Kinetic and Thermodynamic Study of the Liquid-Phase Etherification of Isoamylenes with Methanol

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The kinetics and thermodynamics of liquid-phase etherification of isoamylenes with methanol on ion exchange catalyst (Amberlyst 15) were studied. Thermodynamic properties and rate data were obtained in a batch reactor operating under 1013 kPa and 323–353 K. The kinetic equation was modeled following the Langmuir–Hinshelwood–Hougen–Watson formalism according to a proposed surface mechanism where the rate-controlling step is the surface reaction. According to the experimental results, methanol adsorbs very strongly on the active sites, covering them completely, and thus the reaction follows an apparent first-order behavior. The isoamylenes, according to the proposed mechanism, adsorb simultaneously on the same single active center already occupied by methanol, migrating through the liquid layer formed by the alcohol around the catalyst to react in the acidic site. From the proposed mechanism a model was suggested and the kinetic and thermodynamic parameters were obtained using nonlinear estimation methods.

Introduction

The most important oxygen-containing compound used today as an octane booster for gasoline blends is methyl *tert*-butyl ether (MTBE). The worldwide increasing interest in its production in the last decade has been pushed by new environmental regulations for better unleaded gasoline (Prezelj, 1987; Lange et al., 1985). On the other hand, the high cost associated with MTBE production by using C4 dehydrogenation units and the trend toward lower vapor pressure components within gasoline have spurred development of other ethers as potential additives. In particular, there is a more aggressive move toward the C5 analogs *tert*-amyl methyl ether (TAME), which exhibits a vapor pressure lower than that of MTBE. Many observers see the emergence of more TAME units in United States following the move to limit the olefin content of gasoline (Royse, 1992).

Since the etherification of isoamylenes to TAME production is a relatively new process, there are few published works concerning its kinetic and thermodynamic properties (Randriamahefa et al., 1988; Krause and Hammarstrom, 1987), which will be the subject of this work.

Fundamentals of the Reactions

TAME is formed by the reaction of 2-methyl-1-butene (2M1B) or 2-methyl-2-butene (2M2B) with methanol on an acidic catalyst where a carbocation is the same intermediate for both reactions (March, 1985) (see Scheme 1). The reaction is reversible and fairly exothermic. In industry it is performed in liquid phase on sulfonic acid resins. The operating conditions and equipment design are very similar to that of the MTBE process (Iborra et al., 1992; Cavados and Almeida, 1985; Baratella et al., 1981; Trevale and Buzze, 1981).

The need for a molecular mechanism to describe the reaction and a surface mechanism for the adsorption–

Scheme 1
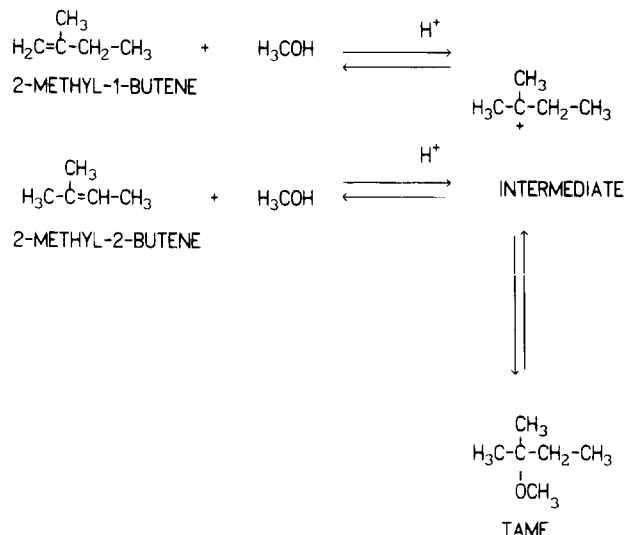
desorption steps on the catalyst surface is quickly apparent when deriving kinetic models. To develop the kinetic expression, a model is required to relate the rate and amount of adsorption to the concentration of the component of the fluid in contact with the surface (Froment and Bischoff, 1990). That is the basis of the Hougen–Watson methodology, widely employed to formulate rate equations, which will be proposed for this etherification reaction.

