Enhancing MTBE Rate Equation by Considering Reaction Medium Influence

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Rate data are reanalyzed for MTBE synthesis in the liquid phase at 318–363 K on the sulfonic macroporous resin Bayer K-2631. The data were obtained in a continuous upflow packed-bed reactor fed with isobutene (IB)-methanol (MeOH) mixtures with an IB/MeOH molar ratio ranging from 0.5 to 2.0. Rate equations based on LHHW and ER mechanisms do not predict rate data accurately, because of the influence of the reaction medium on the catalyst activity. A factor evaluating the resin-medium affinity has been introduced in the rate equations which, as a result, fit the data with a good agreement. Fitted parameters were the overall kinetic constant and the resin solubility parameter. The apparent activation energy agrees with the values quoted in the literature, and the resin solubility parameter and its temperature dependence are plausible.

Introduction

The synthesis of methyl tert-butyl ether (MTBE) is performed by the addition of methanol (MeOH) to isobutene (IB) in the presence of an acidic catalyst. Industrially, sulfonic macroporous ion-exchange resins are preferred as the catalyst and the reaction takes place in the liquid phase under mild conditions. The MTBE synthesis has been encouraged in order to obtain less polluting gasolines. It is a good octane enhancer, allowing the replacement of the tetraethyl lead content, and it reduces the carbon monoxide, hydrocarbon and evaporative emissions. In the early 1990s, MTBE production showed the highest growth rate of all major chemicals (Kirschner, 1996) and it is expected that this trend will continue (Absi-Halabi et al., 1997).

The literature is quite rich in kinetic studies for MTBE synthesis in the liquid phase. These studies were performed by using pure isobutene (Zhang and Datta, 1995), C_4 cuts (Ancillotti et al., 1977; Gicquel and Torck, 1983; Parra et al., 1994), and C_4-like streams (Ancillotti et al., 1978; Voloch et al., 1986; Rehfinger and Hoffmann, 1990) as the IB source. The reaction is mainly described as a heterogeneous catalytic one and rate equations are usually derived by the Langmuir-Hinshelwood-Hougen-Watson (LHHW) or Eley-Rideal (ER) formalisms (Gicquel and Torck, 1983; Rehfinger and Hoffmann, 1990; Parra et al., 1994; Zhang and Datta, 1995). Some authors, however, propose a pseudo-homogeneous model (Voloch et al., 1986; Panneman and Beenackers, 1995).

With the aim of finding a rate equation useful in a wide range of IB and MeOH concentrations, and as a consequence of the nonideality of the liquid phase, Rehfinger and Hoffmann (1990) performed their kinetic analysis in terms of the activities of the compounds that take part in the reaction. Recent work shows that the reaction system is more complex. Previous rate expressions (Rehfinger and Hoffmann, 1990; Parra et al., 1994) are quite inaccurate for IB/MeOH molar ratios ($R_{IB/MeOH}$) far from the stoichiometric one. Moreover, it has been realized that liquid-phase composition influences the reaction rate to some extent. Panneman and Beenackers (1995) discussed how forward rate constants vary with $R_{IB/MeOH}$. In a recent article (Fité et al., 1998), we have found better fits to rate data when the solubility parameter of the reaction medium is included as an empirical factor.

The objective of this article is to obtain an enhanced rate equation for the MTBE synthesis by including a factor, as physicochemically sound as possible, accounting for the interaction between the reaction medium and the resin catalyst. Rate data obtained free of mass-transfer effects (catalyst particle diameter < 0.16 mm; LHSV > 35 h^{-1}) are reexamined. Reaction rates were measured in an isothermal continuous packed-bed reactor that operated differentially at 1.6 MPa over a temperature range of 318–363 K by feeding isobutene-methanol mixtures with $R_{IB/MeOH}$ between 0.5 and 2.0. The acidic ion exchange resin Bayer K-2631 was used as

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the catalyst. More detailed information about the setup and the experimental results can be found elsewhere (Fité et al., 1998).

