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Abstract

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Thermodynamics of the Absorption of Propylene by the System $H_2SO_4 - H_2O$

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The absorption of olefins by sulfuric acid has long been studied; however, because of the complexity of the olefin–water–acid system, works devoted to the thermodynamics of this process are few in number ([1–3]).

The present work is devoted to a study of the thermodynamics of the complex process of absorption of propylene by aqueous sulfuric acid, during which, as we showed earlier ([4]), alkylsulfuric acid and alcohol are formed, which entails a sharp change in the properties of the initial solution.

Table 1

Dependence of the equilibrium constant of the alkylation reaction on the concentration of the initial acid; $t = 70°C$, $K_\Gamma^{70°} = 3.27 \cdot 10^{-6}$ mole/l $\cdot$ mm

H_2SO_4, %	$-H_0$	P_{equil} C_3H_6, mm Hg	C_{alk}, mole/l	$C_{H_2SO_4}$, mole/l	$K'_{alk} \cdot 10^{-2}$, $(mole/l)^{-1}$	$\lg K'_{alk} + 0.732\, H_0$	Percent C_3H_6 in iso-$C_3H_7SO_4H$
62.65	4.43	233.0	0.14	9.56	0.1922	−1.959	18
67.70	5.13	191.7	0.641	10.345	1.000	−1.755	24
70.18	5.45	155.5	0.884	10.53	1.651	−1.772	27
74.03	6.02	81.2	1.37	11.214	4.601	−1.743	29

We have studied in detail the equilibrium of the absorption of propylene by sulfuric acid in the concentration range 62.25–74.03% at temperatures of 70–95° and initial gas pressures of 300–600 mm Hg, with determination of the concentrations of alkylsulfuric acid and alcohol in the reaction mixture. The experiments were carried out in the circulating glass apparatus described by us earlier ([4]). The amount of acid in the experiments was about 8 g. The volume of the system in which absorption was carried out was 2000 cm^3. The course of absorption was followed from the fall in the pressure of propylene in the system; attainment of equilibrium was noted by the cessation of pressure change. After saturation, the reaction mixture was rapidly diluted with a large volume of cold water and analyzed for alkylsulfuric acid and alcohol.

The alkylsulfuric acid was determined acidimetrically, and the alcohol by the method of oxidative titration ([5]). Knowledge of the equilibrium concentrations of alkylsulfuric acid and alcohol makes it possible to determine the equilibrium constants, not available in the literature, for the reactions of alkylation of sulfuric acid and hydration of propylene.

The equilibrium of the alkylation reaction

$$C_3H_6 + H_2SO_4 = \text{iso-}C_3H_7SO_4H \qquad \text{(I)}$$

is conveniently characterized by the constant K'_{alk}, expressed through quantities determined in the experiment:

$$K'_{\text{alk}} = \frac{C_{\text{iso-}C_3H_7SO_4H}}{K_\Gamma P_{C_3H_6} C_{H_2SO_4}} = K_{\text{alk}} F, \qquad (1)$$

where $F = f_{H_2SO_4} f_{C_3H_6} / f_{\text{iso-}C_3H_7SO_4H}$; K_{alk} is the thermodynamic constant; f_i are activity coefficients; C_i are concentrations in moles per liter. The Henry constant K_Γ was found by extrapolating literature data on the solubility of propylene in water ([12]) to the temperature of the experiment.

It follows from Table 1 that K'_{alk} is related to H_0 in the following way:

$$\lg K'_{\text{alk}} = -0.732\, H_0 - 1.76. \qquad (2)$$

The temperature dependence of K'_{alk} is presented in Table 2 (67.7% H_2SO_4).

