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LETTERS TO THE EDITORS

On the Kinetics of Dehydration of *tert*-Butyl Alcohol Catalyzed by Ion-exchange Resins

The dehydration in the liquid phase of *tert*-butanol catalyzed by Dowex 50W was experimentally studied by Frilette, Mower and Rubin (*1*). The experimental apparatus employed was a batch reactor, and the course of the reaction was followed by determining the rate of evolution of isobutene.

The authors developed a Langmuir–Hinshelwood model which postulated competitive chemisorption of alcohol and water on the active sites of the catalyst. The development and testing of this model was based on the activities of alcohol and water in the vapor phase in equilibrium with the liquid phase, while the presence of small amounts of isobutene in the vapor phase was assumed inconsequential. No reason for justifying such an analysis was given. Assuming that the kinetics of a reaction taking place in the liquid phase is determined by the activities of reactants and products of that phase, it is not obvious why liquid phase activities should be replaced by vapor phase activities in the kinetic analysis.

It has been shown experimentally by the work of Kenttämmaa *et al.* (*2*) that the *tert*-butanol–water solution is nonideal. Moreover, the range of vapor composition investigated in the kinetic study (*1*) is wide enough for the liquid phase compositions to be significantly different than those of the vapor phase. Both these factors would be taken into account if the kinetic analysis were based on the activities of the components in the liquid phase. This argument, coupled with the fact that the reaction was taking place in the liquid phase, clearly points out the need to use liquid phase activities for kinetic analysis.

The objectives of the present work are (a) estimation of the liquid phase activities corresponding to the experimentally determined vapor compositions and (b) testing the adequacy of the kinetic model proposed by Frilette, Mower and Rubin in the light of the estimated activities in the liquid phase. The presence of isobutene will be considered negligible as in the original study.

NOMENCLATURE

$[A]$	activity of *tert*-butanol
α	activity
p	vapor pressure, mm Hg
P	total pressure, mm Hg
R	Rate of isobutene formation, cc/sec/meg $\times 10^2$
t	temperature, °C
T	temperature, °K
$[W]$	activity of water
x	mole fraction in liquid phase, variable
y	mole fraction in vapour phase, variable
γ	activity coefficient
β	parameter
A	*tert*-butanol
W	water

CALCULATION OF VAPOR–LIQUID EQUILIBRIUM

Brown and Ives (*3*) have shown that the Margules equations adequately describe vapor–liquid equilibrium in the *tert*-butanol–water system at 25°C. It was, therefore, assumed that the three-suffix Margules equations would adequately describe the variation of activity coefficients with composition at the higher temperatures at which the dehydration data were obtained. The variation of activity coefficients over the 2°C temperature range was neglected. The constants of the Margules equations were calculated from the azeotropic point data (*4*). The three-suffix Margules equations for the *tert*-butanol–water system are

$$\log \gamma_W = x_A^2(0.5256 + 0.7702x_W) \quad (1)$$

$$\log \gamma_A = x_W^2(0.9107 - 0.7702x_A). \quad (2)$$

The calculation of vapor–liquid equilibrium requires knowledge of the vapor pressures of the pure components at various temperatures. Data of the vapor pressure of *tert*-butanol were obtained from Parks and Barton (*5*), and the data in the range of 50 to 90°C were correlated with temperature using the Antoine equation. The constants of the Antoine equation were estimated with a Rosenbrock minimization subroutine. The correlation, Eq. (3), predicted the vapor pressure of *tert*-butanol with an average deviation of ±4 mm Hg.

$$\log p_A = 8.8787 - [2059.0/(t + 260.44)] = g_A(t). \quad (3)$$

Data for the vapor pressure of water were obtained from Perry (*6*). These were correlated in the range of 50 to 100°C with reciprocal absolute temperature. Least-squares estimation of the parameters resulted in the correlation given by Eq. (4)

$$\log p_W = 8.7881 - (2203.4/T) = g_W(T) \quad (4)$$

which predicted the vapor pressure of water with an average deviation of ±1.5 mm Hg.