Discussion

Rate equation proposed in the literature

The most widely used rate equation for the liquid phase of MTBE synthesis taking into account the nonideality of the system is that proposed by Rehfinger and Hoffmann (1990). It is based on a LHHW mechanism in which isobutene, methanol, and MTBE adsorb on one catalytic center, with the surface reaction being the rate-limiting step. The sorbed amounts of isobutene and MTBE and also the fraction of unoccupied sites are supposed to be negligible. The reaction was carried out in the presence of n-butane or 1-butene that were assumed to behave as inerts. Later, by using a C_4 cut as the isobutene source, Parra et al. (1994) obtained an equation derived from an ER mechanism in which the methanol adsorbed on the resin reacts with the isobutene free in the liquid-phase to give MTBE, with the surface reaction being the rate-limiting step. If the reactor feed is free of MTBE, both rate equations reduce to the expression

$$r = k\frac{a_{\mathrm{IB}}}{a_{\mathrm{MeOH}}} \tag{1}$$

We have recently shown that Eq. 1 does not accurately represent the rate data. At all the temperatures, reaction rates predicts by Eq. 1 are higher than the experimental ones at $R_{\mathrm{IB/MeOH}} < 1$. On the contrary, they are lower at $R_{\mathrm{IB/MeOH}} > 1$ (Fité et al., 1998).

Consideration of other reaction mechanisms

At a first attempt, biased residuals obtained with Eq. 1 could be explained because Eq. 1 is not suitable when $R_{\mathrm{IB/MeOH}}$ is far from unity. In order to verify this fact, a set of rate equations was systematically obtained through the LHHW and ER formalisms by assuming different adsorption types for isobutene, methanol, and MTBE.

It is a generally accepted fact that methanol adsorbs on ion exchangers; the adsorption enthalpy of methanol was found to be about -3.8 kJ mol^{-1} (Solà et al., 1994). In addition, since at $R_{\mathrm{IB/MeOH}} > 1$ isobutene dimerization occurs in the presence of sulfonic resins (Ancillotti et al., 1978; Rehfinger and Hoffmann, 1990; Izquierdo et al., 1993), it is inferred that isobutene adsorbs on these resins. Finally, MTBE also adsorbs on the resin, because its decomposition is catalyzed by these solids (Gicquel and Torck, 1983; Rehfinger and Hoffmann, 1990).

The different forms of adsorption considered for each compound are:

(i) One molecule adsorbed on one active center (Type I).

(ii) One molecule adsorbed on two active centers (Type II).

(iii) Two molecules adsorbed on one active center (Type III).

LHHW mechanisms involve the adsorption of both reactants on the catalyst. ER mechanisms assume that isobutene from the liquid phase (namely, Adsorption Type 0) reacts with the methanol adsorbed on the resin. The combination of adsorption types 0 to III for IB, and I to III for MeOH and MTBE, leads to 36 different mechanisms: 9 ER mechanisms, and 27 LHHW ones (Table 1). For each mechanism, the rate equation was obtained by assuming that the surface reaction is the rate-controlling step. Afterwards, since the reactor feed was free of MTBE and it operated differentially, by considering that isobutene adsorption is negligible compared with that of methanol (for LHHW rate equations), and that the number of unoccupied sites is also negligible, rate equations reduce to the eleven that follow

$$r = ka_{\mathrm{IB}} \tag{2}$$

$$k\frac{a_{\mathrm{IB}}}{\sqrt{a_{\mathrm{MeOH}}}} \tag{3}$$

$$k\frac{a_{\mathrm{IB}}}{a_{\mathrm{MeOH}}} \tag{4}$$

$$k\frac{a_{\mathrm{IB}}}{a^2_{\mathrm{MeOH}}} \tag{5}$$

Table 1. Surface Reaction Elementary Step for ER (IB Absorption Type 0) and LHHW (IB Adsorption Types I, II, III) Mechanisms Stemming from the Combination of IB, MeOH and MTBE Adsorption Types Taken into Account