Experimental Section

Materials. The reagents utilized in this work were a C5 cut from the naphtha steam cracking unit of COPESUL (Cia Petroquimica do Sul, Brazil), according to the composition shown in Table 1, and methanol PA grade (>99.5% pure, <0.1% water). The catalyst was the sulfonic ion exchange resin Amberlyst 15 from Rohm and Hass, and its properties are listed in Table 2.

Apparatus. The experimental setup consisted of a 1 L steel stirred batch reactor. An outer jacket was provided for circulating water to keep the reaction

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Table 1. Composition of the C5 Cut

component	concn (w/w, %)	component	concn (w/w, %)
C4 components	0.48	2-pentene	17.26
isopentane	8.94	cyclopentene	25.40
n-pentane	15.53	isoprene	0.19
cyclopentane	4.96	1,3-pentadiene	0.22
3-methyl-1-butene	0.49	cyclopentadiene	1.19
2-methyl-2-butene	16.95	C6 components	0.64
2-methyl-1-butene	6.23	water	400 ppm
1-pentene	1.53	sulfur	1.0 ppm

Table 2. Properties of Amberlyst 15

skeleton	styrene−divinylbenzene
structure	macroporous
active group	sulfonic
maximum temperature operation (K)	393
surface area[a] (m^2/g)	43
porosity[a] (%)	53
capacity[b] (mequiv/g)	4.8
mean pore diameter (Å)	240
particle diameter (mm)	0.7
degree of cross-linking (%)	20

[a] From Iborra et al. (1992). [b] Determined by the method of Fischer and Kunin (1955).

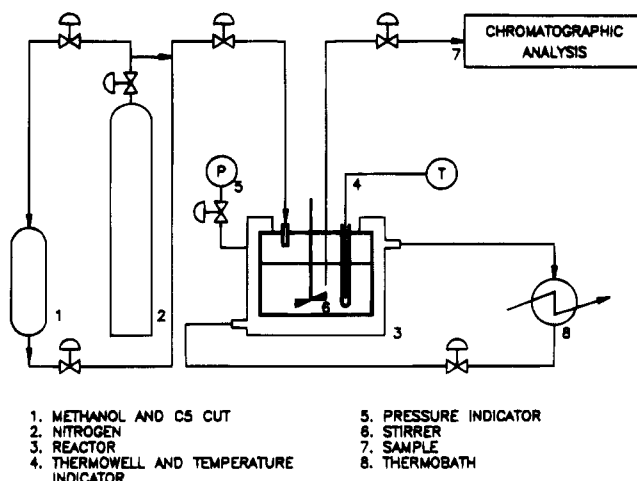**Table 3. Conditions of the Tests and Range of Variables**

agitation speed (rpm)	200
catalyst loading (g)	16, 32, and 48
temperature (K)	323, 333, 343, and 353
pressure (kPa)	1013
molar ratio methanol/ isoamylenes	1.0, 1.3, and 3.0

medium at constant temperature. The reaction temperature was monitored with a thermocouple inside a metallic well according to Figure 1. The conditions for the tests are listed in Table 3.

It was observed from previous experiments (Lovisi and Piccoli, 1992) that the 200 rpm agitation speed gives sufficient turbulence to avoid external mass transfer resistances. On the other hand, the agitation speed should not be too high in order to avoid damage of the catalyst particle, which could obstruct the chromatograph.

Analysis. A Hewlett-Packard gas chromatograph HP5890 equipped with a capillary methyl silicone column (film thickness 0.33 μm with 50 m length and 0.02 mm diameter) and a FID detector was utilized for the analysis of the reaction products. The temperature of the sample injection was constant at 303 K with the oven kept at this level for 9 min. After this time the oven was programmed to increase the temperature at a rate of 10 K/min to 373 K. After 20 min at this temperature all the important components have passed through the column. High-purity Hydrogen (99.9999%) was the carrier gas with a flow rate through the column of 0.6 cm³/min and a 70:1 split ratio. Response factors were determined for methanol, TAME, and hydrocarbons in order to obtain quantitative results.