Vapor–liquid equilibrium curves were calculated with the assumption that the vapor phase was ideal. For any one liquid composition the relation

$$P = \gamma_W p_W x_W + \gamma_A p_A x_A \quad (5)$$

holds at the boiling point of the solution. Or by substitution of p_A and p_W from Eqs. (3) and (4)

$$P = \gamma_W x_W\, 10^{g_W(T)} + \gamma_A x_A\, 10^{g_A(T)}. \quad (6)$$

The activity coefficients were estimated from Eqs. (1) and (2) for the liquid composition under consideration and then Eq. (6) was searched using a Newton–Raphson convergence promotion technique to locate the corresponding boiling point. Having obtained the latter, the vapor compositions could easily be calculated from the following equations

$$y_W = \gamma_W p_W x_W/P, \qquad y_A = \gamma_A p_A x_A/P = 1 - y_W. \quad (7)$$

The equilibrium curves are shown in Fig. 1. The calculation was not carried through to $x_W = 1.0$ because the temperature change would be so great that the assumed independence of activity coefficients on temperature would not be valid. The small (less than 0.3%) overestimation of the boiling point of pure *tert*-butanol, due to the deviation of the correlation of its vapor pressure, should be negligible. The striking similarity of the estimated curves and those experimentally determined [see Ref. (*2*)] provides a further qualitative confirmation of the validity of the assumptions.

Estimation of Liquid-phase Activities

Liquid-phase compositions corresponding to the experimentally determined vapor compositions given in Table 1 of (*1*) were estimated by a two-variable search over x_W and T.

Initial values for water mole fraction and boiling point were assumed and activity coefficients were estimated from the Margules equations for the assumed liquid

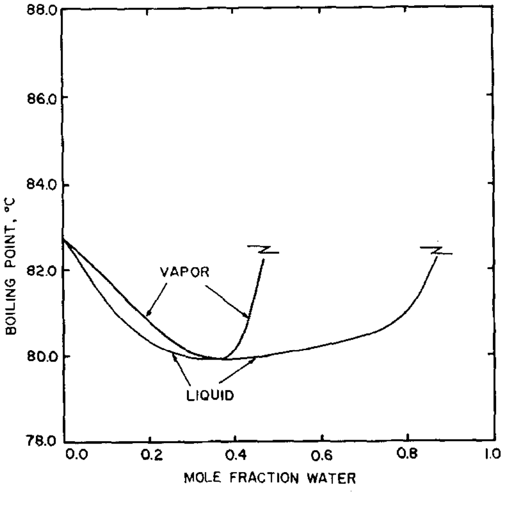

FIG. 1. *tert*-Butanol–Water system equilibrium.

composition. Equation (6) was then searched to determine an improved estimate of the boiling point. Using this better value of the temperature, new improved estimates of the mole fractions were obtained from the transposed forms of Eqs. (7), i.e.

$$x_W = [y_W P/\gamma_W p_W, \quad x_A = y_A P/\gamma_A p_A = 1 - x_W. \quad (8)$$

The procedure was repeated till the absolute difference between successive values for x_W was less than 1×10^{-5}. The temperature corresponding to the converged mole