Adsorption Type		MeOH		
		I	II	III
IB	0	$IB+MeOH\sigma \leftrightarrow MTBE\sigma$ (2,15) $IB+MeOH\sigma+\sigma \leftrightarrow MTBE\sigma_2$ (4,17) $2IB+2MeOH\sigma \leftrightarrow MTBE_2\sigma+\sigma$ (6,19)	$IB+MeOH\sigma_2 \leftrightarrow MTBE\sigma+\sigma$ (2,15) $IB+MeOH\sigma_2 \leftrightarrow MTBE\sigma_2$ (2,15) $2IB+2MeOH\sigma_2 \leftrightarrow MTBE_2\sigma+3\sigma$ (6,19)	$2IB+MeOH_2\sigma+\sigma \leftrightarrow 2MTBE\sigma$ (9,22) $2IB+MeOH_2\sigma+3\sigma \leftrightarrow 2MTBE\sigma_2$ (11,24) $2IB+MeOH_2\sigma \leftrightarrow MTBE_2\sigma$ (6,19)
	I	$IB\sigma+MeOH\sigma \leftrightarrow MTBE\sigma+\sigma$ (4,17) $IB\sigma+MeOH\sigma \leftrightarrow MTBE\sigma_2$ (4,17) $2IB\sigma+2MeOH\sigma \leftrightarrow MTBE_2\sigma+3\sigma$ (9,22)	$IB\sigma+MeOH\sigma_2 \leftrightarrow MTBE\sigma+2\sigma$ (3,16) $IB\sigma+MeOH\sigma_2 \leftrightarrow MTBE\sigma_2+\sigma$ (3,16) $2IB\sigma+2MeOH\sigma_2 \leftrightarrow MTBE_2\sigma+5\sigma$ (8,21)	$2IB\sigma+MeOH_2\sigma \leftrightarrow 2MTBE\sigma+\sigma$ (10,23) $2IB\sigma+MeOH_2\sigma+\sigma \leftrightarrow 2MTBE\sigma_2$ (11,24) $2IB\sigma+MeOH_2\sigma \leftrightarrow MTBE_2\sigma+2\sigma$ (10,23)
	II	$IB\sigma_2+MeOH\sigma \leftrightarrow MTBE\sigma+2\sigma$ (5,18) $IB\sigma_2+MeOH\sigma \leftrightarrow MTBE\sigma_2+\sigma$ (5,18) $2IB\sigma_2+2MeOH\sigma \leftrightarrow MTBE_2\sigma+5\sigma$ (10,23)	$IB\sigma_2+MeOH\sigma_2 \leftrightarrow MTBE\sigma+3\sigma$ (4,17) $IB\sigma_2+MeOH\sigma_2 \leftrightarrow MTBE\sigma_2+2\sigma$ (4,17) $2IB\sigma_2+2MeOH\sigma_2 \leftrightarrow MTBE_2\sigma+7\sigma$ (9,22)	$2IB\sigma_2+MeOH_2\sigma \leftrightarrow 2MTBE\sigma+3\sigma$ (12,25) $2IB\sigma_2+MeOH_2\sigma \leftrightarrow 2MTBE\sigma_2+\sigma$ (12,25) $2IB\sigma_2+MeOH_2\sigma \leftrightarrow MTBE_2\sigma+4\sigma$ (12,25)
	III	$IB_2\sigma+2MeOH\sigma \leftrightarrow 2MTBE\sigma+\sigma$ (8,21) $IB_2\sigma+2MeOH\sigma+\sigma \leftrightarrow 2MTBE\sigma_2$ (9,22) $IB_2\sigma+2MeOH\sigma \leftrightarrow MTBE_2\sigma+2\sigma$ (8,21)	$IB_2\sigma+2MeOH\sigma_2 \leftrightarrow 2MTBE\sigma+3\sigma$ (7,20) $IB_2\sigma+2MeOH\sigma_2 \leftrightarrow 2MTBE\sigma_2+\sigma$ (7,20) $IB_2\sigma+2MeOH\sigma_2 \leftrightarrow MTBE_2\sigma+4\sigma$ (7,20)	$IB_2\sigma+MeOH_2\sigma \leftrightarrow 2MTBE\sigma$ (9,22) $IB_2\sigma+MeOH_2\sigma+2\sigma \leftrightarrow 2MTBE\sigma_2$ (11,24) $IB_2\sigma+MeOH_2\sigma \leftrightarrow MTBE_2\sigma+\sigma$ (9,22)

*In the parentheses rate expressions associated to each mechanism are pointed out (second item points out equations including Ψ factor; first item points out those that do not include it).

$$ka_{\mathrm{IB}}^2 \tag{6}$$

$$k\frac{a_{\mathrm{IB}}^2}{\sqrt{a_{\mathrm{MeOH}}}} \tag{7}$$

$$k\frac{a_{\mathrm{IB}}^2}{a_{\mathrm{MeOH}}} \tag{8}$$

$$k\frac{a_{\mathrm{IB}}^2}{a_{\mathrm{MeOH}}^2} \tag{9}$$

$$k\frac{a_{\mathrm{IB}}^2}{a_{\mathrm{MeOH}}^4} \tag{10}$$

$$k\frac{a_{\mathrm{IB}}^2}{a_{\mathrm{MeOH}}^6} \tag{11}$$

$$k\frac{a_{\mathrm{IB}}^2}{a_{\mathrm{MeOH}}^8} \tag{12}$$

where, as can be seen, Eq. 4 corresponds to Eq. 1. Table 1 shows the rate equation associated with each mechanism. It is to be noted that, as Eqs. 2 to 12 show, reaction rate varies directly as a quotient of isobutene and methanol activities.