Table 2

t, °C	P_{eq} C_3H_6, mm Hg	$K_\Gamma \cdot 10^6$, mol/l · mm	$C_{C_3H_6} \cdot 10^3$, mol/l	C_{alk}, mol/l	$C_{H_2SO_4}$, mol/l	$K'_{\text{alk}} \cdot 10^{-2}$, $(\text{mol/l})^{-1}$	ΔS
70	191.7	3.27	0.627	0.641	10.345	1.001	−17.71
75	209.5	2.94	0.617	0.561	10.425	0.872	−17.52
80	213.0	2.66	0.566	0.483	10.503	0.813	−17.30
85	226.5	2.40	0.543	0.385	10.601	0.668	−17.32
90	225.4	2.16	0.487	0.302	10.684	0.581	−17.23
95	209.6	1.96	0.411	0.201	10.785	0.453	−17.35

Figure 1 gives a plot for calculating the heat of the alkylation reaction. It was found that $\Delta H_{\text{alk}} = (-9.2 \pm 0.2)$ kcal/mol and ΔS is $-(17.4 \pm 0.2)$ e.u.

Fig. 1. Plot for calculating the heat of the alkylation reaction

Of particular interest is the calculation of the equilibrium constant of the hydration reaction of propylene in the liquid phase.

Fig. 1. Plot for calculating the heat of the alkylation reaction

Figure 1: Fig. 1. Plot for calculating the heat of the alkylation reaction

Formation of the alcohol in an acidic medium proceeds according to the equation

$$C_3H_6 + H_2O + H_2SO_4 \rightleftarrows \text{iso-}C_3H_7OH_2^+ + HSO_4^-, \qquad \text{(II)}$$

which is the sum of three equations:

$$C_3H_6 + H_2O \overset{k_{III}}{\rightleftarrows} \text{iso-}C_3H_7OH; \qquad \text{(III)}$$

$$H_2O + H_2SO_4 \overset{k_{IV}}{\rightleftarrows} H_3O^+ + HSO_4^-; \qquad \text{(IV)}$$

$$\text{iso-}C_3H_7OH + H_3O^+ \overset{k_V}{\rightleftarrows} \text{iso-}C_3H_7OH_2^+ + H_2O. \qquad \text{(V)}$$

It is convenient to characterize the equilibrium of reaction (II) by the constant K'_{sp}, expressed through experimentally determined quantities:

$$K'_{sp} = \frac{C_{\text{iso-}C_3H_7OH_2^+}}{C_{C_3H_6}\, a_{H_2O}\, h_0} = K_{sp}\frac{1}{k_{IV}}\frac{f_{C_3H_6}}{f_{\text{iso-}C_3H_7OH}}, \qquad (3)$$

where h_0 is the acidity of the medium, and K_{sp} is the thermodynamic constant.

From the data available in the literature on the basicity of isopropyl alcohol ([6]), it follows that in 67.7% H_2SO_4 practically all the alcohol is in the ionized form, i.e., the value $C_{\text{iso-}C_3H_7OH_2^+}$ in formula (3) is equal to the concentration of all alcohol detected by analysis in the liquid phase. Indeed, analysis of the composition of the gas phase above our system shows that the fraction of alcohol in the vapors does not exceed 10^{-4} of the total amount.

To calculate the equilibrium constant K'_{sp} by equation (3), it is necessary to use the equilibrium values a_{H_2O} and h_0^*, which differ substantially, as was shown by us earlier ([11]), from the corresponding values for the initial acid. In calculating the equilibrium values, we used empirical formulas ([11]) relating a_{H_2O} and h_0^* to the alcohol content in the equilibrium system:

$$h_0^* = h_0\frac{1 + 0.13C_{sp}}{1 + 0.52C_{sp}}, \qquad a_{H_2O} = 55.51\, B\left(C_{sp} + \frac{P_{H_2O}/P_{SH_2O}}{B}\right), \qquad (4)$$

where h_0 and h_0^* are the acidity values of, respectively, the initial acid and the acid with concentration C mol/l alcohol; P_{H_2O} and P_{SH_2O} are the values

Table 3

Dependence of the equilibrium constant of the propylene hydration reaction in the liquid phase on the acidity function of the initial acid. $t = 70°$, $P_{SH_2O} = 233.7$ mm Hg.