TABLE 1

Experimental Data and Calculated Variables

R[a]	y_W[a]	x_W(calc)	γ_W(calc)	γ_A(calc)	α_W(calc)	α_A(calc)
1.14 meq catalyst 75–125 μ particles						
44.6	0.017	0.010	3.3323	1.0000	0.033	0.990
39.1	0.024	0.014	3.3226	1.0001	0.046	0.986
35.1	0.040	0.024	3.2993	1.0002	0.078	0.977
34.0	0.050	0.030	3.2837	1.0003	0.098	0.970
29.2	0.058	0.035	3.2707	1.0005	0.114	0.966
19.9	0.103	0.065	3.1874	1.0018	0.206	0.937
18.8	0.109	0.069	3.1749	1.0021	0.218	0.933
15.5	0.139	0.091	3.1070	1.0040	0.282	0.913
14.4	0.151	0.100	3.0771	1.0050	0.308	0.905
10.6	0.211	0.152	2.8996	1.0137	0.440	0.860
10.3	0.211	0.152	2.8996	1.0137	0.440	0.860
6.66	0.299	0.254	2.5210	1.0510	0.640	0.784
6.10	0.303	0.260	2.4989	1.0542	0.649	0.780
4.44 meq catalyst 75–125 μ particles						
30.4	0.039	0.023	3.3008	1.0002	0.076	0.977
23.0	0.061	0.037	3.2657	1.0005	0.120	0.964
13.6	0.150	0.099	3.0796	1.0049	0.305	0.905
12.2	0.160	0.107	3.0535	1.0059	0.327	0.898
6.78	0.254	0.196	2.7367	1.0262	0.537	0.825
5.68	0.303	0.260	2.4989	1.0542	0.649	0.781
5.47	0.305	0.263	2.4877	1.0559	0.653	0.779
4.77	0.355	0.356	2.1450	1.1290	0.764	0.727
4.19	0.369	0.394	2.0171	1.1715	0.794	0.710
4.21	0.376	0.416	1.9439	1.2013	0.808	0.702
4.01	0.382	0.438	1.8744	1.2343	0.820	0.694
3.92	0.392	0.483	1.7382	1.3164	0.839	0.681
3.78	0.375	0.412	1.9548	1.1966	0.806	0.703
3.58	0.352	0.349	2.1699	1.1220	0.758	0.730
2.82 meq catalyst 150–300 μ particles						
30.8	0.025	0.015	3.3213	1.0001	0.048	0.986
27.0	0.045	0.027	3.2916	1.0003	0.088	0.974
24.0	0.065	0.039	3.2589	1.0006	0.128	0.961
22.6	0.071	0.043	3.2485	1.0007	0.140	0.958
19.5	0.088	0.054	3.2172	1.0012	0.175	0.947
13.2	0.164	0.110	3.0428	1.0063	0.336	0.895
9.22	0.218	0.158	2.8755	1.0153	0.455	0.854
6.56	0.280	0.228	2.6189	1.0384	0.596	0.802
4.57	0.355	0.356	2.1450	1.1290	0.764	0.727
3.22	0.416	0.718	1.2187	2.2760	0.875	0.642

[a] Experimental data from (*1*).

fraction was the boiling point of the solution. The liquid phase compositions corresponding to the vapor phase compositions are given in Table 1. y_A and x_A are equal to $(1 - y_W)$ and $(1 - x_W)$, respectively.

The liquid phase activities of *tert*-butanol and water were obtained from the following equations (7)

$$\alpha_W = \gamma_W x_W, \quad \alpha_A = \gamma_A x_A. \tag{9}$$

Activity coefficients and activities are given in Table 1.

KINETIC ANALYSIS

The development of the model proposed by Frilette, Mower and Rubin [Eq. (7) of (*1*)] will not be repeated here. This is

$$R = k_3[A]/\{[A] + (1/K_A) + (K_W/K_A)[W]\} \tag{10}$$

where R, k_3 K_A and K_W have the same significance as in the original. In the present analysis, however, $[A]$ and $[W]$ stand for the activities in the liquid phase of *tert*-butanol and water, respectively.

The model, Eq. (10), can be transposed to the following form:

$$[A]/R = (1/K_A k_3) + (1/k_3)[A] + (K_W/K_A k_3)[W]; \tag{11}$$

which is of the form:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 \tag{12}$$

and is amenable to linear multiple regression.

Theory (*8*) requires that for model (10) to be acceptable the least-squares estimates of the parameters, provided that least-squares analysis is valid, must be nonnegative. In addition, for model (10) to be acceptable all the parameters must be nonzero because a coefficient of zero value would indicate that some step postulated in the development of the model would not have to be taken into account.

Since, according to the authors of (*1*), the data were not affected by transport processes and were taken at approximately the same temperature, the model may be tested by considering the data of the three experimental runs as one set.