Equations 2 to 12 were fitted to data by minimizing the sum of squares of residuals (SQ). Equation 9 has the lowest SQ, but all the equations have a SQ of the same order of magnitude. Figure 1 shows a plot comparing reaction rates computed by Eq. 9 with the experimental ones. As can be seen, at each temperature predicted rates are higher than experimental ones at $R_{\mathrm{IB/MeOH}} < 1$, whereas the opposite trend is observed at $R_{\mathrm{IB/MeOH}} > 1$. The same behavior is observed for all the equations. This fact suggests that none of the rate equations explains accurately enough rate data. However, apparent activation energies ranged from 82.79 to 85.52 kJ·mol^{-1}, and agreed quite well with the values reported in the literature (Zhang and Datta, 1995; Tejero et al., 1996).

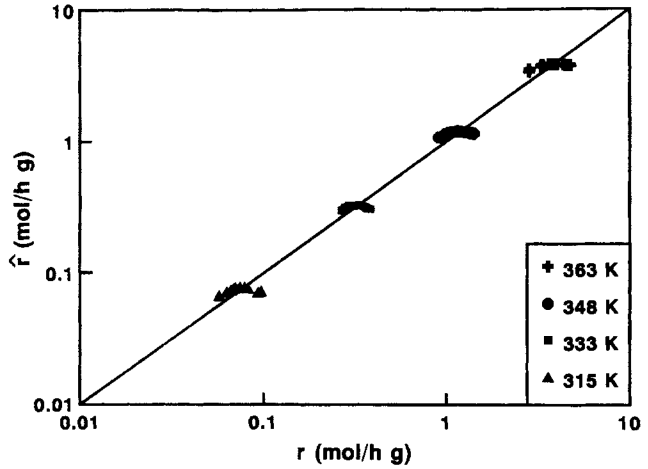

Figure 1. Logarithmic plot of rates estimated by Eq. 9, $\hat{r}$ vs. rate data r.

Points on the lefthand side of the diagonal correspond to $R_{\mathrm{IB/MeOH}} < 1$ and those on the righthand side correspond to $R_{\mathrm{IB/MeOH}} > 1$.

Influence of the reaction medium in the reaction rate

Ion-exchanger catalysts consist of a polymeric backbone on which the sulfonic groups are supported. The resin structure is not wholly rigid in liquid media, so its conformation depends to some extent on the nature of the liquid; reactants with a higher affinity for the resin permeate easily and more deeply into the resin, and they can reach a larger number of active centers (Buttersack, 1989). On the other hand, the acidic strength of sulfonic groups depends on the solvating capacity of the medium. In polar media (good solvating capacity), the sulfonic groups become less acidic and, thus, activity decreases (Tejero et al., 1996). In our case, the reaction medium was exclusively composed of isobutene and methanol, whose polarity and solvating capacity are quite different. Thus, by changing $R_{\mathrm{IB/MeOH}}$, the physical properties of the reaction medium vary significantly and, as a result, the catalytic behavior of the resin varies also.

To characterize the influence of the reaction medium on the catalytic activity, the Hildebrand solubility parameter δ was found to be the most suitable physical property. It is directly related to the swelling of the resin backbone (Errede, 1986) and to the accessibility of active centers of a macroporous sulfonic resin (Buttersack, 1989). For compound i, δ is defined by (Reichardt, 1988)

$$\delta = \sqrt{\frac{\Delta U_V}{\bar{V}_i}} = \sqrt{\frac{\Delta H_V - RT}{\bar{V}_i}} \tag{13}$$

When referred to the reaction medium, δ_M is also related to its polarity, since δ_M^2, known as the *cohesive pressure*, represents the total strength of the intermolecular structure of this medium: δ_M^2 has very high values for solvents of high polarity and low values for nonpolar solvents with weak interaction forces (Reichardt, 1988).

