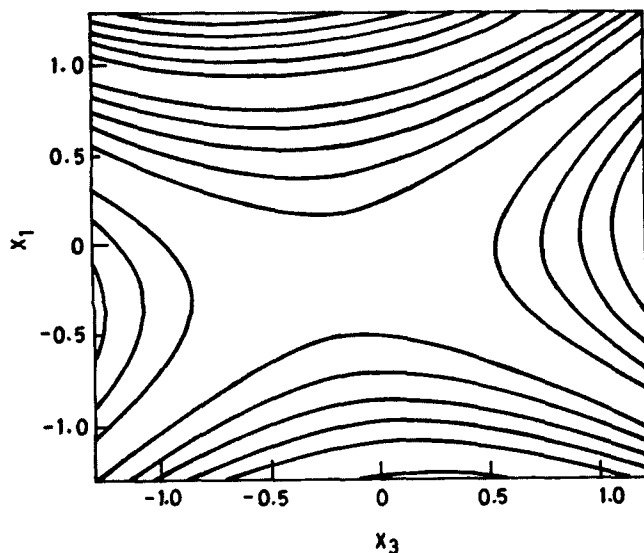

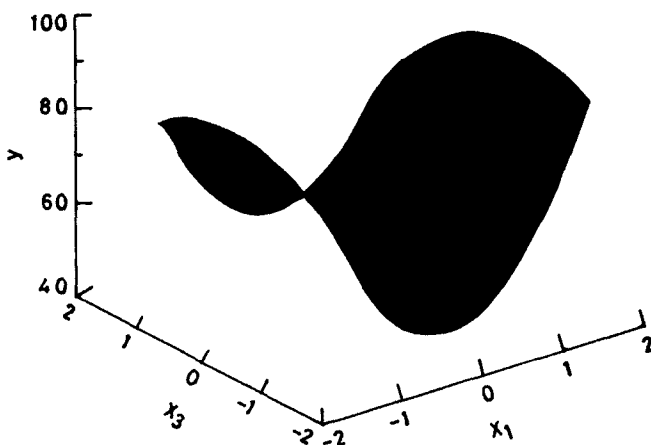**Figure 11.** Hyperbolas of equal yield.

Figure 12. Response surface generated using Equation (20).

Conclusions

A method for the manufacture of diethyl sulfate of better yield has been identified by employing an adsorbing agent. Reactive adsorption has been found to enhance conversion in the system studied. Anhydrous sodium sulfate appears to be a suitable adsorbing agent. The kinetics of the reaction is elucidated and a suitable mechanism is proposed. The parameters of the kinetic model have been estimated. The optimum conditions are obtained by full factorial search and these results are complimented with Box-Wilson composite method. The optimum values by canonical analysis of the response surface are: mole ratio = 9.2; purity = 96%; and sodium sulfate loading = 0.584 of the stoichiometric requirement. The conversion corresponding to these conditions is 97.1%.

Appendix

The various steps involved in the evaluation of the true concentrations of the various species in the reaction mixture is outline below:

1. At time $t = 0$, the number of moles of sulfuric acid (N_{A0}) and alcohol (N_{B0}) present in the reaction mixture is first calculated by multiplying their respective concentrations with the initial volume (V_0) of the reaction mixture. The initial number of EHS (N_{C0}) and water (N_{D0}) are taken as equal to zero. Even though minute quantities of water are present initially, it is assumed that anhydrous sodium sulfate adsorbs the water immediately.

2. Moles of alcohol reacted $= N_{B0} - N_B$
   = moles of sulfuric acid reacted
   = moles of EHS formed
   = moles of water formed

3. Moles of water present = moles of EHS present at time t_i – [moles of water lost at time t_i due to adsorption at time t_{i-1} + moles of water lost between time t_{i-1} and t_i]

4. The volume of the reaction mixture (V) at any instant is then calculated by using the following equation: $V = V_0$ – [moles of water lost up to that instant] $\times 18$.

5. The concentrations of the various species is then calculated by dividing the respective moles by the volume of the reaction mixture.