Linear multiple regression gave the following least-squares estimates for the regression coefficients.

$$\beta_0 = 0.491$$
$$\beta_1 = -0.474 \qquad s(\beta_1) = 0.199$$
$$\beta_2 = 0.020 \qquad s(\beta_2) = 0.128.$$

To test the validity of the least-squares analysis the residuals are plotted against the estimated $\hat{y}$ values in Fig. 2. Inspection of this plot reveals no abnormality which indicates that the analysis is correct and, therefore, the estimated values of the regression coefficients are acceptable from a mathematical point of view.

The value and the 95% confindence range of coefficient β_1 are negative which is sufficient indication to reject the model in the light of the available data. However, the analysis of the implications of the values of the parameters will be carried a little further. The value of β_2 is very close to zero and seems to be much less significant than β_0 and β_1. This raises the question whether this coefficient is actually equal to zero. We, therefore, test the null hypothesis that β_2 is equal to zero.

The null hypothesis is stated (*9*) as

$$H_0{:}\beta_2 = 0, \quad H_1{:}\beta_2 \neq 0$$

and student's t is calculated for β_2

$$t = \beta_2/s(\beta_2) = 0.020/0.128 = 0.156.$$

The value of student's t at (37–3) = 34

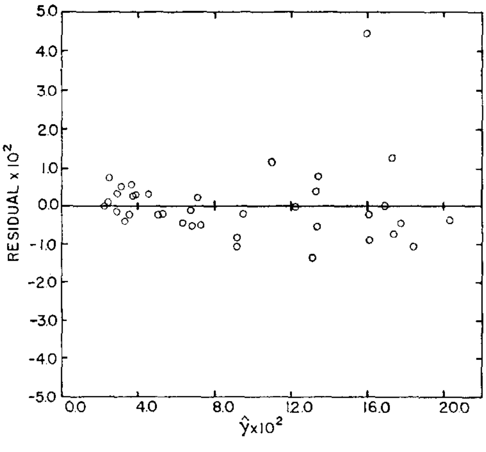

FIG. 2. Plot of residuals.

degrees of freedom and 0.05 probability level is 2.034, and, since this value is larger than the calculated value of t, the hypothesis that $\beta_2 = 0$ is not rejected.

The above analysis indicates that the model proposed by Frilette, Mower and Rubin must be rejected because in the light of the available experimental data the coefficient of *tert*-butanol activity is negative and the coefficient of water activity has a probable value of zero.

It should be pointed out that statistical analysis of the data for each separate run leads to exactly the same conclusions, i.e., rejection of the model.

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Raman Scattering from Water Adsorbed on Oxide Surfaces

Raman spectra recorded using laser excitation have been used to study adsorbed species on oxides (*1*) including, recently, an investigation on silica surfaces (*2*). The use of this technique is reported to be limited by the strong scattering background (SB), which is found to extend over a wide range of wavelengths and to decay when the sample is irradiated with the laser beam for long periods of time. Procedures to eliminate this SB, usually termed "fluorescence," have been given for porous Vycor glass by heating in oxygen at 500°C, because the fluorescence was suggested to arise from a small amount of surface species derived from hydrocarbons (*3*). However, quite similar SB was found in this laboratory in liquid (*4*) and solid proteins (*5*), and was attributed to Raman scattering from the water tightly bound to the protein. The purpose of this letter is to show that the SB observed in oxide surfaces correlates with the presence of water molecules tightly hydrogen-bonded close to Lewis sites, and that it cannot be accounted for in terms of pure fluorescence.

The Raman laser apparatus used in this investigation has already been described (*5*). The photon flux density was kept below 10 mW/cm^2 to eliminate as far as possible the time decay. The samples have been prepared in the conventional way as pressed discs from powdered solids. A metal-Pyrex cell has been constructed in order to heat the pellet to 800°C under vacuum (better than 10^{-4} Torr) without being removed from the Raman laser system. γ-Al_2O_3 samples have been kindly provided by Dr. B. Notari (Laboratori Snam Progetti, Milano), and were prepared according to U.S. Pat. 3,416,888. The other samples were commercial products.