The interaction between the reaction medium and the resin could be considered as a solution process of the resin in the liquid governed by the affinity between both. As close solubility parameter values in a solute–solvent system indicate a high affinity, this physical property could be also applicable to describe the interaction between the resin and the reaction medium. It is thus assumed that when the reaction medium and the resin solubility parameter values are close, there are more active centers accessible to the reactants. Moreover, because of the solvating effects, the polarity of the liquid influences the acidity of the catalytic centers and, therefore, the reaction rate.

By analogy to the solution process of solvents and the liquid phase-resin mixing process, an expression, similar to that which gives the activity of a nonelectrolyte in a solvent (Reichardt, 1988), allows us to quantify the reaction medium-resin affinity by means of the solubility parameters

$$\Psi = \exp\left\{\frac{\bar{V}_M \Phi_P^2}{RT}(\delta_M - \delta_P)^2\right\} \tag{14}$$

In a previous work (Fité et al., 1998), it was shown that including the reciprocal of the solubility parameter of the reaction medium $1/\delta_M$ as an empirical factor efficiently improves the prediction of reaction rates. Figure 2 shows that,

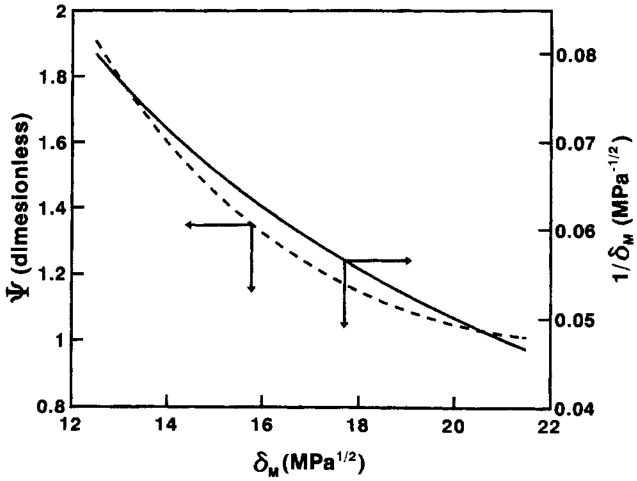

Figure 2. Comparison of the functions $1/\delta_M$ and Ψ calculated at the mean experimental conditions.
(Molar fractions: IB: 0.49, MeOH: 0.51; $T = 340$ K; $P = 1.6$ MPa).

evaluated at the mean experimental conditions, both $1/\delta_M$ and Ψ have a similar shape when plotted vs. δ_M, which suggests that Eq. 14 could be useful to reformulate rate equations. The solubility parameter of the resin δ_P has been estimated at 298 K by a contribution group method (Sourirajan and Matsuura, 1983) to be 22.73 MPa$^{1/2}$.

Reformulation of the kinetic equations

To reformulate Eq. 2 to 12, k was split in an intrinsic kinetic constant k', which is only temperature dependent, and a factor including the influence of the reaction medium on the kinetics; the Ψ function. In this way, Eqs. 2 to 12 were converted to

$$r = k'\Psi a_{\rm IB} \tag{15}$$

$$k'\Psi \frac{a_{\rm IB}}{\sqrt{a_{\rm MeOH}}} \tag{16}$$

$$k'\Psi \frac{a_{\rm IB}}{a_{\rm MeOH}} \tag{17}$$

$$k'\Psi \frac{a_{\rm IB}}{a_{\rm MeOH}^2} \tag{18}$$

$$k'\Psi a_{\rm IB}^2 \tag{19}$$

$$k'\Psi \frac{a_{\rm IB}^2}{\sqrt{a_{\rm MeOH}}} \tag{20}$$

$$k'\Psi \frac{a_{\rm IB}^2}{a_{\rm MeOH}} \tag{21}$$

$$k'\Psi \frac{a_{\rm IB}^2}{a_{\rm MeOH}^2} \tag{22}$$

$$k'\Psi \frac{a_{\rm IB}^2}{a_{\rm MeOH}^4} \tag{23}$$

Table 2. Reduction of SQ from Fit of Eq. 15 to 25 to Rate Data Referred to the SQ Values Obtained for Eqs. 2 to 12

SQ Reduction (%)	T (K)			
	318	333	348	363
Maximum	94.1	98.4	98.9	98.8
Minimum	83.7	83.9	85.8	85.8

$$k'\Psi \frac{a_{\rm IB}^2}{a_{\rm MeOH}^6} \tag{24}$$

$$k'\Psi \frac{a_{\rm IB}^2}{a_{\rm MeOH}^8} \tag{25}$$

Kinetic mechanisms associated with Eqs. 15 to 25 are pointed out in Table 1.