Procedure. The catalyst (0.7 mm particle diameter) was dried at 373 K for 24 h and cooled in a desiccator for 1 h. A sample of the catalyst was charged to the reactor and the system purged with Nitrogen and heated to the desired temperature. The liquid reagents (C5 cut, methanol) were mixed in a separate, auxiliary vessel (without catalyst) and heated to the reaction temperature. This mixture was then added to the reactor under 1013 kPa nitrogen pressure. Stirring started immediately. The first sample was withdrawn just before charging the reagents to the reactor and the second one just after contact of the reagents with the

1. METHANOL AND C5 CUT
2. NITROGEN
3. REACTOR
4. THERMOWELL AND TEMPERATURE INDICATOR
5. PRESSURE INDICATOR
6. STIRRER
7. SAMPLE
8. THERMOBATH

Figure 1. Experimental setup.

catalyst. Other samples were withdrawn in defined times in order to have a plot of conversion versus time.

The rate of the reaction was calculated from the C5 concentration. The kinetic data were analyzed via integral procedures. To avoid further difficulties in the calculation, the experiments for kinetic studies were performed far from chemical equilibrium at the conditions given in Table 3. Care was taken to ensure that no significant amount of product was stripped from the system for the analysis, avoiding experimental errors.

Results and Discussion

Preliminary experiments were performed to study the adsorption of methanol on the catalyst. It was observed that methanol adsorbs strongly over the catalyst, which suggests a Langmuir−Hinselwood−Hougen−Watson (LHHW) model (Froment and Bischoff, 1990). It is known that water adsorbs more strongly than methanol and can inhibit its reaction (Ancilotti et al., 1977, 1978) and for this reason the water content in the reactants was kept below 0.1% to minimize this inhibition effect. The analysis indicated 2M1B to be much more reactive than 2M2B, which was already observed by Krause and Hammarstrom (1987). Byproducts were not observed in significant amounts, indicating the high selectivity of the catalyst for this etherification.

Effect of Methanol Concentration. This work confirms the assertion of some authors (Ancillotti et al., 1977; Gates and Johnson, 1971) that methanol has little influence on the etherification rate (pseudo first order) since it adsorbs strongly on the catalyst, having a very high adsorption constant. According to the mechanism proposed here methanol completely covers the active sites solvating the sulfonic group and forming a methanol liquid layer around the active site. The isoamylenes should migrate through that "methanol layer" to react on the same acidic site already occupied by methanol. In that case, the influence of the methanol concentration is no longer felt and the reaction follows a first-order mechanism.

Thermodynamic Equilibrium. 2M1B is much more reactive than 2M2B and the equilibrium constants for 2M1B are also higher than for 2M2B. The difference in reactivity occurs due to the easier protonation of the less stereohindered double bond of 2M1B. The thermodynamic equilibrium constants are obtained by using eq 1, when the reactions reach chemical equilibrium (Smith and Van Ness, 1980). The equations should be

Table 4. Activity Coefficients Calculated by UNIFAC Method at 1013 kPa

	molar fraction in equilibrium (×1000)				activity coeff (UNIFAC)				equil const (UNIFAC)	
T (K)	x_{2M1B}	x_{2M2B}	x_{MeOH}	x_{TAME}	γ_{2H1B}	γ_{2H2B}	γ_{MeOH}	γ_{TAME}	K_{eq_1}	K_{eq_2}
323	5.9	70.0	29.0	174	1.05	1.05	9.43	1.09	112.0	9.44
	4.6	58.0	58.0	183	1.07	1.07	7.56	1.04	88.2	6.99
	4.6	52.0	75.0	195	1.08	1.08	6.87	1.02	70.9	6.27
333	6.1	65.0	67.0	167	1.07	1.07	6.97	1.03	58.1	5.46
	7.8	83.0	33.0	162	1.05	1.05	8.97	1.08	69.5	6.53
	7.5	80.0	35.0	158	1.05	1.05	8.82	1.08	70.2	6.58
343	3.9	39.0	309	132	1.42	1.42	2.55	0.93	29.0	2.90
	7.0	71.0	98.0	151	1.09	1.09	5.81	1.00	34.8	3.43
	7.4	73.0	86.0	151	1.08	1.08	6.22	1.01	35.7	3.62
	7.2	73.0	84.0	148	1.08	1.08	6.32	1.01	36.2	3.57
	8.0	79.0	68.0	150	1.07	1.07	6.88	1.03	38.6	3.91
	9.2	91.0	44.0	137	1.05	1.05	8.16	1.07	42.3	4.27
	9.1	91.0	42.0	150	1.05	1.05	8.09	1.07	49.4	4.94
353	12.0	106	47.0	145	1.05	1.05	7.89	1.07	27.0	3.06
	9.5	87.0	78.0	137	1.07	1.07	6.38	1.02	27.6	3.02
	9.3	85.0	98.0	145	1.08	1.08	5.78	1.00	23.2	2.54
	4.8	45.0	351	128	1.50	1.50	2.24	0.97	21.9	2.34
	9.4	85.0	98.0	150	1.09	1.09	5.71	1.00	24.2	2.68
	10.3	97.0	48.0	125	1.05	1.05	7.74	1.06	33.0	3.50

