

Kinetics and thermodynamics of 2-propanol dehydration in supercritical water

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Abstract

Kinetics and thermodynamics of 2-propanol dehydration in supercritical water (SCW) and the effect of density on this reaction have been investigated in a batch reactor. The studies were performed at water densities between 0.24 and 0.58 g/cm³ and temperatures between 654 and 686 K. The main reaction products of 2-propanol dehydration were propene and water. Rate of the reaction was found to depend essentially on the water density.

Two models are used to predict the effect of SCW density on the rate constant of 2-propanol dehydration reaction: a thermodynamic model (the model of activated complex) and a model of acid-catalyzed reaction. Redlich–Kwong–Soave equation of state was used for calculation of the partial molar volumes of the reaction participants in SCW including a transition state and activation volume of the reaction. Application of the activated complex model demonstrated that the calculated values of the activation volume depend strongly on pressure at fixed temperature, which contradicts the experimental data where the activation volume is independent of pressure. At the same time, the mechanism of 2-propanol dehydration reaction in SCW was shown to correlate well with the acid-catalyzed mechanism in solutions. Rate of the reaction is directly proportional to the concentration of 2-propanol and H₃O⁺ ions. An increase in the H₃O⁺ concentration in SCW with density correlates unequivocally with an increase in the reaction rate.

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1. Introduction

Application of supercritical fluids (SCF) in catalytic and non-catalytic chemical reactions of various types [1–7] attracts particular interest. Taking into consideration the effect of supercritical (SC) fluids on chemical conversion of both organic and inorganic species, studies on kinetics, mechanism and thermodynamics of chemical reactions come to the front. In contrast to chemical reactions in the gas and liquid phases, the kinetics of chemical reactions in SC fluids most strongly depends on pressure, or more properly, on density of supercritical environment [8–11]. (De)hydration, hydrolysis, hydrogenation and oxidation of organic compounds are the chemical reactions in supercritical water (SCW) that deserve particular attention [1–7,9,11–17].

Among numerous SC solvents, water attracts the major attention as an environment for chemical reactions. Water in a supercritical condition near the critical point ($T_{cr} =$

647.096 K, $P_{cr} = 220.64$ MPa) has a number of special properties providing high efficiency of the above mentioned reactions. Such properties of water may be caused by its structural changes under supercritical conditions [18–20], yielding high concentrations of H₃O⁺ (H⁺) and OH[−] ions. For example, the ionic product of water (K_w) is known to increase by several orders of magnitude when approaching a critical point [21]. As a result, dehydration of alcohols and alkylation reactions [22–24], catalyzed by acids under conventional conditions, proceed intensively in SCW without addition of acids.

The effect of pressure on the rate of chemical reactions was originally revealed in solutions under pressure. These researches were initiated much earlier than the researches in supercritical solvents. So the fundamental knowledge, laws and equations were transferred to chemical reactions conducted in supercritical conditions. Such researches showed that an increase in the solvent density can increase or decrease the reaction rate [1,8–10,25–29] depending on the reagent and the nature of supercritical solvent.

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A change in the reaction rate in supercritical solvent with the change in pressure near the critical point can be explained by two factors: changes in some macroscopic physical properties of the solvent, for example, dielectric constant, and changes in concentration and structure of activated complexes formed in the reaction.

The aims of the present work are first, to investigate experimentally the kinetics, thermodynamics and chemical equilibrium of reversible 2-propanol dehydration reaction depending on density and temperature in the batch reactor in supercritical water near its critical point in the absence of homogeneous catalyst; and second, to model the effect of solvent density on the rate of a selected chemical reaction. It is fair to note that the authors of previous works [9,12,13] studied the mechanism and kinetics of 1-propanol and 2-propanol dehydration reactions in “hot” and supercritical water in a flow reactor in the presence of a homogeneous acid catalyst.

2. Experimental

2.1. Experimental technique

The experiments were performed at the US National Institute of Standards and Technologies (NIST) within the joint scientific studies. Chemical reactions of organics in SCW were conducted in a modernized reactor (Autoclave Engineers), namely, in an autoclave of ca. 126 cm³ volume equipped with a marine type magnetically driven agitator [11]. The maximal operating pressure at 770 K was about 430 bar.

Reactors of two types—batch (autoclave) and continuous (flow) reactors, are commonly used in studies on kinetics, mechanism and thermodynamics of chemical reactions in SCF. The choice of reactor depends on the planned purposes, reaction type, participation of the catalyst, etc. However, when the main research task is to study the mechanism and kinetics of chemical reactions in supercritical fluids near the critical point, an autoclave reactor seems to be most appropriate. There are many arguments in support of this choice [11].

The reagent under study was injected into SCW when its steady state condition (specified temperature and pressure) is reached. The reagent, located in a sampling loop of the known volume, was supplied to the SCW volume by the water delivered to this loop by a syringe pump at a given rate.

The reaction products were sampled for the analysis in the loop of 6.10⁻³ ml volume at specified intervals, then a sample was placed in a Hewlett-Packard 5890 gas chromatograph with the flame-ionization detector equipped with capillary and packed columns. This loop was vacuumed before sampling. Unfortunately, light gases, such as H₂, CO and CO₂, were not analyzed.

2.2. Density of supercritical water in the batch reactor

Density of SCW, an important independent parameter, can be determined with high accuracy in the batch reactor. To calculate the density, one need to know the reactor volume, its “dead” volume (less than 5% of the reactor volume), and weight of water injected to the reactor. Here, the “dead” volume is a space between the shaft of the mixer and wall of the reactor. The reactor and “dead” volumes, as well as the amount of water fed to the reactor were measured with high accuracy.

The SCW pressure, measured with two pressure transducers within the error of ± 0.2 bar, was set in the reactor depending on the given temperature and amount of injected water. Hence, the density of SCW can be modified by varying the water quantity injected into the reactor at specified temperature. Note, when we change the temperature of SCW at the same amount of water in the reactor, the pressure changes also, whereas the density of SCW should remain practically constant.

Predicted by the same procedure, the densities of SCW were compared to the densities calculated from the NIST water steam thermodynamic data [30]. Comparison of the densities obtained under isothermal [11] and isobaric conditions (Fig. 1) showed the essential difference between the theoretical and experimentally found values. At the same time, high experimental reproducibility of these data was obtained.

In our opinion, the difference between experimental and calculated densities may be caused by two factors: first, by the essential non-ideality of SCW under real conditions due to formation of local condensation clusters, whose density exceeds considerably the bulk-average fluid density [10,31]; second, by high compressibility of fluid near the critical point and formation of regular hydrodynamic condensations of fluid due to propeller rotation at a speed up to 2300 rpm. Note that such high speed of hashing is necessary to achieve the isothermal condition of fluid and fast hashing of reagent injected to the SCW. Certainly, one may assume the existence in the reactor volume of the “cold” spots or stagnant zones with much greater density than volumetric density of

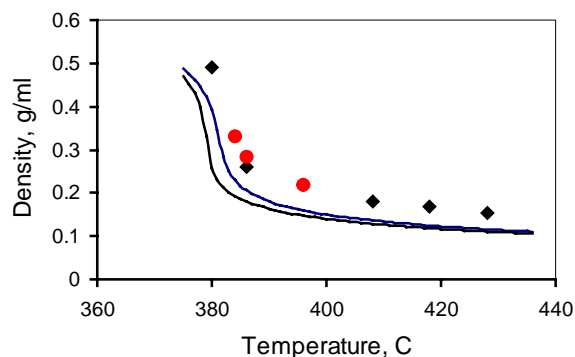


Fig. 1. The temperature dependence of SCW density. Lines: calculated data at 234.6 and 240.86 bar; Symbols: the experimental data.

