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Articles

Reaction of Glyoxal with Aliphatic Alcohols Using Cationic Exchange Resins as Catalysts

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Abstract:
The applicability of cationic exchange resins, such as Indion 130, Amberlyst-15, and Amberlite IR-120, as catalysts was evaluated for the reactions of glyoxal with different aliphatic alcohols to give mono- and diacetals. The alcohols studied in the present work were methanol, *n*-butanol, isoamyl alcohol, and 2-ethylhexanol. In all cases, the presence of water in the reaction mixture was found to have a strong impact on the equilibrium conversion and the reaction kinetics. The removal of water results in a significant enhancement in the conversion levels. Reaction parameters such as mole ratio of reactants, temperature, and catalyst loading were studied to maximize the selectivity towards the industrially more important product, *i.e.*, monoacetals of glyoxal. Experimental data for the batch reactions of methanol are very well explained by a simple pseudohomogeneous model. A simplified lumped parameter model, consisting of four parameters, based on the Langmuir−Hinshelwood−Hougen−Watson mechanism, has been proposed for the reactions of glyoxal with less reactive alcohols (*n*-butanol, isoamyl alcohol, and 2-ethylhexanol), as the effect of water concentration on the kinetics of these reactions cannot be explained by a pseudohomogeneous model.

Introduction

Reaction of alcohols with glyoxal, in the presence of acid catalysts, results in various products such as mono- and diacetals of monomeric, dimeric, and trimeric glyoxal and glycolates. Their yields depend on the conditions employed while the reaction is being carried out. Out of these products, the monoacetal of glyoxal, *i.e.*, 2,2-dialkoxyethanal, has been found to be an important intermediate in the synthesis of various industrial organic compounds, as it possesses double functionality due to a free aldehyde group and an acetal group which can be conveniently converted back to the aldehyde under certain conditions.[1,2] The monoacetals, apart from their role in organic syntheses, also find application as cross-linking agents for cellulosic materials as substitutes for formaldehyde, which is not favoured due to health reasons. Hence, the present work was undertaken to study, in detail, the reaction kinetics of acetalization of glyoxal with different aliphatic alcohols such as methanol, *n*-butanol, isoamyl alcohol and 2-ethylhexanol, particularly in the context of the selectivity with respect to the corresponding monoacetal.

The acetalization reaction is reversible and yields one molecule of water along with one molecule of monoacetal, and hence the equilibrium conversion and the rate of reaction in the forward direction are strongly affected by the presence of water in the reaction mixture. This problem is further compounded by the fact that commercial glyoxal is available in the form of its aqueous solution (40% w/w). Hence, in order to obtain higher conversions, especially in the case of the less reactive alcohols like *n*-butanol, isoamyl alcohol, and 2-ethylhexanol, simultaneous removal of water during the course of the reaction may be essential. It is always desired to have a high conversion level in the reaction of glyoxal, as unreacted glyoxal is difficult to separate from the reaction mixture by conventional separation techniques like distillation.

Cationic exchange resins, especially the macroporous resins such as Indion-130 and Amberlyst-15 as catalysts, have the ability to work in both polar and nonpolar media. These catalysts have gained considerable importance because of various engineering benefits they offer over the homogeneous acid catalysts such as sulfuric acid and *p*-toluenesulfonic acid (PTSA).[3,4] Hence, in the present work, the performance of such resins was assessed for the acetalization reactions of glyoxal wherein, because of the simultaneous removal of water, dielectric properties of the reaction mixture are likely to vary significantly, as the reaction proceeds.

Previous Studies

The observation that glyoxal readily reacts with alcohols in the presence of acid catalyst to form the corresponding diacetals and glycolates is well documented in the literature.[5] It has been reported that, under certain conditions, higher molecular weight products are also formed in the reaction. These products come from the dimeric and trimeric forms

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* Author to whom correspondence should be addressed.

(1) Blanc, A.; Wilhelm, D.; Calbot, B. *Perform. Chem.* **1994**, April/May, 43.

(2) Blanc, A.; Wilhelm, D.; Calbot, B. *Spec. Chem.* **1995**, 53.

(3) Chakrabarti, A.; Sharma, M. M. *React. Polym.* **1993**, *20*, 1.

(4) Sharma, M. M. *React. Polym.* **1995**, *26*, 3.

(5) *Glyoxal*; Societe Francaise Hoechst Product Information Brochure, 1994; p 9.

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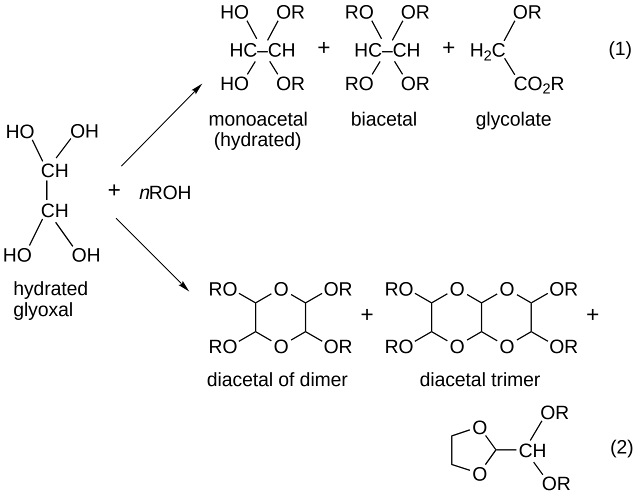
Scheme 1



of glyoxal. These forms of glyoxal are always in equilibrium with monomeric glyoxal and exist in high proportions at high concentrations of glyoxal.[6] Kliegman and co-workers[7−9] have identified various products resulting from the reaction of glyoxal with different alcohols such as ethanol, *n*-butanol, 2-ethylhexanol, and allyl alcohol in the presence of a homogeneous acid catalyst like PTSA. They have not reported the formation of the monoacetal of glyoxal which may form by acetalization of only one of the two carbonyl groups of glyoxal.