utilized for each isoamylene separately.

$$K_{eq} = \frac{a_{TAME}}{a_{iC5}a_{Me}} = \frac{(x\gamma)_{TAME}}{(x\gamma)_{iC5}(x\gamma)_{Me}} \quad (1)$$

$$K_{eq} = K_x K_\gamma \quad (2)$$

where γ_i is the activity coefficient of component i and K_{eq} is the equilibrium constant.

The UNIFAC method (Gmehling et al., 1982) was utilized to calculate the value of the liquid activity coefficients of all compounds according to the same procedure utilized by Colombo et al., (1993), Delion (1985), Safranov et al. (1989), and Gicquel (1981, 1983). It was observed that, using eq 1 above, with γ_i predicted by UNIFAC, the values of the equilibrium constant (K_{eq}) obtained were not consistent. According to Table 4, K_{eq} decreases when the methanol molar fraction increases, for all tested temperatures. That experimental observation is not in good agreement with the thermodynamics. It was suggested that the lack of consistency of the K_{eq} values (calculated using γ_i from UNIFAC) was due to the methanol activity coefficient, which could be influenced by the ionic strength of the solution and by the strong adsorption of methanol on the acidic centers.

Considering the influence of the ionic strength of the acidic catalyst on the methanol properties and the strong adsorption of methanol on the active sites, the following empirical equation was suggested for the activity coefficient of methanol, at the conditions of the tests:

$$\gamma_{MeOH} = (x_{MeOH})^b \quad (3)$$

To check the mathematical consistency of this empirical equation, it is necessary to calculate the value of constant b. For a low methanol concentration (see Table 4), γ_{TAME} and γ_{iC5} are approximately constant and equal 1.0. As γ_{MeOH} were not measured, eq 3 was added to eq 1, and the following expression is obtained for the equilibrium constant of each reaction.

$$K_{eq} = K_x/(x_{MeOH})^b \quad (4)$$

where

$$K_x = x_T/x_{Me}x_{iC5} \quad (4a)$$

With some mathematical transformation of eq 4 the
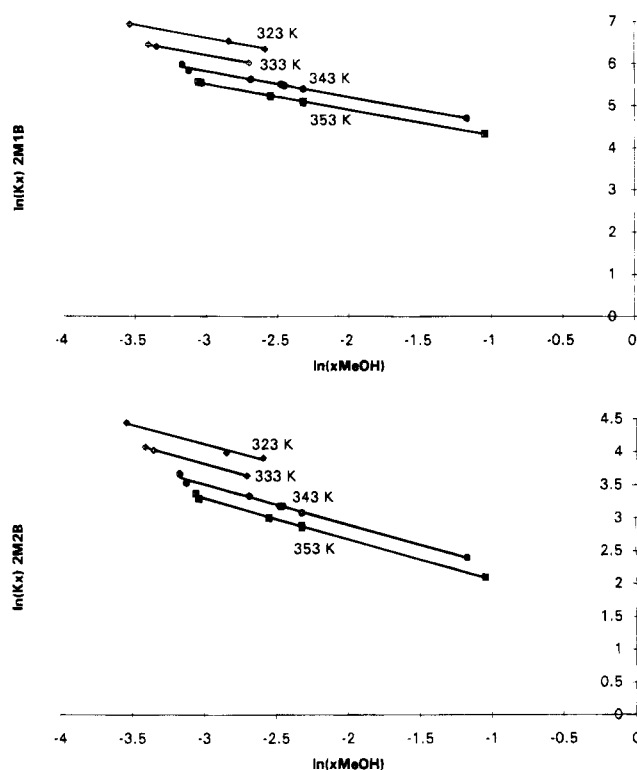
Figure 2. Logarithm of K_x versus logarithm of methanol fraction in solution (a, top) for 2M1B etherification and (b, bottom) for 2M2B etherification.