SCW at a given temperature. However, this assumption was not confirmed experimentally.

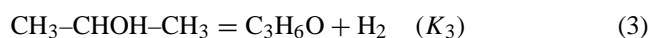
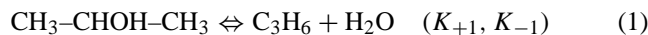
2.3. Experimental results

Among many studied chemical reactions in SCW (conversion of methyl-ethyl acetate, ethers and lowest alcohols), the 2-propanol dehydration reaction was chosen for the detailed study of the way the SCW density and temperature affect the kinetics and equilibrium of chemical reactions. Kinetic studies of this reaction in SCW were performed in the temperature interval of 651–686 K at SCW density of 0.24–0.59 g/ml. The pressure varied in the range of 227–350 bar. The initial concentration of 2-propanol in SCW varied within the limits of $3\text{--}4.5 \times 10^{-6}$ mol/cm³.

The primary experimental data (molar fractions of reactants) on 2-propanol dehydration in SCW at 666 K and density of 0.42 g/ml ($P = 270$ bar) at various residence times are presented in [11].

It was shown experimentally that propylene (C₃H₆), propane (C₃H₈), propyne (C₃H₄), acetone (C₃H₆O), and 1-propanol (C₃H₈O) are the main products of 2-propanol dehydration in SCW. Methane and ethane were detected in insignificant quantities.

To determine main reaction stages resulting in the formation of the above listed products, 1-propanol dehydration, propylene hydration, propyne, propylene and acetone hydrogenation were carried out under the similar conditions in SCW. The experimental data and analysis of the previously published data allow the basic reactions occurring at 2-propanol dehydration in SCW to be written as follows:



Here, the initial 2-propanol decomposes by two parallel reactions (1) and (3). The propylene formed in reaction (1) can participate in reactions (2), (4) and (5).

A more detailed description of the additional experiments aimed at confirmation of the chosen reaction scheme is given below.

2.3.1. 1-Propanol dehydration in SCW

1-Propanol dehydration in SCW was carried out at 670 K and two densities of SCW equal to 0.28 and 0.48 g/ml. Propylene and insignificant amounts of 2-propanol, propane and acetone were detected among the products of 1-propanol dehydration. Hence, it can be concluded that 1-propanol is formed in 2-propanol dehydration as a result of propylene

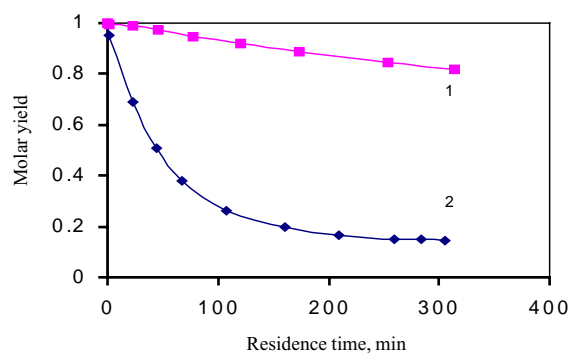


Fig. 2. Molar fractions of (1) 1-propanol and (2) 2-propanol vs. residence time at the same temperature 670 K and density 0.48 g/ml.

hydration (reaction (2)). Note also that the rate of 1-propanol dehydration is lower than the rate of 2-propanol dehydration under similar conditions (Fig. 2).

2.3.2. Propylene and propyne hydration in SCW

The experiments showed that the propylene hydration reaction in SCW proceeds by 99% to yield 2-propanol. A small amount of acetone is detected in the reaction products only when the concentration of 2-propanol in SCW is high, which is the only consequence of reaction (3) and/or (6). Hence, one may suggest that under the given experimental conditions, acetone does not form directly from propylene, but it is formed most likely from propylene hydration products by reactions (3) and (6).

At the same time, hydration of propyne in SCW results in the formation of acetone only. Moreover, the rate of this reaction (6) is several times higher than the rate of reaction (1). As mentioned above, propyne is present in the reaction products, so one may assume that the acetone formation occurs by propyne hydration reaction, with propyne being an intermediate component of 2-propanol dehydration reaction. Unfortunately, we did not manage to identify experimentally the reaction resulting in the propyne formation.

2.3.3. Propylene and acetone hydrogenation by hydrogen in SCW

It is carried out by a technique slightly differing from that described above [11]. Results of these experiments allow two main conclusions to be suggested. First, hydrogenation of C₃H₆ by hydrogen present in SCW leads to the formation of C₃H₈. Second, the acetone, injected to the SCW containing hydrogen, undergoes hydrogenation with 2-propanol formation. But the rate of this reaction is low in spite of the high initial concentration of acetone. Besides, the formed 2-propanol is spent in reaction (1), forming propylene, which is hydrogenated up to propane by excess hydrogen. As a result, propylene, propane and 2-propanol are present in the reaction mixture in approximately equal amounts.

Available experimental data are not sufficient to separate the contributions of reactions (3) and (6) to the acetone formation. Certainly acetone is formed by reverse reaction (6),

Table 1
Equilibrium composition of the reaction mixture, $T = 666$ K, $P = 280$ bar

Component	Equilibrium composition (mole)	
	Variant I	Variant II
H ₂	0.2170	0.0000
C ₃ H ₄	0.0000	0.0091
C ₃ H ₆	0.0083	0.9004
C ₃ H ₈	0.3870	0.0101
CH ₂ OHCH ₂ CH ₃	0.0001	0.0223
CH ₃ CHOHCH ₃	0.0005	0.0581
C ₃ H ₆ O	0.6050	–
H ₂ O	1000.3943	1000.9169

as, first, C₃H₄ is present in the products of 2-propanol dehydration reaction in SCW; second, according to the experiment, the propyne hydration in SCW results in the formation of acetone only. Besides, the rate of this reaction is much higher than the rate of reaction (1), so propyne is not accumulated in the reaction mixture and passes through a maximum in special experiments. Third, propyne can be formed by reaction (5), however, we do not have direct proof of this assumption.

It is necessary to pay attention to another possible reaction (3), resulting in acetone formation. Most probably, this stage is the slowest one among the above mentioned reactions (1)–(6). To confirm this statement, we calculated the equilibrium composition of the two reaction mixtures, taking into account their non-ideality. The calculation showed (Table 1) that when acetone is included in the list of reaction products variant I, the equilibrium mixture contains mainly acetone, which is not confirmed by our experiment. When acetone is excluded from the list of products variant II, the calculated equilibrium composition under supercritical conditions is rather close to the experimental equilibrium. Thus, reaction (3), yielding acetone, is the slowest stage as compared to the other reactions, especially reaction (6).

Therefore, the studies showed that dehydration of 2-propanol in SCW proceeds mainly by six consecutive-parallel reactions, three of them being the well reversible reactions under the chosen experimental conditions.