Blanc and co-workers[1,2,10,11] have investigated this reaction to obtain the monoacetal with high selectivity. The homogeneous as well as heterogeneous acid catalysts such as H_2SO_4, $ZrSO_4{\cdot}4H_2O$, and sulfonic resin have been successfully used for these reactions. The monoacetal of glyoxal, according to them, is formed selectively with a high conversion level if a large excess of alcohol is used for the reaction. Very recently, a patent has been taken by SFH[12] for a continuous process to manufacture dimethoxyethanal from methanol and aqueous glyoxal solution.

The previous studies, particularly those for the synthesis of glyoxal, encouraged us to investigate these reactions in detail for the effect of different parameters and to perform some modelling work to get a better insight into its kinetic and thermodynamic aspects.

Mechanism of Reaction

The acid-catalyzed addition of alcohol on glyoxal as mentioned in the previous section, yields various products represented by eqs 1 and 2 (Scheme 1).

The reaction mechanism for acetalization of a carbonyl compound such as glyoxal involves formation of an intermediate compound called a hemiacetal. Hemiacetal possesses functional groups of both an ether and an alcohol attached to the same carbon atom. It is formed by the nucleophilic addition of an alcohol molecule to a carbonyl group, which in the presence of acid catalyst acquires a positive charge. The hemiacetal then subsequently reacts with a second molecule of alcohol to form a monoacetal of glyoxal (*i.e.*, di-*n*-alkoxyethanal). Here, the hydroxyl group of the hemiacetal gets etherified in the presence of acid catalyst. The mechanism is shown in Figure 1. Similarly, diacetal (1,1,2,2-tetraalkoxyethane) is formed by acetalization of the second carbonyl group of the glyoxal molecule. Acetalization of the dimer and trimer of glyoxal should follow the same mechanism.

In the presence of heterogeneous catalysts such as ion exchange resins, all the steps mentioned above take place on the surface of the resin particle, if the reaction medium is sufficiently nonpolar. In a polar medium such as water, the resin is believed to dissociate, thereby releasing protons, which results in reaction occuring in the liquid medium present in the pore volume.[13]

Table 1. **Physical properties of ion exchange resin used in the present work**

	catalyst		
physical properties	Amberlyst-15	Indion-130	Amberlite IR-120
shape	beads	beads	beads
size (mm)	0.5	0.55	0.5
internal surface area (m^2/g)	55	*a*	*a*
wt capacity (mequiv of H^+/g)	4.7	4.8	4.4
cross-linking density (% DVB)	20−25	*a*	8
porosity (%)	36	*a*	*b*
temp stability (K)	393	403	393

[a] Data not available. [b] Not applicable.

Experimental Section

Materials. Glyoxal (40% w/w aqueous solution), methanol, *n*-butanol, isoamyl alcohol, 2-ethylhexanol, and solvent *n*-hexane were obtained from s.d. Fine Chemicals Pvt. Ltd. Indion 130 was obtained from Ion Exchange Ltd., and Amberlite IR-120 and Amberlyst-15 were obtained from Fluka. The physical properties of the cation exchange resins are given in Table 1. Since water constitutes a major proportion of the reaction mixture, drying of macroporous resins prior to their use was not necessary. Amberlite IR-120, a gel type resin which is available with a substantial moisture content (40−45% w/w), was dried at 373 K for 6 h under vacuum (1−2 mmHg) prior to its use.

Apparatus and Procedure. *Reactions in the Batch Mode.* All the reactions of glyoxal with methanol and some with *n*-butanol, isoamyl alcohol, and 2-ethylhexanol were carried out in the batch mode. A 1×10^{-4} m^3 capacity autoclave (Parr Instruments) with 0.05 m i.d., equipped with an automatic temperature controller, was used for this purpose. The working volume of the reactor was typically

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(6) Profile: Glyoxal Chemistry—Properties and potential uses of a versatile crosslinking agent. *Hoechst High Chem Magazine* **1994**, 40.

(7) Kliegman, J. M.; Whipple, E. B.; Ruta, M.; Barnes, R. K. *J. Org. Chem.* **1972**, *37* (8), 1276.

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(10) Blanc, A.; Hemadi-Sangsari, F.; Chastrette, F. Eur. Pat. EP 249,530, 1986; *Chem. Abstr.* **1988**; *109*, 22537.

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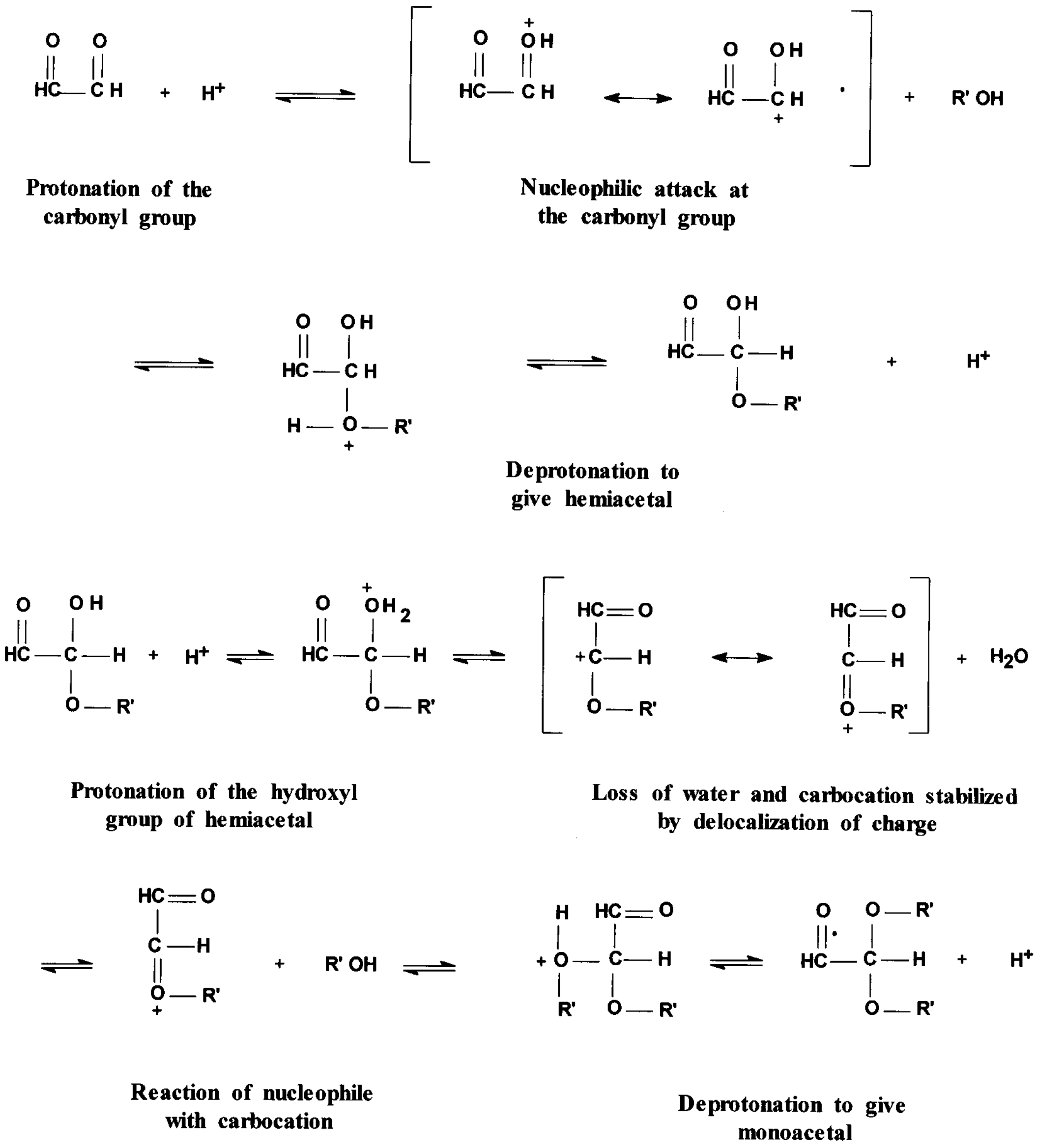