H_2SO_4, %	$-H_0$	$h_0 \cdot 10^{-5}$	P_{eq} of C_3H_6, mm Hg	P_{H_2O}, mm Hg	C_{sp}, mol/l	a_{H_2O}, mol/l	$h_0 \cdot 10^{-5}$	$K'_{sp} \cdot 10^3$, (mol/l)	$\lg K'_{sp} - 0.319H_0$	Percent of C_3H_6 in iso-C_3H_7OH
62.25	4.43	0.269	233.0	41.0	0.62	16.84	0.220	2.196	−1.246	80
67.70	5.13	1.51	191.7	23.0	1.80	23.97	0.960	1.239	−1.261	69
70.18	5.45	2.82	155.5	17.0	2.38	27.78	1.650	1.022	−1.253	70
74.03	6.02	10.22	81.2	9.0	3.38	33.04	5.334	0.721	−1.222	67

the vapor pressures of water, respectively over the initial acid and the saturated space; for 70° an extrapolation yielded $B = 16.47 \cdot 10^{-2}$.

It follows from Table 3 that the values of $\lg K'_{sp}$ are related to H_0 by

$$\lg K'_{sp} = 0.319H_0 - 1.245. \tag{5}$$

The temperature dependence of K'_{sp} is presented in Table 4.

Table 4

Dependence of the equilibrium constant of the propylene hydration reaction in the liquid phase on temperature. 67.7% H_2SO_4

t, °C	P_{eq} of C_3H_6, mm Hg	$K_T \cdot 10^3$, mol/l·mm	$C_{C_3H_6} \cdot 10^3$, mol/l	P_{H_2O}, mm Hg	P_{SH_2O}, mm Hg	$B \cdot 10^2$ from equation (4)	C_{sp}, mol/l	a_{H_2O}, mol/l	$h_0 \cdot 10^{-5}$	$h_0^* \cdot 10^{-5}$	$K'_{sp} \cdot 10^3$, (mol/l)	$\Delta S^{\ddagger}$
70	191.7	3.27	0.627	23.0	233.7	16.47	1.80	23.97	1.51	0.960	1.239	−23.32
75	209.5	2.94	0.617	27.5	294.4	22.11	1.25	20.52	1.41	0.993	0.994	−23.49
80	213.0	2.66	0.566	35.5	355.1	27.75	1.32	25.88	1.35	0.9172	0.9828	−23.38
85	226.5	2.40	0.543	46.5	440.4	37.25	1.30	32.74	1.26	0.898	0.851	−23.53
90	225.4	2.16	0.487	58.0	525.7	46.76	1.32	40.38	1.20	0.834	0.803	−23.51
95	209.6	1.96	411	73.3	633.9	62.77	1.29	51.36	1.12	0.7826	0.780	−23.41

t, °C	P_{eq} of C_3H_6, mm Hg	$K_T \cdot 10^3$, mol/l·mm	$C_{C_3H_6} \cdot 10^3$, mol/l	P_{H_2O}, mm Hg	P_{SH_2O}, mm Hg	$B \cdot 10^2$ from equation (4)	C_{sp}, mol/l	a_{H_2O}, mol/l	$h_0 \cdot 10^{-5}$	$h_0^* \cdot 10^{-5}$	$K'_{sp} \cdot 10^3$, (mol/l)$^{-1}$	ΔV

Figure 2 gives a graph for calculating the heat of hydration. It was found that $\Delta H_{sp} = -(3.7 \pm 0.3)$ kcal/mol, $\Delta S = -(23.44 \pm 0.12)$ e.u.

From Tables 1 and 3 and Fig. 3 it is seen how the fraction of propylene converted into alcohol and alkyl acid changes with the concentration of the initial H_2SO_4, which agrees with literature data ([2,3]).

Table 5 presents the values of the equilibrium constants for the gross absorption of propylene, $K = \Delta P_\infty / P_{eq}$, where ΔP_∞ is the equilibrium pressure drop in the system, and P_{eq} is the equilibrium pressure. K is related to the constants of alkylation K'_{alk} and alcohol formation K'_{sp} by the equation

$$K = \frac{K_\Gamma RTV_{acid}}{2000}\left(K'_{sp}a_{H_2O}h_0 + K'_{alk}C_{H_2SO_4}\right), \qquad (6)$$

where V_{acid} is the volume of acid in liters. It was found that the effective heat $\Delta H = -(8.7 \pm 0.8)$ kcal/mol, and $\Delta S = -(15.14 \pm 0.3)$ e.u.