2.4. Effect of SCW density and temperature on the rate of 2-propanol dehydration reaction

As noted above, the isothermal change of SCF density near the critical point can lead to a significant change in the rate of some chemical reactions. Therefore, it seemed reasonable to study the effect of SCW density on the rate of 2-propanol dehydration reaction. All the runs were carried out at 666 K and SCW density varying from 0.24 to 0.58 g/ml. The investigated interval of SCW densities corresponds to the area of parameters T and P , in which main properties of SCW, including ionization and dielectric constants [30], vary most considerably. The results in the form of dependences of the molar fractions of 2-propanol, propy-

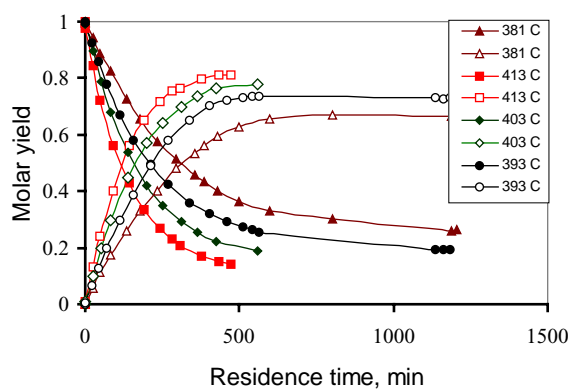


Fig. 3. 2-Propanol dehydration reaction in SCW. Molar fractions of 2-propanol (filled symbols) and propylene (empty symbols) vs. residence time at various temperatures. Density of SCW is 0.34 g/ml.

lene presented in the Fig. 3. Other results as dependences of reaction products on the residence time are reported in detail in our previous paper [11].

The rate of 2-propanol dehydration reaction was shown to increase considerably when SCW density changes from 0.34 to 0.5 g/ml at a constant temperature. The further increase in SCW density from 0.5 g/ml has a weak effect on raising the rate of reaction (1). The experiments showed also that the rates of 2-propanol dehydration reaction at SCW densities of 0.24 and 0.34 g/ml are almost similar. Molar fraction of acetone in reaction products decreases essentially with an increase in the fluid density, while molar fraction of 1-propanol increases in the same measure. Molar fraction of propane does not depend on the density in the studied interval.

Temperature effect on the rate of 2-propanol dehydration reaction in supercritical water was studied at three densities of supercritical water equal to 0.24, 0.34 and 0.42 g/ml. At the same time, in the present work we shall deal with the kinetics of 2-propanol dehydration at SCW density of 0.34 g/ml, as this density is nearest to the critical density of water.

Fig. 4 shows the trends of molar fractions of 2-propanol and propylene depending on the residence time at SCW density of 0.34 g/ml and temperature varying from 654 to 686 K. The behavior of 2-propanol and propylene molar fractions at the residence time exceeding 1200 min confirms the attainment of the equilibrium state of the reaction. However, it is hardly possible to reach the “pure” equilibrium state for reaction (1) at large residence time owing to secondary reactions (2)–(6).

2.5. Processing of experimental data

Mathematical processing of experimental data was performed using our software package KINET II [32–34]. Reactions (1)–(4) selected for mathematical processing of kinetic data and finding the rate constants. According to reactions scheme, the system of five differential equations

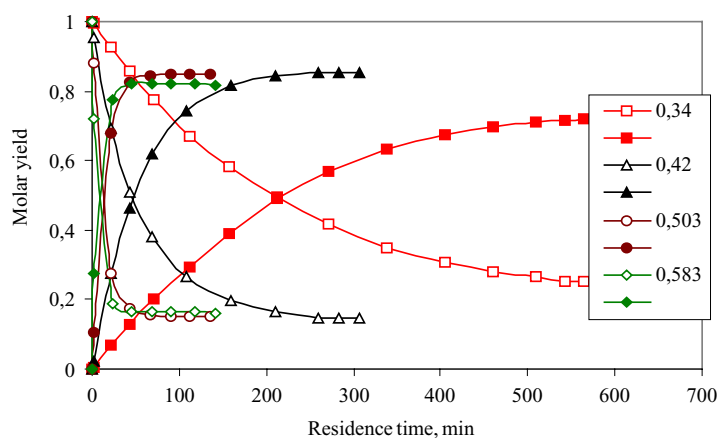


Fig. 4. 2-Propanol dehydration reaction in SCW. Molar fractions of 2-propanol (filled symbols) and propylene (empty symbols) vs. residence time at various densities. Temperature of SCW is 666 K.

Table 2

Apparent rate constants of 2-propanol dehydration reaction at various SCW densities, temperature 666 K

Density (g/ml)	K_{+1} (s^{-1})	K_{-1} (s^{-1})	K_{eq}	K_2 (s^{-1})	K_3 (s^{-1})	K_4 (s^{-1})
0.34	$5.8E-5 \pm 6.9E-7$	$1.3E-5 \pm 8.1E-7$	4.57	$7.2E-7 \pm 2.6E-7$	$7.9E-7 \pm 2.1E-7$	$7.2E-8 \pm 3.1E-8$
0.424	$2.8E-4 \pm 2.5E-6$	$4.8E-5 \pm 1.4E-6$	5.78	$6.5E-7^*$	$4.7E-7^*$	$1.4E-7^*$
0.503	$1.3E-3 \pm 1.2E-5$	$2.3E-4 \pm 4E-6$	5.65	$9.5E-7^*$	$5.3E-7^*$	$7.0E-7^*$
0.583	$1.9E-3 \pm 2.5E-5$	$3.5E-4 \pm 7.7E-6$	5.35	$1.5E-6^*$	$3.4E-6 \pm 1.7E-6$	$2.0E-6^*$

* Here, the confidence interval is approximately equal to the constant value.

in the assumption of the first order reaction rates was used for the estimation of the rate constant values. Good agreement between the experimental data and the data calculated with the model is observed in all cases [11]. The predicted apparent rate constants and the equilibrium constant of reaction (1) at different densities of SCW are given in Table 2. These data demonstrate that, first, the apparent rate constant of reaction (1) increased by more than an order of magnitude as the density increased from 0.3 to 0.58 g/ml; second, the equilibrium constant of reaction (1) also varies with increasing density. Appreciable changes in the equilibrium constant occur when the density of SCW changes from 0.34 to 0.42 g/ml. At the same time, such change in the equilibrium constant with the density can be caused by both experimental and calculation errors.

The apparent rate constants of the reaction and 95% confidence intervals at temperature variation from 654 to 686 K and constant SCW density 0.34 g/ml are given in Table 3. Since the concentration of 1-propanol in the reaction products in the discussed runs was considerably lower than the concentration of other products, $K_3 = 0$ was accepted for the processing of kinetic data.

Table 3

Rate constants of 2-propanol dehydration reactions in SCW at various temperatures, density of SCW is 0.34 g/ml

T (K) (s^{-1})	654	666	676	686
K_{+1}	$4.0E-5 \pm 4.6E-7$	$6.0E-5 \pm 1.13E-6$	$8.0E-5 \pm 7.8E-7$	$1.1E-4 \pm 1.0E-6$
K_{-1}	$6.7E-6 \pm 1.0E-6$	$1.3E-5 \pm 1.3E-6$	$1.5E-5 \pm 7.7E-7$	$1.5E-5 \pm 8.0E-7$
K_2	$3.7E-7 \pm 1.6E-7$	$6.3E-7 \pm 2.5E-7$	$9.8E-7 \pm 1.7E-7$	$1.7E-6 \pm 4.0E-7$
K_4	$5.6E-7 \pm 2.1E-7$	$7.0E-7 \pm 3.3E-7$	$6.8E-7 \pm 2.3E-7$	$1.1E-6 \pm 2.5E-7$

The Arrhenius plots of apparent rate constant (K_{+1}) of the forward reaction (1) at SCW densities of 0.24 and 0.34 g/ml were constructed. With the first order differential equations being used for data processing, activation energies of the reaction at two SCW densities were obtained: 20 kJ/mol at 0.24 g/ml density, and 26 kJ/mol at 0.34 g/ml density. Such difference in the activation energies at various densities may be caused by both the experimental and data processing errors.