Figure 1. **Mechanism of monoacetalization of glyoxal.**

around 8 × 10^{-5} m^3, and 0.2−0.5 mL samples were withdrawn six to seven times during the course of the reaction.

Reactions with Water Removal. A majority of the reactions of *n*-butanol, isoamyl alcohol, and 2-ethylhexanol were carried out in a fully baffled agitated glass reactor of capacity 1 × 10^{-4} m^3, equipped with a stuffing box and cooling water condenser. A six-bladed glass disc turbine was used for agitation. A Dean and Stark apparatus was used for the removal of water during the course of reaction. The condensate collected in the Dean and Stark trays contained no compound other than alcohol, water, and solvent, if any.

Analysis. Glyoxal concentration can be determined by reacting a known volume of sample with a known amount of standard sodium hydroxide solution (intramolecular Cannizzaro reaction) and titrating the reaction mixture with standard oxalic acid using phenolphthalein as an indicator.[5] Alcohols and products (*e.g.*, mono- and diacetals) were analysed on a gas chromatograph (Chemito 8510, Toshniwal Brothers, Pvt. Ltd., India) fitted with a flame ionization detector. A 4 m × 3.175 × 10^{-3} m i.d. stainless steel column packed with 10% OV-17 on Chromosorb was used for the analysis. The temperature of the oven was programmed as 388 K for 60 s at a ramp rate of 0.5 K/s up to 658 K for 480 s for the reactions of *n*-butanol, isoamyl alcohol, and 2-ethylhexanol whereas, for the reactions with methanol, analysis was carried out at constant oven temperature, *i.e.*, 378 K. Nitrogen was used as a carrier gas at a flow rate of 4.1 × 10^{-7} m^3/s. The conversion values obtained by chemical analysis and that calculated by GC analysis match with slight deviation.

Results and Discussion

Glyoxal, when reacted with alcohol according to the procedure described in the previous section with a sufficiently high alcohol:glyoxal mole ratio (~10:1), gives only two products, and these were mono- and diacetals of monomeric glyoxal.

The profiles of conversion *vs* time for the batch reactions with different alcohols are shown in Figure 2. The selectivity towards the monoacetal in all the batch reactions, at moderate temperatures (~353 K) was substantially high (>92%). However, quantitative conversion of glyoxal was never

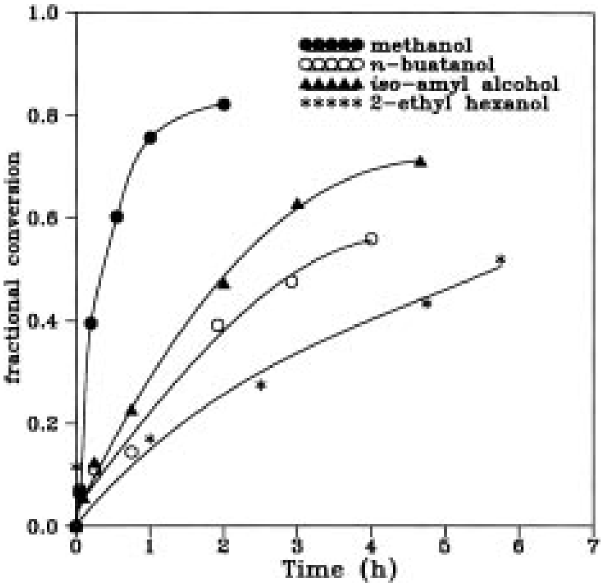

Figure 2. **Batch reactions of glyoxal with different alcohols: catalyst, Indion-130 (10% w/w); mole ratio (alcohol:glyoxal), 10:1; temperature, 353 K.**