following expression is obtained:

$$\ln K_x = \ln K_{eq} + b \ln x_{MeOH} \quad (5)$$

where K_{eq} should be constant for all x_{MeOH}.

Plotting $\ln K_x$ against $\ln x_{MeOH}$, according to Figure 2, b is obtained from the angular coefficient and the equilibrium constants from the linear coefficient. By this methodology it was possible to calculate the value of the constant b and the values of the equilibrium constants knowing the composition of the reaction medium at equilibrium.

The value of the b was found to be -0.6 at 343 K. Values around -0.6 were also found for other temperatures (Figure 2). Equation 4 then becomes

$$K_{eq} = x_{TAME}/x_{iC5}(x_{Me})^{0.4} \quad (6)$$

Table 5. Equilibrium Constants Calculated by Using Equation 6 and Figure 2

T (K)	$K_{eq_{2M1B}}$	$K_{eq_{2M2B}}$
323	119 ± 6.5	10.7 ± 0.2
333	79.7 ± 1.0	7.5 ± 0.1
343	53.4 ± 4.1	5.3 ± 0.4
353	39.9 ± 1.2	4.2 ± 0.2

Equation 6 is valid for the conditions of the test. The equilibrium constants of each reaction, calculated by eq 6, are listed in Table 5. Using this methodology, the equilibrium constants for each studied temperature could be calculated precisely. The values of the equilibrium constants are consistent for all ranges of methanol/isoamylene studied, which indicates the goodness of fit of the methodology.

Reaction Enthalpy. The reaction enthalpy is obtained by applying the Van't Hoff equation (Smith and van Ness, 1975) to the data of Table 5.

$$\frac{d[\ln K_{eq}]}{d[1/T]} = -\frac{\Delta H_r^\circ}{R} \qquad (7)$$

The standard enthalpy variation of the two reactions in the liquid phase obtained (with a 95% confidence interval) from the angular coefficient of the straight line obtained from Figure 3 (van't Hoff plotting) is −8.7 ± 0.6 kcal/mol for the 2-methyl-1-butene and −6.8 ± 0.6 kcal/mol for the 2-methyl-2-butene etherification. From the same figure, the value of the standard reaction entropy is obtained, for a 95% confidence interval, by the linear coefficient, respectively, −17.4 ± 1.8 and −16.5 ± 1.9 cal/mol K (Smith and van Ness, 1975). The value of the entropy variation is negative because two molecules react to give only one, decreasing the degrees of freedom of the system.

The following equations are obtained from Figure 3, for both reactions, still considering the van't Hoff plotting:

$$\ln K_{eq_{2M1B}} = -8.64 + 4330/T \qquad (8)$$

$$\ln K_{eq_{2M2B}} = -8.10 + 3360/T \qquad (9)$$

Reaction Mechanism. In the liquid phase and with low methanol concentration the reaction occurs through a very quick concerted mechanism (Ancilotti et al., 1977; Gates and Rodrigues, 1973) with the reactant molecules adsorbing in four to six acidic centers (Gates and Rodrigues, 1973). The rate-controlling step is the reaction of the olefin with alcohol (Lovisi and Piccoli, 1992). In such a condition, the reaction is very fast (Ancillotti et al., 1977, 1978; Tejero, 1986; Tejero et al., 1987, 1988a, 1988b), however, side reactions such as isomerization and polymerization are favored.
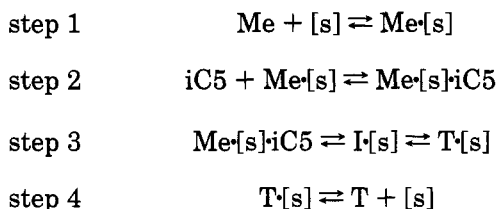
At high methanol concentration and high polarity of the solution (molar ratio methanol/isoamylene > 1.0), the hydrogen bondings of the sulfonic resin start a process of dissociation. The methanol molecules enter this hydrogen network completely dissociating and solvating the H⁺ ion. In that case, the reaction becomes catalyzed by the solvated proton, which has a lower catalytic activity than the sulfonic proton. In such an ionic mechanism the reaction is slower (Gates and Rodrigues, 1973), obeying an apparent homogeneous kinetics (Lovisi and Piccoli, 1992). The rate-controlling step is the protonation of the olefin, which generates a carbocation (Lovisi and Piccoli, 1992).

In the present work, the operating conditions are such that the ionic mechanism is predominant. Methanol
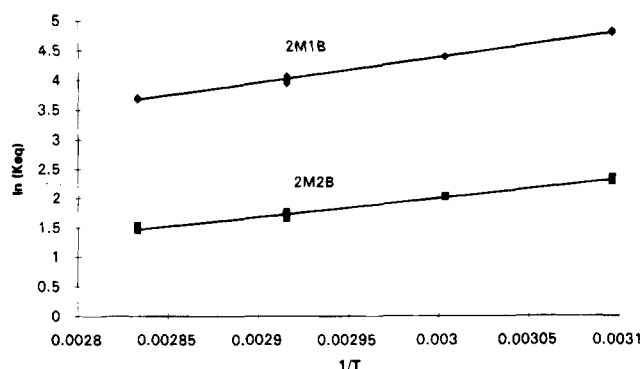
Figure 3. Van't Hoff plotting for the two etherifications.

forms a solvated layer around the catalyst site through which the isoamylene should migrate to adsorb on the same site already occupied by methanol. The reaction occurs by transference of an H⁺ ion to the double bond of the isoolefin forming an intermediate carbocation which is the same for each reaction.

The surface mechanism, which will be the basis of the kinetic equation, is proposed as follows:

step 1	$Me + [s] \rightleftharpoons Me{\cdot}[s]$
step 2	$iC5 + Me{\cdot}[s] \rightleftharpoons Me{\cdot}[s]{\cdot}iC5$
step 3	$Me{\cdot}[s]{\cdot}iC5 \rightleftharpoons I{\cdot}[s] \rightleftharpoons T{\cdot}[s]$
step 4	$T{\cdot}[s] \rightleftharpoons T + [s]$

where [s] is the active site and Me·[s] is the methanol adsorbed on the active site.

Kinetic Model. The strong adsorption of methanol on the catalyst suggests the Hougen−Watson formalism represents the kinetics (Froment and Bischoff, 1990). In order to propose a mechanism, it is necessary first to know the rate-determining step of the reaction in order to suggest the appropriate kinetic equation. It is clear that the adsorption of methanol on the acidic sites is not the rate-controlling step since it adsorbs strongly on the catalyst but permits the isoamylenes to adsorb and react on the same active site. No inhibition was experimentally observed due to its adsorption. In this case, the adsorption of the isoamylenes is not the rate-controlling step because the acidic sites of the resin are available for isoamylene coadsorption, according to the mechanism proposed. The diffusion of the isoamylenes through the methanol layer around the active sites is not the rate-controlling step because no influence of the agitation was observed on the reaction rate. It was also experimentally observed that the TAME product does not inhibit the reaction by obstruction of the active sites. We found its adsorption constant to be not mathematically significant. This means that step 4 (TAME desorption) is not the rate-controlling step either. The reaction is only thermodynamically limited by the equilibrium. We suggest that the rate-controlling step (for the conditions of the tests) is the surface reaction (step 3), also in accordance with the molecular mechanism proposed above where the solvated proton is effectively the catalyst.