On the basis of the data obtained, a number of interesting quantities can be calculated. Knowledge of the heat of the alkylation reaction of sulfuric acid by propylene makes it possible to calculate the heat of formation of isopropylsulfuric acid from the elements $(\Delta H_{form})_{iso\text{-}C_3H_7SO_4H}$ by the formula:

$$(\Delta H_{form})_{iso\text{-}C_3H_7SO_4H} = \Delta H_{alk} + (\Delta H_{form})_{C_3H_6(l)} + (\Delta H_{form})_{H_2SO_4(2.68)},$$

where $(\Delta H_{form})_{C_3H_6(l)}$ is the heat of formation of liquid propylene; $(\Delta H_{form})_{H_2SO_4(2.68)}$ is the heat of formation of sulfuric acid at a molar

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···of water to sulfuric acid in the solution $2.68 : 1 \simeq 3.1$, equal to -205.6 kcal/mole ([8]):

$$(\Delta H_{form})_{iso\text{-}C_3H_7SO_4H} = (-9.2 + 0.48 - 205.6) \text{ kcal/mole} = -214.32 \text{ kcal/mole}.$$

Using the obtained value of the heat of formation of the protonated form of the alcohol, one can calculate by difference the heat of protonation of isopropyl alcohol: $\Delta H_V = \Delta H_{sp} - \Delta H_{III}$.

Fig. 2. Plot for calculating the heat of the hydration reaction

Figure 2: Fig. 2. Plot for calculating the heat of the hydration reaction

Fig. 3. Dependence of the percentage conversion of C3H6 into iso-C3H7OH (1) and iso-C3H7SO4H (2) on acid concentration

Figure 3: Fig. 3. Dependence of the percentage conversion of C3H6 into iso-C3H7OH (1) and iso-C3H7SO4H (2) on acid concentration

The heat of reaction (III), ΔH_{III}, is found from tabulated data

$$\Delta H_{\text{III}} = (\Delta H_{\text{form}})_{\text{iso-C}_3\text{H}_7\text{OH}(\ell)} - (\Delta H_{\text{form}})_{\text{H2O}(\ell)} - (\Delta H_{\text{form}})_{\text{C3H}_6(\ell)};$$

$$\Delta H_{\text{III}} = (68.4 - 0.5 - 76.6) \text{ kcal/mole} = -8.7 \text{ kcal/mole},$$

Fig. 2. Plot for calculating the heat of the hydration reaction

Fig. 3. Dependence of the percentage conversion of C_3H_6 into iso-C_3H_7OH (1) and iso-$C_3H_7SO_4H$ (2) on the acid concentration

whence the heat of protonation of isopropyl alcohol is

$$\Delta H_{\text{V}} = (-3.7 + 8.7) \text{ kcal/mole} = 5 \text{ kcal/mole}.$$

The heat of protonation of isopropyl alcohol found by us is close to the heat of protonation of methyl alcohol, $\Delta H = 4.6$ kcal/mole, calculated from Smith' s data ([10]).

Table 5

Dependence of the gross-absorption equilibrium constant on temperature, 67.7% H_2SO_4

t, °C	Acid, g	P_0 C_3H_6, mm Hg	ΔP_∞, mm Hg	P_{eq} C_3H_6, mm Hg	K_{tot}	$K_{\text{pr}} = \frac{K_{\text{tot}} \cdot 2000}{\text{g acid}} \cdot 10^{-2}$
70	7.64	322.5	130.8	191.7	0.682	1.783
75	7.79	318.5	109.0	209.5	0.520	1.335
80	7.87	313.5	100.5	213.0	0.472	1.200
85	7.53	316.8	90.3	226.5	0.398	1.054
90	7.34	291.0	65.6	225.4	0.291	0.794
95	7.16	269.0	59.6	209.6	0.285	0.798

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Note: Figure translations are in progress. See original paper for figures.