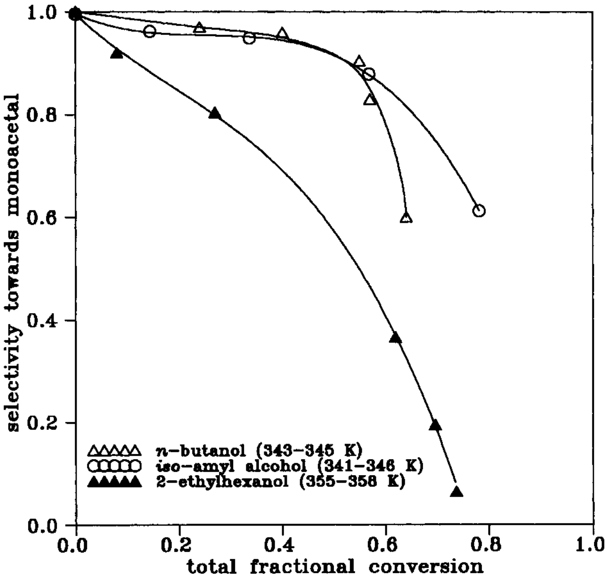

Figure 3. **Reaction of glyoxal with alcohols with simultaneous water removal: catalyst, Indion-130 (10% w/w); mole ratio (alcohol:glyoxal), 10:1.**

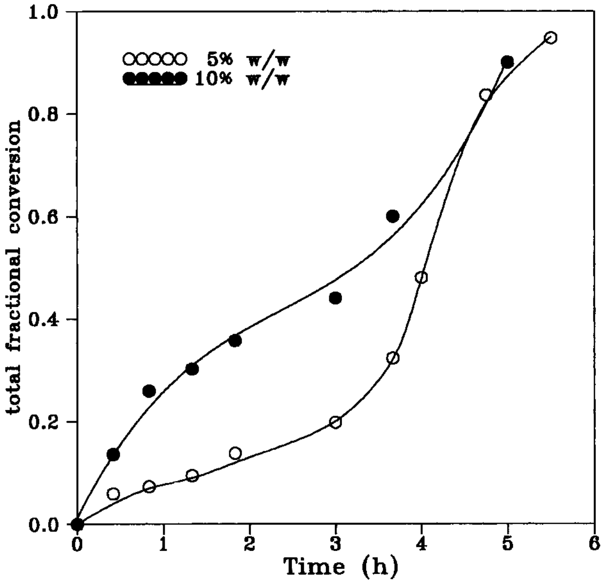

Figure 4. **Effect of catalyst loading on the reaction of glyoxal with *n*-butanol with simultaneous water removal: catalyst, Indion-130; temperature, 353 K; mole ratio (alcohol:glyoxal), 10:1; average rate of water removal, 680 g·mol/h·m^3.**

obtained if glyoxal was used in the form of 40% w/w aqueous solution. It is evident from Figure 2 that methanol is the most reactive of all the alcohols studied. The rates of the reactions for less reactive alcohols such as *n*-butanol, isoamyl alcohol, and 2-ethylhexanol were very low without simultaneous water removal. Hence, in order to enhance the rate of these reactions, water was removed from the reaction mixture during the course of the reaction.

In all the reactions with simultaneous water removal, it was observed that conversion to monoacetal increases up to a certain reaction time and then decreases due to the formation of the diacetal of glyoxal, thereby resulting in a decline in the selectivity toward the monoacetal. In the absence of any solvent, the boiling temperature of the reaction mixture rises as the reaction proceeds (*e.g.*, 370−395 K in the reaction with *n*-butanol). However, when solvents such as *n*-hexane were used, the temperature of the reaction mixture was nearly constant.

It was observed that the conversion *vs* time and selectivity *vs* conversion plots for the reactions of both *n*-butanol and isoamyl alcohol, carried out under identical conditions, match with slight deviation, as shown in Figure 3. Hence, it can be concluded that the reactivities of both the alcohols are almost equal under the conditions employed. Though significant rates were realised for the reaction of 2-ethylhexanol with glyoxal, the selectivity obtained toward the corresponding monoacetal in this case was least among all the alcohols.

The effect of different parameters on profiles of conversion and selectivity was studied and is discussed in the following sections.

Effect of Speed of Agitation. Reactions were carried out over a wide range of speed of agitation (8−18 rps), and it was found that, beyond 15 rps, the conversion and selectivity are independent of the speed of agitation. Hence, all the runs were carried at 15 rps to ensure that there was no resistance to external mass transfer at the solid−liquid interface. It was also ensured that at moderate catalyst loading (<10% w/w) attrition of the resin particles did not take place at this speed of agitation.

Effect of Catalyst Loading. The reactions in the batch and semibatch modes were studied over a wide range of catalyst loading, *i.e.*, from 1.5% (w/w) to 20% (w/w). It was observed that in the batch mode the rate increases significantly as catalyst loading increases. However, beyond 10% w/w loading, the enhancement in the rate was not appreciable.

In the reactions with simultaneous water removal at lower catalyst loading, the rate of the reaction in the initial period was less than that at higher catalyst loading, as shown in Figure 4. However, as time proceeds, even in the case of low catalyst loading, the rate increases and the conversion level nearly matches the conversion at higher catalyst loading. This increase in the rate at lower catalyst loading

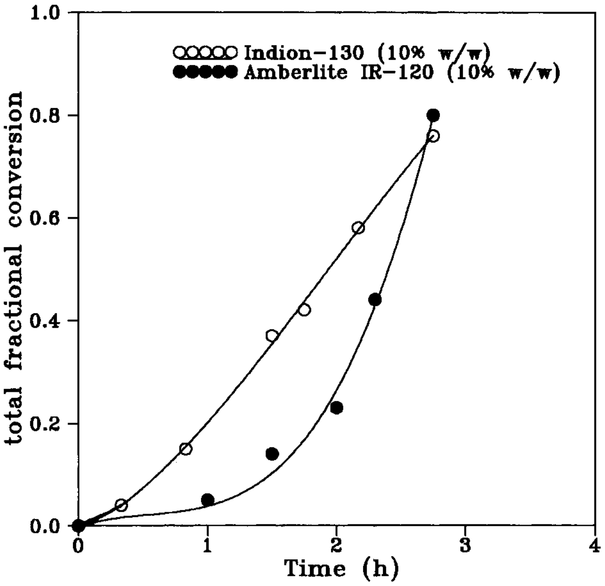

Figure 5. **Effect of type of catalyst on the reaction of glyoxal with *n*-butanol: mole ratio (alcohol:glyoxal), 7.5:1; average rate of water removal, 1000 g·mol/h·m^3.**