The equation obtained by using the LHHW formalism, assuming the surface reaction as the rate-controlling step, is the following:

$$r = \frac{kK_{Me}C_{Me}(C_{iC5} - (C_T/K_{eq}'C_{Me}))}{1 + K_{Me}C_{Me} + (K_{Me}K_{iC5}C_T/K_{eq}') + K_TC_T} \qquad (10)$$

Table 6. Calculated Kinetic Constants for the Two Etherifications

T (K)	$k_{2M1B} \times 1000$ (s^{-1})	$k_{2M2B} \times 1000$ (s^{-1})
323	8.5 ± 0.2	0.72 ± 0.02
333	22 ± 0.8	2.1 ± 0.1
343	52 ± 1.2	5.4 ± 0.2
353	125 ± 1.5	13.4 ± 0.2

It was mathematically observed that the adsorption constants of isoamylenes (K_{iC5}) and TAME (K_T) were not significant while the methanol adsorption constant (K_{Me}) was very high. In that case, the equation can be simplified to

$$r = k(C_{iC5} - (C_T/K_{eq}' \, C_{Me})) \quad (11)$$

Now it is clear that the reaction is pseudo zero order in relation to methanol concentration. As can be easily observed, this rule is true only when the methanol concentration is not very low. When the methanol/isoamylene ratio is decreased, the polarity of the reaction medium decreases and the mechanism changes from the ionic to the concerted one.

Since the reaction takes place in the liquid phase, the activity coefficient of methanol has a very strong deviation from unity and it should be considered in the kinetic equation. The activity coefficient of the isoamylenes and TAME are approximately 1 (Table 4) and eq 11 becomes

$$r = k(C_{iC5} - (C_T/K_{eq}' x_{Me} \gamma_{Me})) \quad (12)$$

Combining this with eq 4, the following expression is obtained:

$$r = k(C_{iC5} - (C_T/K_{eq}' x_M^{0.4})) \quad (13)$$

The kinetic constants of the above model, fitted for several temperatures using nonlinear methods, are listed in Table 6. The results are in very good agreement with the experiments according to Figure 4, where points represent the experimental data and lines represent the simulation results.

The activation energy is obtained from the values of the kinetic constants at various temperatures, using the Arrhenius equation:

$$\ln k = \ln A - E_a/RT \quad (14)$$

The values obtained for the activation energy are 20.2 ± 0.6 kcal/mol for the 2-methyl-butene-1 and 22.1 ± 0.3 kcal/mol for the 2-methyl-butene-2 etherification.

In the reaction of these two olefins with methanol, the same intermediate compound is obtained and, of course, the same product TAME. This means that the difference between the two calculated activation energies should give the same value as the difference of the two reaction enthalpies.

$$E_{a_{2M1B}} - E_{a_{2M2B}} = \Delta H°_{r_{2M1B}} - \Delta H°_{r_{2M2B}} \quad (15)$$

The value obtained experimentally for the difference of activation energies was 1.90 kcal/mol whereas the difference of reaction enthalpies was 1.85 kcal/mol. The error is only ~2.8%. This shows that the experimental data are adequate and the parameters estimated are mathematically as well as physically consistent.

Byproducts. Byproducts were not observed in significant amounts, showing the high selectivity of the catalyst. It should be assured that no water is present in the system in order to avoid formation of *tert*-amyl
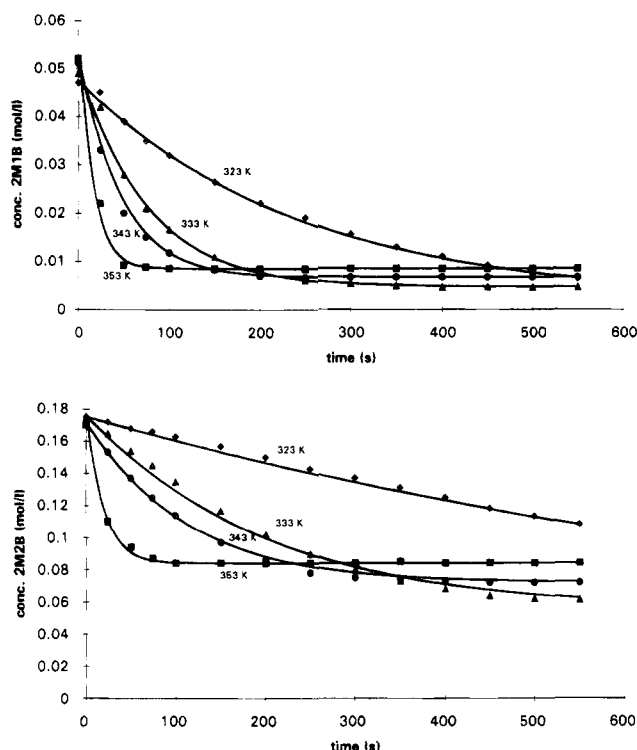
Figure 4. Experimental versus predicted data using eq 13 (a, top) for 2M1B etherification and (b, bottom) for 2M2B etherification.