3. Prediction of SCW density effect on the rate constants of 2-propanol dehydration reaction

The nature of interaction between reactants and solvent determines the extent to which the pressure/density of SCW affects the chemical reaction rate. Several mechanisms of such interaction are examined in the literature, among them are formation of an activated complex, density or concentration augmentation, and clustering solvent around a dilute solute [31,35,36]. Two approaches are used in our studies of SCW density effect on the rate constant of 2-propanol

dehydration reaction: the thermodynamic model (transition state theory) and the model of acid-catalyzed reaction.

3.1. Thermodynamic pressure effect

According to the thermodynamic model, the effect of pressure/density on the reaction rate constant is described using the transition-state theory. Within this theory, reactants and activated complex or transition state are assumed to be in equilibrium, and for a unimolecular decomposition reaction it is possible to write:



where A is 2-propanol, and [TS] is transition state or activated complex.

When the thermodynamic approach is used, the [TS] should be considered as an ordinary molecule having the macroscopic thermodynamic properties, such as critical pressure and temperature. It is supposed also that reagent A is in equilibrium with [TS]. But, being in equilibrium with the reagent, the [TS] decomposes with the formation of the reaction products as well. The stage of [TS] destruction with the formation of the products is a limiting stage of the chemical reaction.

3.2. Structure of activated complex for 2-propanol—supercritical water system

Molecules in gases and solutions can form complexes as a result of various weak chemical interactions, yielding, for example, bonds $\text{O}-\text{H} \cdots \text{H}$, $\text{C}-\text{H} \cdots \text{O}$, $\text{C}-\text{H} \cdots \text{C}$. Hydrogen bonds, representing weak chemical interactions, differ insignificantly from the common valence bonds. Therefore, the formed molecules, complexes, should not qualitatively differ from the molecules formed by strong chemical bonds.

An activated complex for chemical reactions in SCW may consist of the reagent molecule solvated with non-dissociated molecules of water, and include a hydronium cation (C_3H_7^+). The hydronium cation can exchange proton with both water molecules and molecules of reagent in the solution. The closer the hydronium cation comes to the other molecule, the more probable is the proton transition.

Probably, the presence of hydroxyl groups in alcohols and their ability to form complexes is the reason for strong dependence of chemical reaction rate on the density of supercritical fluid.

The structure of the activated complex formed by 2-propanol molecule in SCW and containing at least one strongly bonded water molecule and a proton may be presented as



The activated complex can be formed also at the interaction of two or more molecules among themselves in a supercritical solvent. Nevertheless, for 2-propanol dehydration in

SCW, we chose the activated complex formed by the interaction of one 2-propanol molecule and at least one molecule of water. Formation of the activated complex via the interaction of two or more 2-propanol molecules in SCW is unlikely, since, first, the concentration of 2-propanol in SCW is low (≤ 0.0045 mol/l), and, second, it was shown experimentally that the reaction rate increased with increasing the water concentration, which resulted in an increase of its density. This experimental fact testifies obviously for the benefit of the above assumption about the structure of activated complex.

3.3. Transition-state theory in modeling the influence of SCW density on the reaction rate constant

Based on the theory of an elementary reaction, the equation that determines coupling between the reaction rate constant and Gibbs free energy of activated complex or equilibrium constant for reaction (7) can be written as

$$k = \chi \frac{k_b T}{h} \exp\left(\frac{-\Delta G^\ddagger}{RT}\right) = \chi \frac{k_b T}{h} K_f^\ddagger \quad (8)$$

Here, χ is the transmission coefficient; it does not depend on temperature and pressure and serves mainly for the coordination of dimensions, in calculations it is commonly taken as a unit; k_b the Boltzmann constant, and h the Planck constant. K_f^\ddagger is the equilibrium constant of reversible reaction $A \rightleftharpoons [\text{TS}]$ expressed through the fugacity of components. ΔG^\ddagger is the free energy of activation at the formation of transition state.

Consecutive logarithmation and differentiation of Eq. (8) with respect to pressure at a constant temperature result in the basic equation of the transition-state theory for unimolecular reaction:

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^\ddagger}{RT} \quad (9)$$

Here, ΔV^\ddagger is the activation volume (cm^3/mol) expressed as a difference between partial molar volumes of [TS] and the reactant. The ΔV^\ddagger value can be calculated using the thermodynamic model based on the equations of state describing the P - V - T properties of the reaction mixture.

Thus, the transition state theory gives a relation between the chemical reaction rate constant and the activation volume. Partial molar volumes of transition state and reactants in a solvent play a key role in this formalism.

The absolute value of activation volume of the chemical reaction near to the critical point of the solvent, i.e. in its strongly compressed area, can be very large. There are many examples in the literature when the activation volumes of reaction can change in the limits from +15,000 to -15,000 cm^3/mol [29,37]. It is just the high compressibility of fluid that can lead to large absolute values of the partial molar volumes.

Let us return to the data of Table 2 and plot the dependence of the apparent rate constant of reaction (1) on density in the

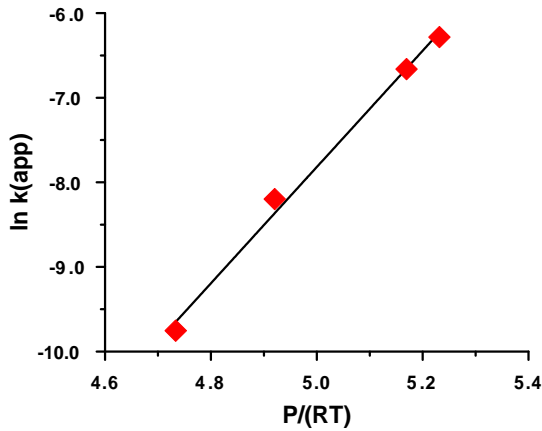


Fig. 5. The dependence of the natural logarithm of an apparent rate constant of reaction (1) on P/RT , $T = 666$ K.

forward direction (Fig. 5). Fig. 5 shows $\ln k_{\text{app}}$ as a function of P/RT that falls on a straight line with good accuracy:

$$\ln k_{\text{app}} = 6.875 \frac{P}{RT} - 34.00 \quad (10)$$

Slope of the straight line has the dimensions of molar volume, l/mol, and according to Eq. (10) is $-\Delta V^{\#}$. Thus, the 2-propanol dehydration in SCW has a large negative activation volume equal to $-6875 \text{ cm}^3/\text{mol}$. Moreover, this value is constant in the studied pressure interval. To estimate the value of $\Delta V^{\#}$ and its dependence on density and partial molar volumes, we used the cubic equation of state.