6. Finally, the conversion of sulfuric acid (X_A) is calculated using the relation $X_A = (N_{A0} - N_A)/N_{A0}$

Nomenclature

A	frequency factor, $[\text{s}^{-1} \cdot (\text{mol/m}^3)^{1-n}]$
b_0, b_1, b_2, b_3	regression coefficients
b_{12}, b_{13}, b_{23}	regression coefficients
b_{11}, b_{22}, b_{33}	regression coefficients
C_{A0}, C_{B0}	initial concentration of sulfuric acid and ethanol respectively, (mol/m^3)
C_A, C_B, C_C, C_D	concentration of sulfuric acid, ethanol, ethyl hydrogen sulfate and water respectively, (mol/m^3)
E_a	activation energy, (kJ/mol)
F	Fisher's variance ratio
F_D	rate of adsorption, (mol/min)
k	rate constant, $[\text{s}^{-1} \cdot (\text{mol/m}^3)^{1-n}]$
k_1	rate constant for the forward reaction, $[\text{s}^{-1} \cdot (\text{mol/m}^3)^{1-n}]$
k_2	rate constant for the reverse reaction, $[\text{s}^{-1} \cdot (\text{mol/m}^3)^{1-n}]$
K	equilibrium constant

M	initial mole ratio of ethanol and sulfuric acid
N	number of experiments according to the design matrix
N_A, N_B, N_C, N_D	number of moles sulfuric acid, ethanol, ethyl hydrogen sulfate and water, respectively
$N_{AO}, N_{BO}, N_{CO}, N_{DO}$	initial number of sulfuric acid, ethanol, ethyl hydrogen sulfate and water, respectively
p	$2[1-(1/K)] C_C$
r	$[-(C_{A0} + C_{B0}) - \{(C_{A0} + C_{B0})^2 - 4(C_{A0} \cdot C_{B0}) [1-(1/K)]\}^{1/2}]$
s	$[-(C_{A0} + C_{B0}) + \{(C_{A0} + C_{B0})^2 - 4(C_{A0} \cdot C_{B0}) [1-(1/K)]\}^{1/2}]$
S_{bi}^2	sample variance
S_R^2	error mean square for all points
S_y^2	error mean square at the center point of the matrix
t	time, (min)
T	temperature, (K)
V	volume of the reaction mixture at any time, (mL)
V_0	initial volume of the reaction mixture, (mL)
X_A	conversion of sulfuric acid, (%)
X_{Ae}	equilibrium conversion of sulfuric acid, (%)
X_1, X_2, X_3	canonical variables
x_1, x_2, x_3	coded factors for mole ratio, anhydrous sodium sulfate loading and purity of the reactants
y	yield of ethyl hydrogen sulfate, (%)
y_p	predicted yield, (%)
y_s	predicted response at the centre point of the surface

Greek Symbols

α	star arm of Box-Wilson composite design
λ_1, λ_2	Eigen values of the characteristic polynomial
$\lambda_{11}, \lambda_{22}, \lambda_{33}$	Canonical form coefficients

Abbreviation

MR	mole ratio

References

Akhnazarova, S. and V. Kafarov, "Experiment Optimization in Chemistry and Chemical Engineering", Mir Publishers, Moscow, Russia (1982), pp. 151–189.

Chaudhuri, S.K. and M.M. Sharma, "Absorption of Ethylene in Concentrated Sulfuric Acid", Ind. Eng. Chem. Res. 30, 339–345 (1991).

Deno, N.C. and M.S. Newman,"Mechanism of Sulfation of Alcohols", J. Am. Chem. Soc. 72, 3852–3856 (1956).

Dunnicliff, H.B. and G.S. Butler, "Ethyl Hydrogen Sulfate", J. Chem. Soc. 119, 1384–1393 (1921).

Kraft, M.Ya. and F.V. Lyutina, "Action of Chlorosulfurous Esters on Alkylsulfuric Acid", J. Gen. Chem. USSR. 32, 3429–3430 (1962).