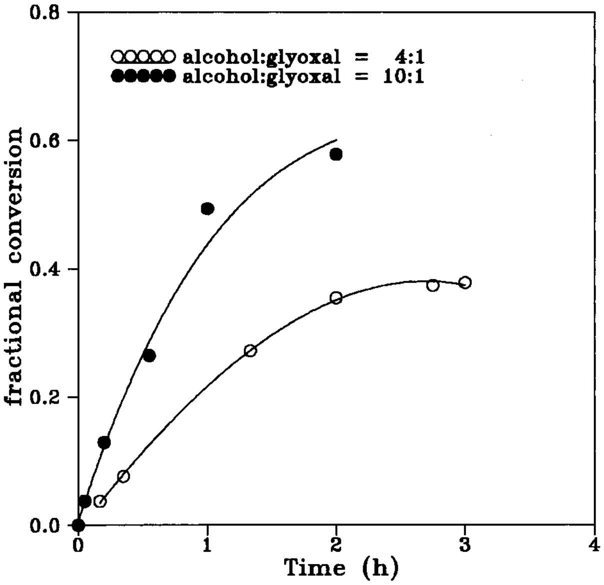

Figure 6. **Effect of mole ratio on the reaction of glyoxal with methanol: catalyst, Indion-130 (10% w/w); temperature, 343 K.**

can be attributed to the simultaneous water removal, which after a certain limit strongly dominates the adverse effect due to low catalyst loading. In this period rapid formation of diacetal takes place, leading to almost complete conversion of glyoxal.

Effect of Type of Catalyst. The reaction was carried out using ion exchange resins having different properties. In all the reactions, macroporous resins, *i.e.*, Indion-130 and Amberlyst-15, which have almost similar properties (refer to Table 1), exhibit similar performance with respect to the overall rate and selectivity.

The gellular resin Amberlite IR-120 and macroporous resins offered almost equal rates for the reactions of methanol whereas, in the case of the reactions of nonpolar alcohols, it was observed that in the initial period the overall rate of the reaction with Amberlite IR-120 was lower than that with the macroporous resins, as shown in Figure 5. This result can be attributed to the sluggish response of gellular resins to the nonpolar system because of poor swelling. The reactive system consisting of less reactive alcohols is comparatively less polar than that in the case of the reaction with methanol.

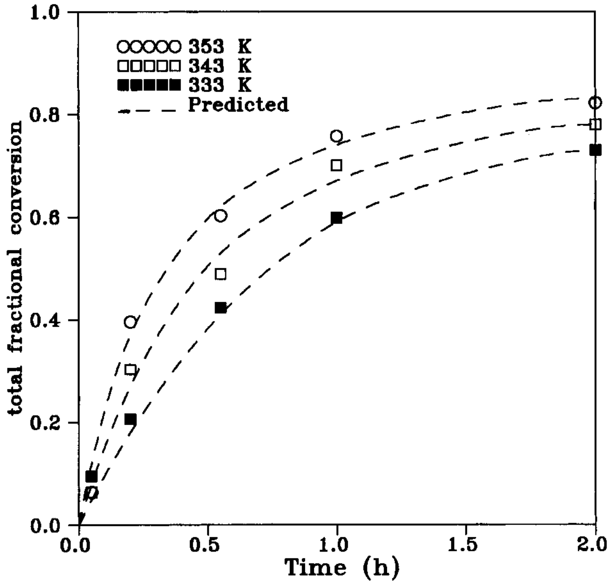

Figure 7. **Experimental and predicted profiles for the reaction of glyoxal with methanol: mole ratio (alcohol:glyoxal), 10:1; catalyst, Indion-130 (10% w/w).**

Effect of Mole Ratio. The overall rate of the reaction and equilibrium conversion with respect to glyoxal were found to increase with an increase in mole ratio, as is shown in Figure 6 for the reaction of methanol with glyoxal. It was observed that, at higher alcohol:glyoxal mole ratios (>8:1), monoacetal can be obtained selectively. This observation is in agreement with that reported by Stambouli *et al.*[11] At lower mole ratios, formation of the acetal of dimer was found to take place, as has been reported by Kliegman *et al.*,[7] who used PTSA as catalyst for the same reaction. Hence, subsequent reactions were carried out with a 10:1 alcohol:glyoxal mole ratio.

Effect of Temperature. Reactions of methanol with glyoxal in the batch mode were carried out in the temperature range 333−353 K, and it was observed that the rate of reaction increases with an increase in temperature (see Figure 7). The selectivity with respect to monoacetal in the batch reactions was found to decrease slightly with an increase in the reaction temperature.

The effect of temperature on the reactions of *n*-butanol, isoamyl alcohol, and 2-ethylhexanol, with simultaneous water removal, can be studied by deliberately adding an external solvent, thereby maintaining the boiling temperature of the reaction mixture at a lower level. Hence, reactions were carried out using *n*-hexane as a solvent wherein, instead of an alcohol−water azeotrope, water was removed from the reaction mixture along with *n*-hexane. The volume of the reaction mixture was maintained at a constant level by the continuous recycling of *n*-hexane. It was observed that the selectivity obtained at lower reaction temperature was significantly high (>90%) even at a high conversion level (~80%), as shown in Figure 8 for the reaction of glyoxal with *n*-butanol. At higher temperature, *i.e.*, in the absence of solvent, a sharp decline in the selectivity was observed

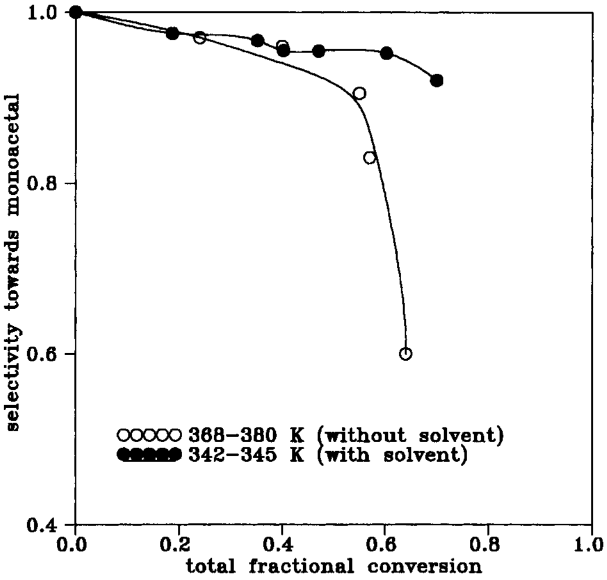

Figure 8. **Effect of temperature on the reaction of glyoxal with *n*-butanol: catalyst, Indion-130 (10% w/w); mole ratio (alcohol: glyoxal), 10:1; average rate of water removal, 800 g·mol/h·m^3.**