3.3.1. The equation of state

There are many methods to calculate the partial molar volumes, nevertheless, the cubic equations of state (EOS) [29,35,38] are used most frequently. In the present work, the Redlix–Kwong–Soave (RKS) EOS was used for this purpose:

$$P = \frac{RT}{V_m - b_i} - \frac{a_m(T)}{V_m(V_m + b_{mi})} \quad (11)$$

where V_m is the molar volume of a mixture (l/mol).

Coefficients a_m and b_m for a mixture with the given molar fraction vector y are determined as follows:

$$a_m = \sum_{j=1}^{N_s} \sum_{i=1}^{N_s} y_i y_j a_{ij}; \quad b_m = \sum_{j=1}^{N_s} \sum_{i=1}^{N_s} y_i y_j b_{ij} \quad (12)$$

$$a_{ii} = \alpha_i(T) \left(\frac{0.42748 R^2 T_{ci}^2}{P_{ci}} \right) \quad (13)$$

$$b_{ii} = \frac{0.08664 RT_{ci}}{P_{ci}} \quad (14)$$

$$a_{ij} = (1 - k_{ij}) \sqrt{a_{ii} a_{jj}} \quad (15)$$

$$b_{ij} = (1 - c_{ij}) \left(\frac{b_{ii} + b_{jj}}{2} \right) \quad (16)$$

$$\alpha_i(T) = \left[\left(1 + d_i \left(1 - \sqrt{\frac{T}{T_{ci}}} \right) \right) \right]^2 \quad (17)$$

$$d_i = 0.480 + 1.574 \omega_i - 0.176 \omega_i^2 \quad (18)$$

where T_{ci} and P_{ci} are the critical temperature and pressure of the i -th component in a mixture. Parameter ω_i is the acentric factor of the component.

A distinctive feature of the above mentioned RKS equation of state is the presence of two binary interaction coefficients k_{ij} and c_{ij} in Eqs. (15) and (16). It will be shown that these coefficients are important for increasing the calculation accuracy. Their values can be found from experimental data on the phase equilibrium in binary systems.

3.3.2. Definition of binary interaction coefficients

It was shown in our previous work [39] that a correct prediction of binary interaction coefficients $k_{i,j}$ and $c_{i,j}$ allows the above RKS equation of state to describe well the P – V – T properties of multicomponent mixes, including the field of high and super high pressures. Applying the technique described in [39], we calculated the binary interaction parameters for 2-propanol–water system using the experimental data on the phase equilibrium of this binary pair [40] in critical area. The predicted critical temperature and critical pressure versus 2-propanol concentration in water are plotted in Fig. 6a and b. Here, solid curves are a result of calculation at $K_{ij} = 0$ and $c_{ij} = 0.125$, and filled circles denote the equilibrium experimental data [40]. Fig. 7 presents the P – V isotherms at 573 K for a mixture containing 27.3% of 2-propanol in water, calculated at various values of c_{ij} and $k_{ij} = 0$. One may see from this figure that the calculation data are very sensitive to the c_{ij} values. The correct course of isotherm with a horizontal platform at pressure $P_{cr} = 121$ bar (isotherm 4 in Fig. 7 is critical for the chosen mixture) is derived only when c_{ij} is equal to 0.125. Note, we could not find experimental data on the vapor–liquid equilibrium for the propylene–water binary pair, which would allow the binary interaction coefficients for this system to be defined.

3.3.3. Prediction of the partial molar volumes

According to the definition, partial molar volume of the i -th component in a mixture can be determined from the standard thermodynamic expression:

$$\bar{V}_i = \left[\frac{\partial(nV_m)}{\partial n_i} \right]_{P,T,n_j} = V_m + \frac{\partial V_m}{\partial y_i} (1 - y_i) \quad (19)$$

Here

$$\frac{\partial V_m}{\partial y_i} = - \frac{\partial P / \partial y_i}{\partial P / \partial V_m} \quad (20)$$

Derivatives in numerator and denominator of expression (20) can be found in the analytical form at differentiation of

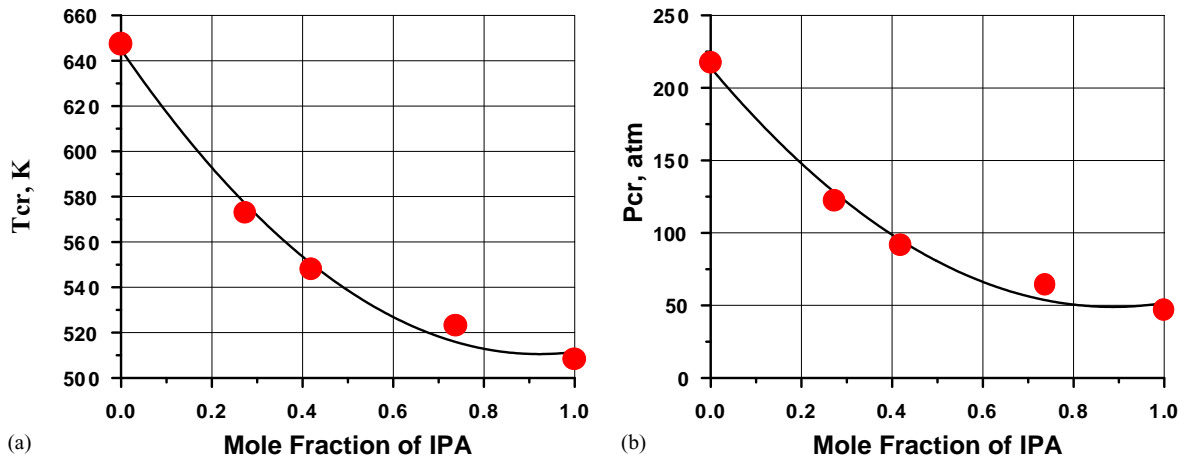


Fig. 6. Critical temperature (a) and pressure (b) of 2-propanol–water mixture vs. its composition. Solid lines: the calculated values; filled circles: the experimental data.

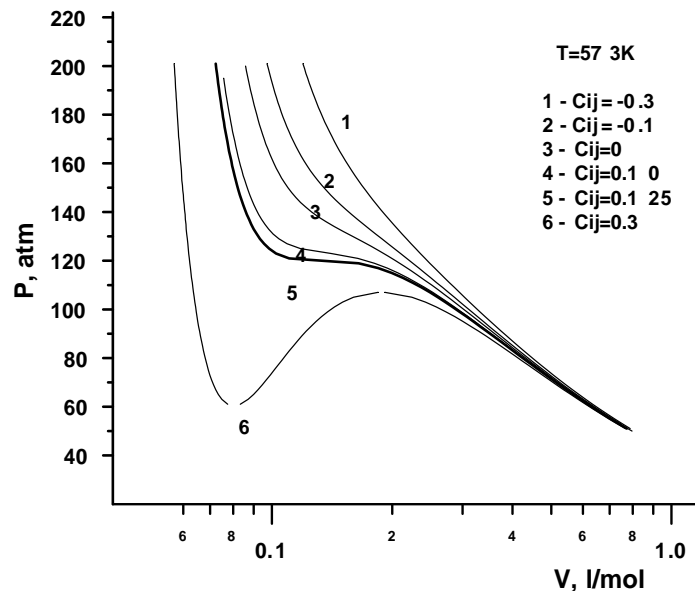


Fig. 7. P – V isotherm ($T = 573$ K) of 2-propanol–water binary mixture plotted at various values of $C_{1,2}$; $k_{1,2} = 0$. (1) $C_{1,2} = -0.3$; (2) -0.1 ; (3) 0; (4) 0.125 (critical); (5) 0.3.