These equations were fitted to the reaction rate data by optimizing k' and δ_M, the function to minimize being SQ. At all the temperatures, a significant reduction of SQ was achieved for each one of the equations, as shown in Table 2. For instance, Figure 3 plots the reaction rates predicted by Eq. 22 with rate data. In comparison to Figure 1 we can see how the predictions of the reaction rates have been improved. Thus, including the Ψ function in the rate equation greatly decreases SQ. This strong reduction cannot be only attributed to the introduction of a new parameter δ_M. The resin-reaction medium interaction is an important feature of the catalytic behavior of ion-exchange resins. Equation 16 has the lowest SQ, but Eqs. 15 to 22 yield a close SQ. It is therefore not possible to distinguish the best model.

The apparent activation energy of the reaction E_{ap} was found for Eqs. 15 to 25 from the temperature dependence of k' according to the Arrhenius law. For all the equations, the Arrhenius plot yields a very good straight line and the standard error associated to E_{ap} is lower than 1%. As can be seen in Table 3, all the E_{ap} values agree with those quoted in the literature (Zhang and Datta, 1995; Tejero et al., 1996). It

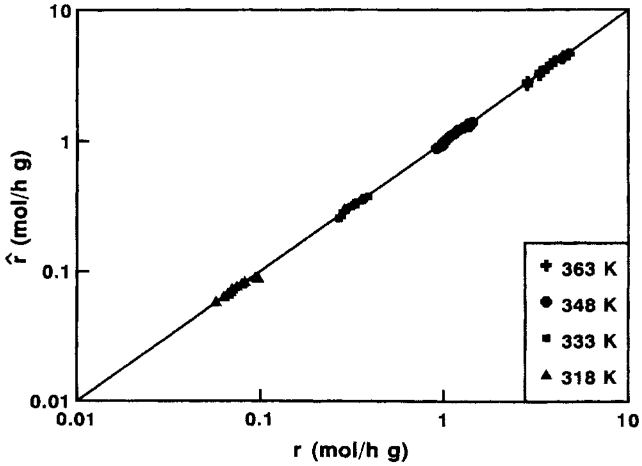

Figure 3. Logarithmic plot of rates computed by Eq. 22 $\hat{r}$ vs. rate data r.

Table 3. Apparent Activation Energy Values and Associated Standard Error Obtained from Fit of Experimental Data to Kinetic Eqs. 15 to 25

Eq.	$E_{ap}\pm$s.e. (kJ·mol^{-1})
15	79.53±0.80
16	79.68±0.76
17	79.82±0.72
18	80.13±0.66
19	81.31±0.68
20	81.46±0.65
21	81.60±0.62
22	81.91±0.57
23	82.58±0.52
24	83.33±0.53
25	84.16±0.58

Table 4. Results of Fit to Eq. 26 of Resin Solubility Parameter Values Obtained for Eqs. 15 to 25

Eq.	$m\pm$s.e. (10^2 MPa$^{1/2}$ K^{-1})	$n\pm$s.e. (MPa$^{1/2}$)	R^2 Coefficient	$\hat{\delta}_{298\,\mathrm{K}}\pm$s.e. (MPa$^{1/2}$)
15	−1.135±0.060	25.97±0.20	0.994	22.59±0.38
16	−1.604±0.048	27.585±0.164	0.998	22.80±0.31
17	−2.074±0.037	29.205±0.125	0.9994	23.02±0.23
18	−3.0180±0.0141	32.459±0.048	0.99996	23.461±0.090
19	−1.922±0.034	28.535±0.116	0.9994	22.81±0.22
20	−2.396±0.022	30.171±0.076	0.9998	23.027±0.142
21	−2.8714±0.0108	31.810±0.037	0.99997	23.249±0.069
22	−3.8253±0.0119	35.101±0.040	0.99998	23.696±0.075
23	−5.746±0.055	41.732±0.189	0.9998	24.60±0.35
24	−7.682±0.096	48.42±0.33	0.9997	25.52±0.62
25	−9.633±0.135	55.17±0.46	0.9996	26.45±0.86

is to be noted that, with the exception of Eq. 25, the inclusion of the parameter Ψ in the rate equation reduces by 1.5% to 6.2% the E_{ap} value. This fact can be explained by the slight temperature dependence of the solubility parameter.