Table 2. **Regressed values of the parameters for the reaction of glyoxal with different alcohols**

regressed parameter	glyoxal and methanol (333 K)	glyoxal and *n*-butanol (343–345 K)	glyoxal and isoamyl alcohol (343–346 K)	glyoxal and 2-ethylhexanol (355–358 K)
Kf$_1$	3.4×10^{-2}	6.74×10^{-2}	1.15×10^{-1}	1.24×10^{-1}
Kb$_1$	4.4×10^{-2}	1.09×10^{-1}	1.29×10^{-1}	5.56×10^{-1}
Kf$_2$	8.5×10^{-3}	8.14×10^{-3}	2.12×10^{-2}	2.65×10^{-1}
Kb$_2$	1.4×10^{-1}	1.95×10^{-1}	5.02×10^{-1}	1.18×10^{-1}

[a] Kf$_1$ = k_1, Kb$_1$ = k_2, Kf$_2$ = k_3, Kb$_2$ = k_4 for methanol (pseudohomogeneous model). Kf$_1$ = $k_1K_GK_A^2/K_W$, Kb$_1$ = k_2K_M, Kf$_2$ = $k_3K_MK_A^2/K_W$, Kb$_2$ = k_4K_D for *n*-butanol, isoamyl alcohol, and 2-ethylhexanol (LHHW model).

after a certain conversion level; during this reaction period the boiling temperature of the reaction mixture (without solvent) increases rapidly, as was already discussed.

Effect of Rate of Water Removal. The average rate of water removal was varied in the range 600–1500 g·mol/h·m^3 of reactor. It was found that, with an increase in the rate of water removal, total reaction time was reduced without much change in the plot of conversion *vs* selectivity. The overall rate of reaction was found to be a linear function of rate of the water removal in the range studied.

Effect of Initial Concentration of Water in the Reaction of Methanol. Reactions of methanol were carried out at different initial concentrations of water in the reaction mixture with the same alcohol:glyoxal; mole ratio 40–80% (w/w) aqueous solutions were used as the sources of glyoxal. The rate and equilibrium conversion increase significantly with a decrease in the initial concentration of water. When 80% w/w glyoxal was reacted with methanol in the presence of Indion-130 (10% w/w) and a 10:1 alcohol:glyoxal mole ratio at 343 K, 80% conversion of glyoxal was realized in 0.5 h compared to 30% conversion obtained with 40% w/w glyoxal in the same period under otherwise similar conditions. Hence, to attain maximum conversion, dehydrated glyoxal may be used for the reactions of methanol.

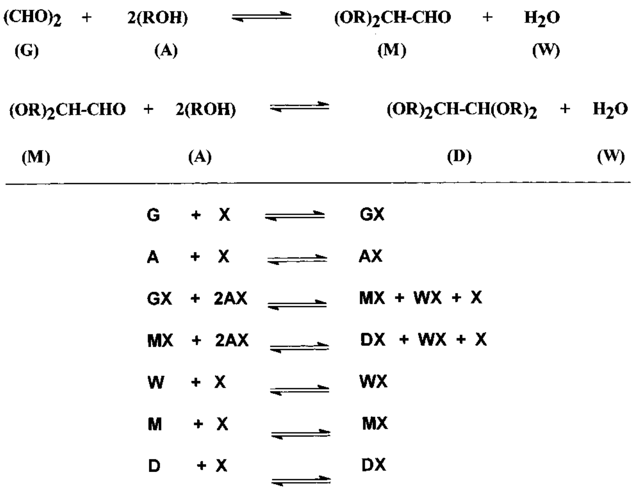

Figure 9. **Langmuir–Hinshelwood–Watson mechanism for acetalization of glyoxal.**

Kinetic Modelling

Reactions of Methanol in the Batch Mode. A simple pseudohomogeneous model can be applied to the reactive system consisting of sufficiently polar compounds such as methanol, water, glyoxal, and corresponding acetals. In this mechanism, resin can be assumed to exist in the dissociated form and reaction is catalysed by the protons which form an electrical double layer near the resin surface. The rate expression in this case is directly written in terms of the solution concentrations of the components involved. Hence, the depletion in the concentration of glyoxal is given by

$$C_{G_o}\frac{dx_1}{dt} = k_1C_GC_A^{\ 2} - k_2C_MC_W \tag{3a}$$

$$C_{G_o}\frac{d(x_1+x_2)}{dt} = k_3C_MC_A^{\ 2} - k_4C_DC_W \tag{3b}$$

$$C_G = C_{G_o}(1 - x_1 - x_2) \tag{4a}$$

$$C_A = C_{G_o}(R - 2x_1 - 4x_2) \tag{4b}$$

$$C_M = C_{G_o}x_1 \tag{4c}$$

$$C_D = C_{G_o}x_2 \tag{4d}$$

$$C_W = C_{W_o} + C_{G_o}(x_1 + 2x_2) - \zeta t \tag{4e}$$

where the k's, the parameters of the proposed pseudohomogeneous model, represent the apparent rate constants. ζ is the average rate of water removal, and its value is equal to 0 for the batch reactions. The values of the rate constants were regressed by a least-squares method. Rosenbrock's optimisation technique was used for minimising the objective function. The values of parameters thus obtained are given in Table 2. A match between the predicted profiles based on the regressed values of the parameters and the experimental results is shown in Figure 7. Apparent values of activation energies for the monoacetalization of glyoxal with methanol are 41.2 and 56.1 kJ/g·mol for forward and backward reactions, respectively.