alcohol (TAA). Water reacts with isoamylenes, but it is also adsorbed much more strongly on the catalyst surface than methanol. For this reason, TAA is formed only when water is present in low concentration in the feed (less than 1%). When the amount of water is high, the reaction is inhibited due to obstruction of the active centers. In that case, it is difficult for the isoamylenes to diffuse through the aqueous film around the active center. The dienes present in the C5 cut also react with methanol, producing ethers. They can also polymerize producing gum components. The best way to avoid this gum formation is by keeping the diene concentration in the feed below 0.1%. Operating conditions, mainly temperature, can increase this byproduct significantly.

Conclusions

Liquid-phase etherification of isoamylenes with methanol were studied at 1013 kPa in 323–353 K on the ion exchange resin Amberlyst 15. The large deviation from unity of the methanol activity coefficient and the strong adsorption of methanol on the catalyst are the most important factors that should be carefully considered when this reaction is studied. There is no previous work in the literature considering these phenomena. The ion exchange resin solvated by methanol is the main factor causing deviation in the thermodynamic properties. Analysis of the experimental data suggests that the best LHHW rate equation can be deduced from a reaction mechanism where methanol adsorbs on an acidic active center and the isoamylenes adsorb on the same site already occupied by methanol. In that case, the H$^+$ ion (from the sulfonic group) first protonate the methanol molecule. In a second stage, the H$^+$ is transferred to the isoamylene forming the intermediate complex which will generate the TAME molecule according to the classical nucleophilic mechanism. It is important to observe that the mechanism here proposed as well as the rate-controlling step, kinetics, and other properties

remain valid only for reaction in liquid phase with a molar ratio Methanol/Isoamylenes > 1. If the molar ratio is substoichiometric, the isoamylenes can adsorb alone on the acidic site and the mechanism will change considerably.

We conclude that sulfonic ion exchange resin is adequate for the TAME synthesis in liquid phase due to its high activity and selectivity. It is widely used for MTBE synthesis corroborating its useful properties. Byproducts as gum compounds should be controlled by C5 cuts free of dienes.

This work is complete in considering the TAME synthesis since it accounts for all important phenomena occurring in the reaction, giving the values for the thermodynamic and kinetic parameters.

Notation

A = coefficient of the Arrhenius equation
a = activity
b = empiric constant for the methanol activity coefficient
C5 = isoamylene
E_a = activation energy (kcal/kmol)
H^+ = ionized hydrogen (acidic proton)
$H_r°$ = standard reaction enthalpy (kcal/kmol)
I = intermediate carbocation
K_{eq} = equilibrium constant (m³/kmol)
K_{eq}' = modified equilibrium constant considering the total concentration of the solution (dimensionless)
K_j = adsorption equilibrium constant for component j in liquid phase
k = rate coefficient of the etherification (M$_T$/kg of cat s)
MeOH, Me = methanol
R = universal gas constant (kcal/kmol K)
r = rate of reaction per catalyst mass unit related to C5 consumption (kmol/kg of cat s)
[s] = active site
T = TAME
x = molar fraction

Greek Letters

γ = activity coefficient (liquid phase)

Subscripts

iC5 = isoolefin C5 (isoamylene)
MeOH or Me = methanol
2M1B = 2-methyl-1-butene
2M2B = 2-methyl-2-butene
TAME or T = *tert*-amyl methyl ether

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