Eq. (11) as

$$\frac{\partial P}{\partial V_m} = - \left[\frac{RT}{V_m(V_m + b_m)^2} - \frac{a_m(2V_m + b_m)}{V_m^2(V_m + b_m)^2} \right] \quad (21)$$

$$\frac{\partial P}{\partial y_i} = \frac{\partial b_m}{\partial y_i} \left[\frac{a_m}{V_m(V_m + b_m)^2} + \frac{RT}{(V_m - b_m)^2} \right] - \frac{\partial a_m}{\partial y_i} \frac{1}{V_m(V_m + b_m)} \quad (22)$$

$$\frac{\partial a_m}{\partial y_i} = 2 \sum_{k=1}^N y_k a_{ik}; \quad \frac{\partial b_m}{\partial y_i} = 2 \sum_{k=1}^N y_k b_{ik}$$

For a binary mixture with large contents of the solvent (y_1) and infinite dilution of the solute (y_2), expression (22)

becomes

$$\left(\frac{\partial P}{\partial y_1} \right)^\infty = Ab_{11} + Ba_{11}b_{11} - Ca_{11};$$

$$\left(\frac{\partial P}{\partial y_2} \right)^\infty = Ab_{12} + Ba_{11}b_{12} - Ca_{12} \quad (23)$$

where parameters A , B , C are the functions of molar volume of the mixture, temperature and coefficient b_m

$$A = 2 \frac{RT}{(V_m - b_m)^2}; \quad B = 2 \frac{V_m}{(V_m^2 - V_m b_m)^2};$$

$$C = 2 \frac{1}{V_m^2 - V_m b_m} \quad (24)$$

According to Eqs. (13) and (14), values a_{11} and b_{11} determine only the individual component properties. Coefficient $a_{1,2}$ is defined by mixing rules (15) and (16). Coefficients a_m and b_m at infinite dilution of solute come to appropriate coefficients a_{11} and b_{11} for the pure solvent.

Eqs. (21)–(24) show that the partial molar volume of the solute depends strongly on its nature and physico-chemical properties, and properties of the solvent. At the same time, the partial molar volume of the solvent is actually equal to molar volume of the mixture.

Unfortunately, it seems impossible to estimate the partial molar volume of an activated complex with good accuracy without knowledge of its structure. However, the task of finding or calculating the detailed structure of a transition state has not been solved even for the most simple molecular interactions. Therefore, in practical calculations it is usually assumed that thermodynamic properties of an activated complex are not strongly different, for example, from the properties of one of the reaction products [35,38]. Alternatively, a substance with the known thermodynamic properties and the structure close to the structure of hypothetical [TS] is chosen as the transition state or activated complex.

3.4. Results and discussion

The knowledge of the activated complex structure is required for the calculation of its critical parameters. The molecule formed by chemical interactions between 2-propanol molecule and hydronium cation with formation of the weak O–H...O bond was taken as a model for the transition state structure. The group contribution Lydersen's method [41] was used for the calculation of critical properties of the selected transition state. These estimations gave the critical parameters $T_{cr} = 980$ K and $P_{cr} = 66$ bar, which were used further to calculate the partial molar volume of the activated complex.

Activation volume of chemical reaction ΔV^\ddagger , or the difference between partial molar volume of the transition state and partial molar volume of a solute, was calculated for the accepted structure of an activated complex. Figs. 8–10 show the dependencies of partial molar volumes for 2-propanol–water (\bar{V}_{IPA}), propylene–water ($\bar{V}_{C_3H_6}$) and [TS]–water binary pairs versus pressure in SCW at $T = 666$ K. The obtained result shows that the 2-propanol–water and propylene–water infinite diluted mixes have rather low values of the partial molar volumes. In addition, this value is negative for the first pair, and positive for the second one.

Since the binary interaction coefficients are the experimentally determined values and there are no available data for [TS]–water system, we have to choose such coefficients. Fig. 10 presents changes in the partial molar volumes of [TS] in SCW with pressure at various binary interaction coefficients. It was found that the partial molar volumes of [TS]–water are most sensitive (as compared to sensi-

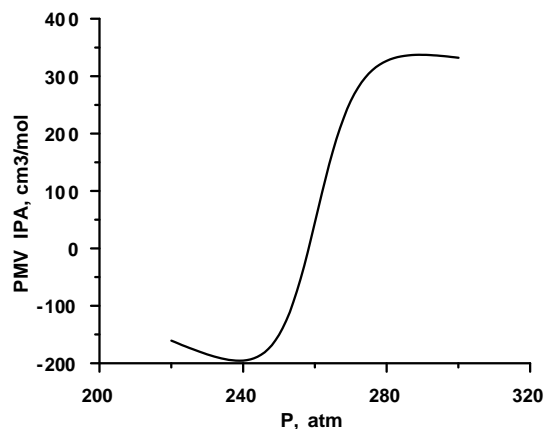


Fig. 8. The dependence of the partial molar volume of 2-propanol in the indefinitely diluted solution of water on pressure, $T = 666$ K.

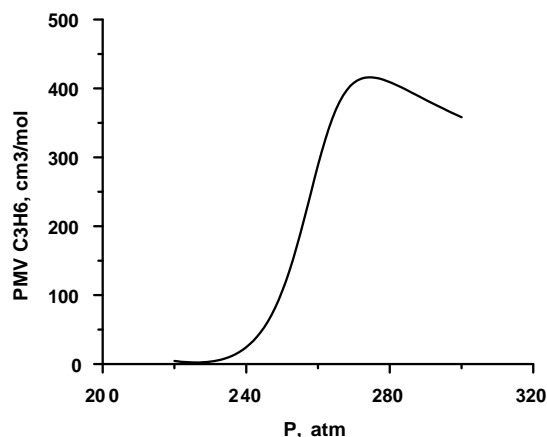


Fig. 9. The dependence of partial molar volume of propene in the indefinitely diluted solution of water on pressure, $T = 666$ K.

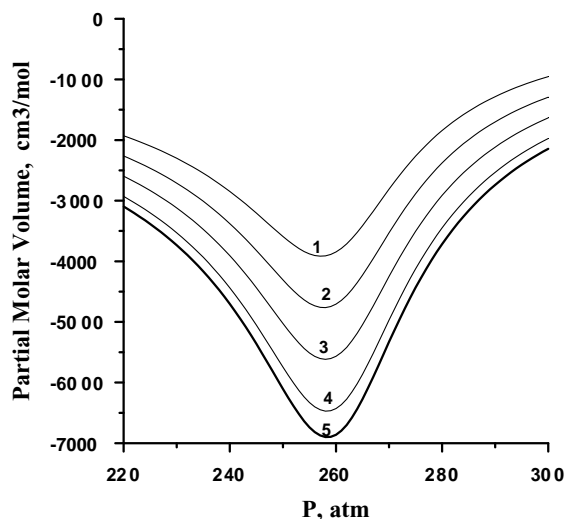


Fig. 10. The dependence of partial molar volume of TS in the indefinitely diluted solution of water on pressure. Effect of $k_{1,2}$ and $c_{1,2}$. $T = 666$ K. (1) $C_{1,2} = 0.2$, $k_{1,2} = -0.2$; (2) 0.3, -0.3 ; (3) 0.4, -0.4 ; (4) 0.5, -0.5 ; (5) 0.55, -0.55 .