Reactions of Less Reactive Alcohols. The profiles of conversion *vs* time for mono- and diacetals in the case of

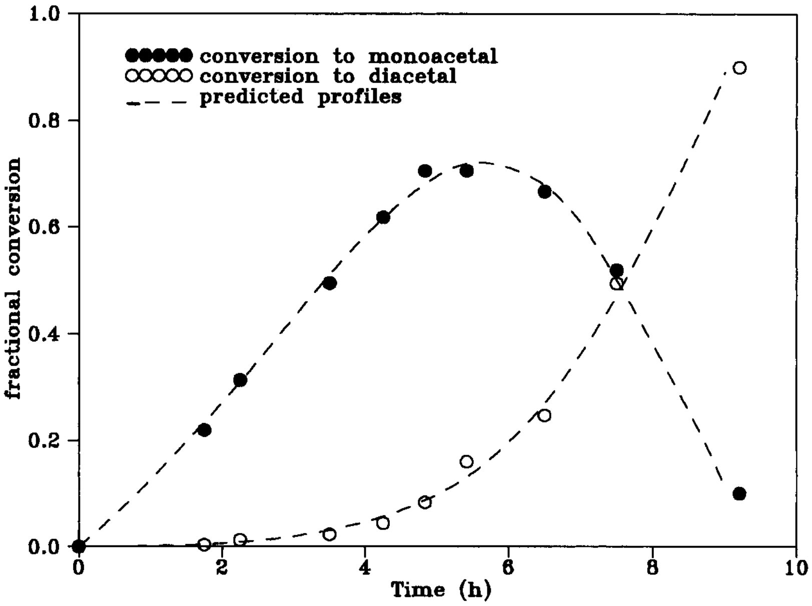

Figure 10. **Comparison of experimental and predicted profiles for the reaction of glyoxal with *n*-butanol: catalyst, Indion-130 (10% w/w); solvent, *n*-hexane; temperature, 343−345 K; average rate of water removal, 333 g·mol/h·m^3; mole ratio (alcohol: glyoxal), 10:1; initial concentration of water, 2.5 × 10^3 g·mol/m^3.**

the reactions with water removal indicate that the path followed by the reaction kinetics is strongly influenced by the presence of water and its concentration in the reaction mixture. This behaviour of the reactive system cannot be just explained by a simple pseudohomogeneous model, and hence it was thought necessary to propose a model based on the Langmuir−Hinshelwood−Hougen−Watson (LHHW) mechanism for heterogeneous catalysis. The mechanism assumes that the reactants adsorb on the surface of solid catalyst and the reaction takes place between the adsorbed reactant species on the surface. The rate of the reaction depends on the activity of the adsorbed species and the surface rate constants. The different steps involved in this mechanism are shown in Figure 9. The rate expressions which indicate the change in the conversion of glyoxal to mono and diacetal with respect to time can be obtained as follows:

$$C_{G_o}\frac{dx_1}{dt} = \frac{k_1K_GK_A^{\,2}C_GC_A^{\,2} - k_2K_MK_WC_MC_W}{(1 + K_WC_W + K_AC_A + K_GC_G + K_MC_M + K_DC_D)^3} \tag{5a}$$

$$C_{G_o}\frac{d(x_1+x_2)}{dt} = \frac{k_3K_MK_A^{\,2}C_MC_A^{\,2} - k_4K_DK_WC_DC_W}{(1 + K_WC_W + K_AC_A + K_GC_G + K_MC_M + K_DC_D)^3} \tag{5b}$$

where K represents the adsorption coefficient of the corresponding species. ζ, the average rate of water removal per unit volume of reactor, is obtained experimentally as follows:

$$\zeta = \frac{\text{(amount of total water removed in gram moles)}}{\text{(reaction time)} \times \text{(reaction volume)}} \tag{6}$$

The value of ζ was maintained constant and the slight deviation, especially in the beginning and at the end of reaction, was taken into account while the model equations were solved. Equations 5a and 5b consist of nine parameters, the values of which can be regressed with the help of a least-squares method. However, it was observed that, because of the large number of parameters and the nonlinear objective function, multiple solutions (*i.e.*, multiple sets of parameters) were obtained. It was also observed that in the nine-parameter model the predicted profiles were sometimes insensitive to the values of one or more than one parameter. Hence, it was thought to be essential to reduce the number of parameters by making some valid assumptions. The original LHHW model was thus simplified to a four-parameter model as follows.

The numerator and denominator of eqs 5a and 5b were divided by K_W, and since water has a strong affinity towards the resin sites, the value of K_W is expected to be quite high compared to the values of all other adsorption coefficients. Hence, $1/K_W$, K_M/K_W, K_G/K_W, K_D/K_W, and K_A/K_W can be neglected from the denominator terms. Equations 5a and 5b can then be reduced to the following form:

$$C_{G_o}\frac{dx_1}{dt} = (k_1K_GK_A^{\,2}/K_W)C_GC_A^{\,2}C_W^{\,-3} - (k_2K_M)C_MC_W^{\,-2} \tag{7a}$$

$$C_{G_o}\frac{d(x_1+x_2)}{dt} = (k_3K_MK_A^{\,2}/K_W)C_MC_A^{\,2}C_W^{\,-3} - (k_4K_D)C_DC_W^{\,-2} \tag{7b}$$

The model equations 4a−e and 7a,b represent a simplified (lumped parameter) model based on the LHHW mechanism consisting of four parameters. Activity coefficients of different compounds were determined with the help of the UNIFAC method, and it was found that the coefficients of any of the compounds do not change significantly over the entire reaction period. For instance, in the reaction of glyoxal with *n*-butanol, the values of activity coefficients of different compounds are the following: water, 2−2.06; glyoxal, 1.02−1.08; alcohol, 0.97−1.01; monoacetal, 0.91−0.94; diacetal, 0.71−0.77. Hence, the activity coefficients were also lumped into the parameters. The differential equations were solved