The solubility parameter values for IB, MeOH and MTBE, calculated by means of Eq. 13, were plotted against the temperature (Figure 4). A practically linear temperature dependence is observed for each compound, with the solubility parameter decreasing with increasing temperature, as follows from its definition (Barton, 1991).

Similarly, we assume that the temperature dependence for the solubility parameter of the resin should be a quasi-linear one in the temperature range explored. The slope of that function should be negative or zero, that is,

$$\delta_p = mT + n, \quad m \leq 0, \tag{26}$$

This was checked for Eqs. 15 to 25 by plotting the fitted values of δ_P vs. temperature. δ_P values fulfill Eq. 26 for each rate equation in the temperature range explored. For instance, Figure 4 plots the fitted values for δ_P vs. temperature for Eq. 21. The calculated values of the slope and the intercept, as well as the associated standard errors are given in Table 4. Errors for the slope and the intercept are smallest for Eqs. 21 and 22. Nevertheless, taking into account the experimental error, a choice between models cannot be safely made.

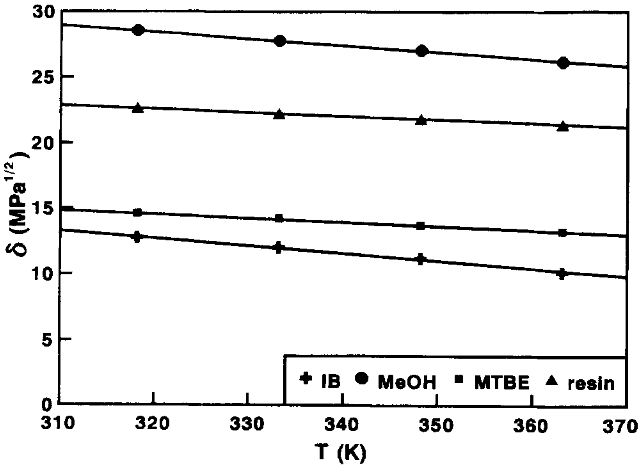

Figure 4. Temperature dependence of the solubility parameter of isobutene, methanol, and MTBE, computed by Eq. 13, and of the resin solubility parameter obtained from the fit of Eq. 21.

No experimental values for the resin Bayer K-2631 were found in the open literature. Therefore, as indicated above, at 298 K, δ_P has been estimated to be 22.73 MPa$^{1/2}$. Computed values of δ_P at 298 K through Eq. 26 are close to the estimated one, especially for Eqs. 15 to 22. Again, a significantly best model cannot be distinguished.

To discriminate among Eqs. 15 to 25, two additional experiments were carried out at IB and MeOH concentrations far from the initial experimental design. In order to hinder olefin dimerization that takes place readily when isobutene is in a large excess and at high temperatures (Izquierdo et al., 1993), both experiments were done at a low IB/MeOH molar ratio ($R_{\mathrm{IB/MeOH}} = 0.29$) and at 318 and 333 K.

Estimates of the reaction rate were computed by means of Eqs. 15 to 25 for the new experiments and compared with the new rate data. Deviations between calculated and experimental rates are listed in Table 5. As can be seen, lower errors were obtained at 318 K, respectively, for Eqs. 18, 19, 20 and 21, and at 333 K for Eqs. 20 and 21.

On the whole, it seems that Eqs. 20 to 22 better fit the experimental data. Also, their parameters show a better temperature dependence. Therefore, mechanisms associated with

Table 5. Relative Errors of Reaction Rates Predicted by Eqs. 15 to 25 for Supplementary Experiments Performed at $R_{\mathrm{IB/MeOH}} = 0.29$

	Relative Error (%)	
Eq.	$T = 318$ K	$T = 333$ K
15	14.92	19.79
16	11.83	16.55
17	8.81	13.39
18	2.95	7.29
19	2.44	6.39
20	0.36	3.49
21	3.09	0.66
22	8.38	4.79
23	18.27	14.90
24	27.29	24.03
25	35.49	32.27