Table 4

Partial molar volume in extreme point of function (20) vs. [TS] critical pressure at $T_{cr} = 980$, $k_{12} = -0.5$, $c_{12} = 0.5$

P_{cr} (bar)	\bar{V}_{TS} (cm ³ /mol)
40	-7939
50	-7267
60	-6739
70	-6311
80	-5955
90	-5625

tivity to critical parameters) to the change of the binary interaction coefficients $k_{1,2}$ and $c_{1,2}$. The activation volume of reaction (7) approaches the experimentally measured value at the chosen coefficients $c_{1,2} = 0.55$ and $k_{1,2} = -0.55$. The tendency of these coefficients variation is obvious also from expression (23). The curves in Fig. 10 have the clearly expressed minimum and negative partial molar volume. The absolute values \bar{V}_{TS} exceed considerably the \bar{V}_{IPA} and $\bar{V}_{C_3H_6}$ values.

The calculations showed that variation of [TS] critical pressure affects weakly the value of the partial molar volume (Table 4). At the same time, \bar{V}_{TS} is more sensitive to [TS] critical temperature (Table 5).

The predicted partial molar volumes of [TS] are always negative and close to the experimentally found value equal to -6875 cm³/mol. Hence, the structure of the chosen [TS] complex seems to be designed correctly. It should have a larger molecular weight than 2-propanol, a higher critical temperature and a lower critical pressure than the solvent. The negative sign of the partial molar volume indicates the prevalence of attractive forces at [TS] formation in SCW.

Analysis of the results presented in Figs. 8 and 10 shows that the calculated values of the activation volumes depend strongly on the pressure at the fixed temperature and their difference, i.e. ΔV^\ddagger is not constant that contradicts the experimental data on 2-propanol dehydration in SCW. This result suggests that the effect of density on the rate constant of 2-propanol dehydration in SCW cannot be explained solely by the thermodynamic pressure effect or the transition state theory.

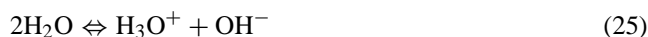
Table 5

Partial molar volume in extreme point of function (20) vs. [TS] critical temperature at $P_{cr} = 66$ bar, $k_{12} = -0.5$, $c_{12} = 0.5$

P_{cr} (bar)	\bar{V}_{TS} (cm ³ /mol)
750	-4065
770	-4269
800	-4577
900	-5621
1000	-6687
1100	-7773

3.5. Acid-catalyzed reaction mechanism for 2-propanol hydration reaction

Water dissociation constant and ionic product of water near its critical point are important properties of chemical reactions. Water near the critical point is strongly ionized with formation of H_3O^+ and OH^- ions by equilibrium reaction:



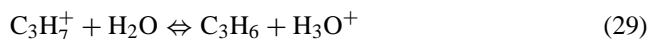
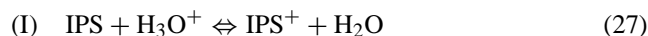
The ionic product of water K_w expressed as

$$K_w = [H_3O^+] \times [OH^-] \quad (26)$$

increases by more than three-orders of magnitude when going from ambient to supercritical conditions. K_w and the dissociation constant in near-critical region are also a strong function of density at constant temperature. Therefore, the changes in these properties can strongly affect the 2-propanol dehydration reaction rate according to acid-catalyzed reaction mechanism in solutions.

Here, $[H_3O^+]$ and $[OH^-]$ are the hydronium ion and the anion concentrations in water.

Elementary reaction steps in the acid-catalyzed 2-propanol dehydration in SCW according to [13] can be written as



where IPS is 2-propanol, IPS^+ and $C_3H_7^+$ are the intermediate reaction products, charged molecules of 2-propanol and propylene, respectively. The sum of reactions (27)–(29) gives the gross reaction (1).

Each of (27)–(29) steps is characterized by the rates of the forward and reverse reactions, r_i , r_{-i} , with their expressions under the mass action law being the products of the rate constant k_i or k_{-i} by the appropriate concentrations. The equilibrium constant of each reaction is determined as $K_i = k_i/k_{-i}$, $i = 1, 2, 3$.

Eqs. (27)–(29) are supplemented by the expression of electroneutrality of a solvent as

$$[IPS^+] + [C_3H_7^+] + [H_3O^+] = [OH^-] \quad [OH^-] = \frac{K_w}{[H_3O^+]} \quad (30)$$

The concentrations of species are expressed hereinafter in the units of molality, i.e. as gram moles per kilogram or gram ion per kilogram. As a result, the concentration of water in the reactor-autoclave for all the runs performed at various densities is $[H_2O] = 55.55 = \text{const}$.

The above reaction pathway (27)–(29) shows that the H_3O^+ ions affect directly the rate of both forward and reverse 2-propanol dehydration reactions. An approach, assuming one limiting stage in (27)–(29) when the others are equilibrium, is commonly used for the discrimination of kinetic model. This allows the concentrations of the charged

species IPS^+ and C_3H_7^+ to be expressed through the concentrations of H_3O^+ ions, neutral species and equilibrium constants of rapid stages. Simultaneous solution of balance Eqs. (27)–(29) and (30), when reaction (27) is the rate-determining step, allowed us to get expressions for the forward and reverse apparent reaction rate (1) as

$$r_1 = k'_1[\text{IPS}] [\text{H}_3\text{O}^+] = k_1[\text{IPS}] \quad (31)$$

$$r_{-1} = k'_{-1}[\text{C}_3\text{H}_6] [\text{H}_3\text{O}^+] = k_{-1}[\text{C}_3\text{H}_6] \quad (32)$$

There is an important conclusion that the apparent rate constants of forward and reverse gross-reaction (1) are directly proportional to the $[\text{H}_3\text{O}^+]$ ion concentration.

3.5.1. Ionic product of water

Ionic product of water changes dramatically near the critical point. The equation for accurate calculation of K_w variation with density and temperature is proposed in [21] as

$$\log K_w = Q_1(T) + Q_2(T) \log \rho \quad (33)$$

$$Q_1(T) = \frac{A+B}{T} + \frac{C}{T^2} + \frac{D}{T^3}; \quad Q_2(T) = \frac{E+F}{T} + \frac{G}{T^2} \quad (34)$$

The dimensions of K_w (gion/kg^2) are determined by formula (33). The density of water is substituted in formula (33) in terms of gram per cubic centimeter. The concentration of water in the system is a constant value at the chosen units of concentration. Thus, $[\text{H}_2\text{O}]$ enters into the equations for apparent rate constants as a constant value, which is independent from the solvent density.

According to the data presented in [21], the coefficients in Eq. (34) are equal to

$$\begin{aligned} A &= -4.098; & B &= -3245.2/K; \\ C &= 2.2362 \times 105/K^2; & D &= -3.984 \times 107/K^3; \\ E &= 13.957; & F &= -1262.3/K; \\ G &= 8.5641 \times 105/K^2 \end{aligned}$$

Eq. (33) can be used at temperatures from 273 to 1273 K and pressures up to 10,000 bar at $T = 666$ K.

$$Q_1(T) = -8.60138; \quad Q_2(T) = 13.99094 \quad (35)$$

Then the dependence of $[\text{H}_3\text{O}^+]$ on the density is expressed by equation:

$$[\text{H}_3\text{O}^+] = \sqrt{K_w} = 10^{-4.30069} \times \rho^{6.9955} \quad (36)$$

A high sensitivity of the $[\text{H}_3\text{O}^+]$ concentration to the solvent density confirms our assumptions on the mechanism of the density effect on the apparent rate constants.