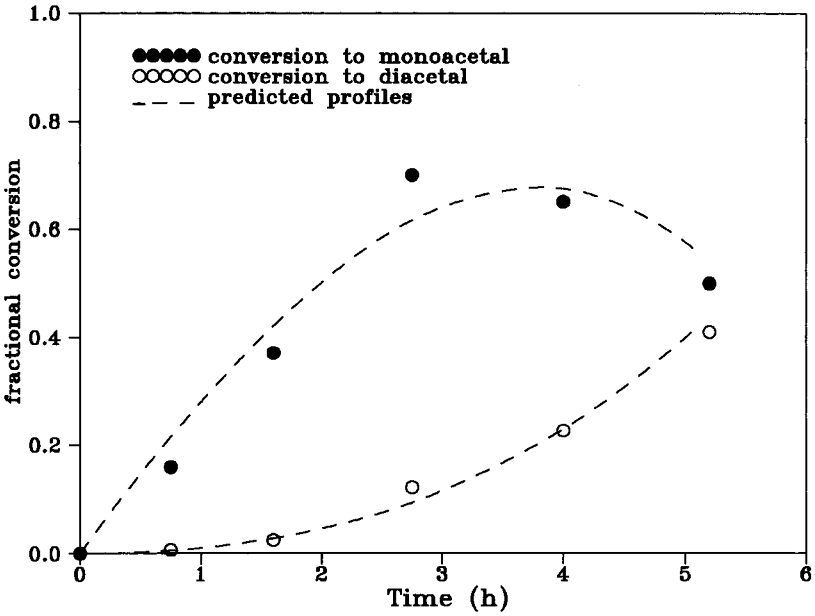

Figure 11. **Comparison of experimental and predicted profiles for the reaction of glyoxal with isoamyl alcohol. Catalyst, Indion-130 (10% w/w); solvent, *n*-hexane; temperature, 343−346 K; average rate of water removal, 670 g·mol/h·m^3; mole ratio (alcohol: glyoxal), 10:1; initial concentration of water, 2.25 × 10^3 g·mol/m^3.**

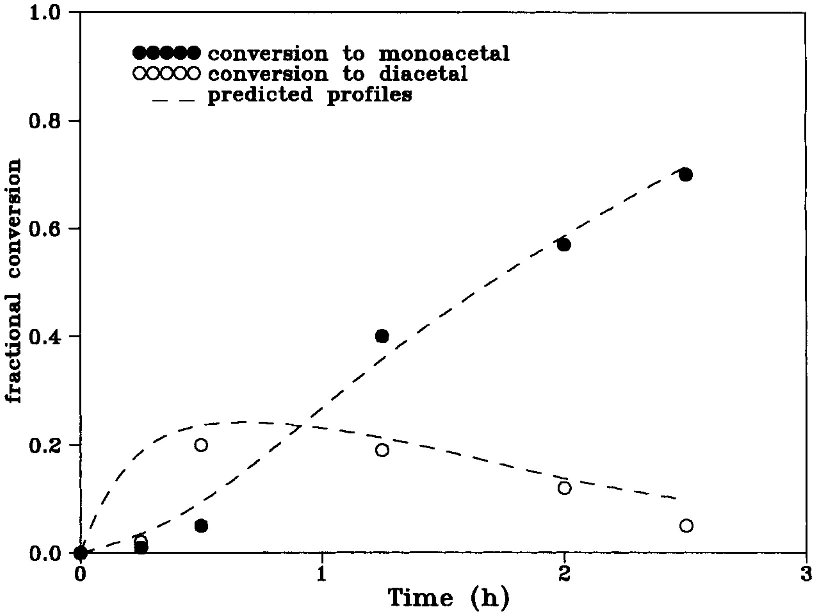

Figure 12. **Comparison of experimental and predicted profiles for the reaction of glyoxal with 2-ethylhexanol: catalyst, Indion-130 (10% w/w); solvent, *n*-hexane; temperature, 355−358 K; average rate of water removal, 670 g·mol/h·m^3; mole ratio (alcohol: glyoxal), 10:1; initial concentration of water, 1.25 × 10^3 g·mol/m^3.**

simultaneously using a fourth-order Runge Kutta method, and the values of the lumped parameters were regressed with the help of a least squares method.

Table 2 gives the values of the regressed parameters. Figures 10−12 show the experimental and predicted profiles of conversions *vs* time for the reactions with the respective alcohols.

This model also very well explains the kinetics of the batch reactions of the less reactive alcohols, carried out at the same temperature. The model equations, when solved by substituting $\zeta = 0.0$ and the respective values of parameters given in Table 2, predict the profiles for batch reaction with slight deviation from the experimental data.

Conclusion

The macroporous as well as gel type resins can be successfully employed for the monoacetalization of glyoxal with methanol at high mole ratios of alcohol to glyoxal (>8: 1) and in the temperature range 333−343 K. Simultaneous removal of water during the course of reaction is not necessary if the initial concentration of water in the reaction mixture is sufficiently low.

The monoacetalization of glyoxal with comparatively less reactive alcohols such as *n*-butanol, isoamyl alcohol, and 2-ethylhexanol needs simultaneous water removal in order to obtain sufficiently high conversion and reaction rates. However, with water removal, selectivity towards the monoacetal decreases significantly as the reaction proceeds.

Macroporous resins with 10% w/w catalyst loading offer satisfactory performance from both conversion and selectivity points of view. The reaction should be carried out in the presence of a volatile solvent such as *n*-hexane so as to bring down the reaction temperature, which enhances the selectivity with respect to the corresponding monoacetal. In the reactions of 2-ethylhexanol with simultaneous water removal, selectivity was lower than that obtained with *n*-butanol or isoamyl alcohol.

NOMENCLATURE

C	concentration (g·mol/m^3)
K	adsorption coefficient ((g·mol/m^3)$^{-1}$)
k	apparent surface rate constant ((g·mol/m^3)$^{-2}$ h^{-1})
R	mole ratio (alcohol:glyoxal)
t	time (h)
x_1	conversion to monoacetal
x_2	conversion to diacetal

Greek Letters

ζ	rate of removal of water per unit volume of reactor (g·mol/h·m^3)

Subscripts

A	alcohol
D	diacetal
G	glyoxal
M	monoacetal
o	initial concentration
W	water

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