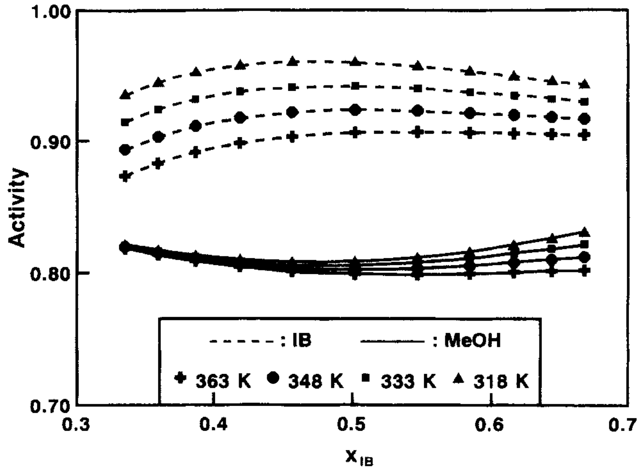

Figure 5. Methanol and isobutene activities in the concentration range explored.

them could be considered as the most plausible ones. In these equations the numerator contains the isobutene activity squared, whereas the denominator is the methanol activity to a power, 1/2, 1, and 2, respectively.

Equations 20 to 22 arise from reaction mechanisms wherein two isobutene molecules react with two methanol molecules to give two MTBE molecules. Surface reaction is assumed to be the rate-limiting step. As several mechanisms lead to Eqs. 20 to 22, it can be hypothesized that the number of active centers that could take part in the reaction varies from two to eight (see Table 1). It is a common fact, however, that a high number of sulfonic groups take part in ion-exchanger catalyzed reactions (Wesley and Gates, 1974). Finally, it is not possible to discriminate further among Eqs. 20 to 22 because the isobutene and methanol activities vary slightly in the concentration range explored, as Figure 5 shows. To distinguish between Eqs. 20 to 22, it would be necessary to carry out supplementary experiments by varying the IB and MeOH activities over a much wider range.

Conclusions

The kinetics of the MTBE synthesis performed in the liquid phase at 318–363 K in the presence of the sulfonic ion-exchange resin Bayer K-2631 was reexamined. Rate equations were developed systematically from LHHW and ER mechanisms, wherein different sets of adsorption steps were considered for IB, MeOH, and MTBE. These equations do not accurately predict rate data in the whole range of IB and MeOH concentrations. By analogy to the solution process of a nonelectrolyte in a solvent, we propose to introduce a factor with physicochemical meaning, which includes the medium solubility parameter, in the rate equations. This factor describes reaction medium-resin interaction responsible greatly for the catalytic behavior of ion-exchange resins in the liquid phase. The modified rate equations fit the rate data with very good agreement. Two parameters were fitted for each equation: the kinetic constant k' and the resin solubility parameter δ_P. For each equation, the apparent activation energy agrees with the values quoted in the literature, and the resin solubility parameter value and its temperature dependence are close to the expected ones. Finally, the extrapolation of the rate equations to predict reaction rates out of the initial range of IB and MeOH concentrations yields good results. The better rate equations are based on reaction mechanisms, wherein surface reaction involves the participation of two IB and two MeOH molecules to give two MTBE molecules. These mechanisms ask a relatively high number of active centers to participate in the rate-limiting step.

Notation

a_i = activity of compound i, dimensionless
E_{ap} = apparent activation energy, kJ mol^{-1}
k, k' = rate coefficient, mol (h·g)$^{-1}$
LHSV = liquid hourly space velocity, h^{-1}
m = slope of Eq. 26, MPa$^{1/2}$K^{-1}
n = constant of Eq. 26, MPa$^{1/2}$
r = intensive reaction rate, mol (h·g)$^{-1}$
$\hat{r}$ = calculated reaction rate, mol (h·g)$^{-1}$
R = gas constant, J (mol·K)$^{-1}$
R^2 = regression coefficient
$R_{IB/MeOH}$ = isobutene/methanol molar ratio in the feed, dimensionless
T = temperature, K
$\bar{V}$ = molar volume, L·mol^{-1}
δ = solubility parameter, MPa$^{1/2}$
ΔH_V = molar enthalpy of vaporization, kJ·mol^{-1}
ΔU_V = molar energy of vaporization, kJ·mol^{-1}
Φ = volume fraction, dimensionless
σ = active center
Ψ = coefficient of the kinetic equation, dimensionless

Subscripts

i = compound i
M = reaction medium
P = resin

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