3.6. Comparison of predicted and experimental data

Based on Eq. (36), the rate constants in expressions (31), (32) can be written as

$$k_1 = k'_1[\text{H}_3\text{O}^+] = k'_1 b \rho^n \quad (37)$$

$$k_{-1} = k'_{-1}[\text{H}_3\text{O}^+] = k'_{-1} b \rho^n \quad (38)$$

where k'_1, k'_{-1} are the rate constants of bimolecular reactions, kilogram-second per mole; $b = 10^{-4.3007}$, $n = 6.996$ are the constants from Eq. (36). The dimensions of the reaction

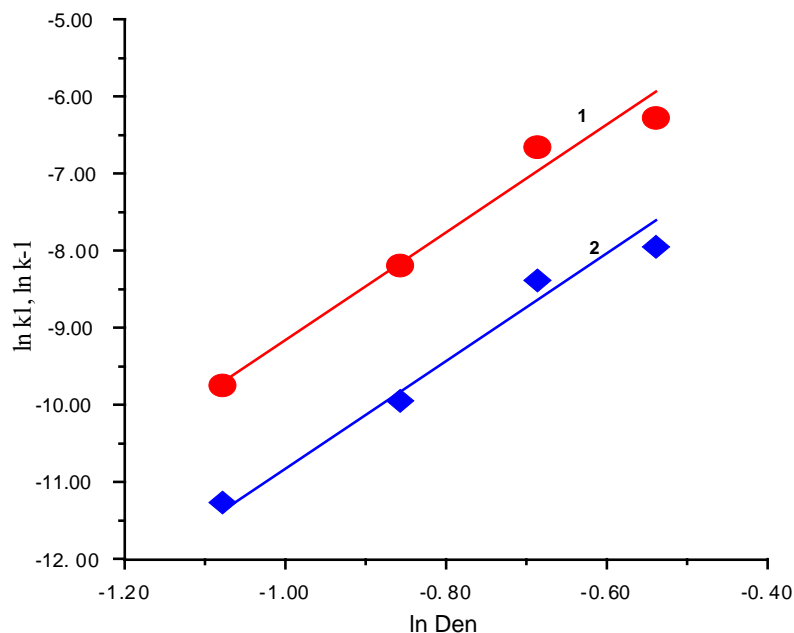


Fig. 11. The dependence of apparent rate constants for direct (1) (k_1) and reverse (2) (k_{-1}) reaction (1) on density. Symbols: the experiment; solid lines: the calculated data.

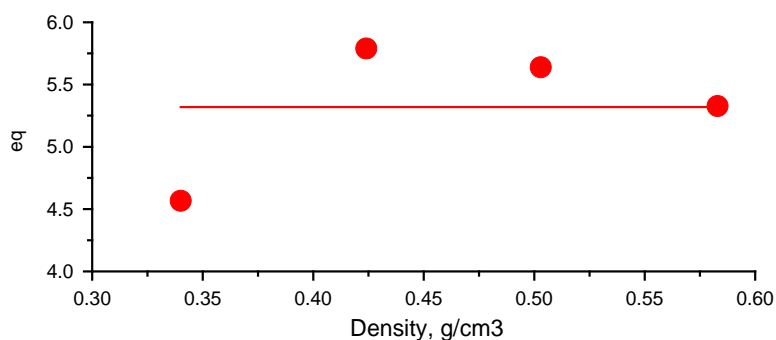


Fig. 12. The dependence of an equilibrium constant of 2-propanol dehydration reaction in SCW on density. Filled circles: the experiment; solid line: the calculated data.

rate are expressed in mole per kilogram second, dimensions of concentrations in mole per kilogram; k'_1 and k'_{-1} values can be found by solving the parameter estimation task using the following linear forms:

$$\ln k_1 = \ln(k'_1 b) + n \ln \rho \quad (39)$$

$$\ln k_{-1} = \ln(k'_{-1} b) + n \ln \rho \quad (40)$$

The estimated k_1 and k_{-1} values are equal to

$$k'_1 = 2295.25 \pm 538.01; \quad k'_{-1} = 431.53 \pm 94.66 \quad (41)$$

The root-mean-square relative deviation of the values of apparent rate constants predicted by formulas (37) and (38) from the measured constants given in Table 2 amounts to 24%. Fig. 11 illustrates the agreement between predicted and experimental data. Here, solid lines are the result of theoretical calculations with the use of Eqs. (39) and (40), filled symbols are the experimental data.

3.7. Equilibrium of 2-propanol dehydration reaction in SCW

In equilibrium of reaction (1) $r_1 = r_{-1}$, or

$$k'_1[\text{IPS}] = k'_{-1}[\text{C}_3\text{H}_6] \quad (42)$$

Apparent equilibrium constant can be expressed as

$$K_{\text{eq}} = \frac{k'_1}{k'_{-1}} = 5.319 \quad (43)$$

The estimation of $\tilde{K}_{\text{app}} = [\text{C}_3\text{H}_6]^{\text{eq}}/[\text{IPS}]^{\text{eq}}$ was made at different densities of SCW (see Table 2). Here, the experimental values of reagent concentrations in an equilibrium are marked with the superscript “eq”. Agreement of predicted and experimental K_{eq} values is shown in Fig. 12. The average \tilde{K}_{app} value estimated in the fourth run is equal to 5.33, which is very close to the value predicted by Eq. (43).

4. Conclusion

The studies of 2-propanol dehydration in supercritical water showed that the reaction rate depends greatly on the density of supercritical water. As a result of special experimental studies of hydration and hydrogenation of the

main products of the target reaction, the reaction route of 2-propanol dehydration in SCW has been proposed. Non-catalytic hydrogenation of olefins by hydrogen dissolved in SCW near its critical point was shown to proceed with high rate. The apparent rate constants, energy and activation volume of 2-propanol dehydration reaction were obtained by variation of temperature and pressure near the critical point of supercritical water. It was shown also that the density of SCW can be used to control the rate and selectivity of chemical reaction.

The influence of SCW density on the rate constant was attributed to the activation volume effect (thermodynamic model or a model based on the transition-state theory) and the effect of water dielectric constant (a model based on the acid-catalyzed mechanism).

Application of the first model showed that the calculated values of the activation volume depend strongly on pressure at fixed temperature that contradicts the experimental data and so this approach or model cannot be used for explanation of pressure effect on the rate of selected reaction. At the same time, prediction based on the acid-catalyzed mechanism describes experiments with good accuracy. It was shown that the rates of direct and reverse apparent reactions of 2-propanol dehydration are directly proportional to the concentration of H_3O^+ ions. The evident linear dependence of logarithms of H_3O^+ concentration in SCW and apparent rate constant on the density/pressure proves the second reaction mechanism to be more preferable. However, the true rate constant of H_3O^+ -catalyzed reaction does not depend on density/pressure.

Acknowledgements

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