

Determination of the adsorption model of alkenes and alcohols on sulfonic copolymer by inverse gas chromatography

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Abstract

The determination of a number of adsorption sites on sulfonated styrene–divinylbenzene copolymer for alkenes (propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, isobutene, 2-methyl-1-butene, 2-methyl-2-butene, 2-methyl-1-pentene, 2-methyl-2-pentene and 2-methyl-2-hexene) and alcohols (methanol, ethanol and *n*-propanol, *n*-butanol, 2-butanol and *tert*-butanol) was performed by the saturation copolymer with vapors of adsorbate, by removing the excess of adsorbate from copolymer by blowing the inert gas through copolymer bed and by the desorption of adsorbed alcohol in the programmed increase of temperature. The adsorption measurements were performed on sulfonated ion-exchange resin (Amberlyst 15) with different concentrations of the acid group, which means with a varying number of adsorption sites. The following adsorption models for alkenes were suggested: the first in which one molecule of alkene is adsorbed by two sulfonic groups, for linear alcohols, the second in which one sulfonic group can adsorb one molecule of alcohol and for non-linear alcohols the third where one molecule of alcohol is adsorbed by two or more sulfonic groups.

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1. Introduction

It is difficult to determine the number of molecules adsorbed on one adsorption center when only the adsorption isotherm is available and therefore it is necessary to adjust a definite adsorption model to the results of measurements based on the analysis of the shape of the adsorption isotherm. Of course, attempts at finding statistical correlations between experimental results and equations describing adsorption models assumed can lead to the case where different models are correlated with experimental results.

The method capable of matching a definite adsorption model up with the results of measurements based on the analysis of the shape of the adsorption isotherm was described in the study [1]. Under static conditions, measurements of the adsorption of compounds of weak bases properties (dimethyl ether and tetrahydrofuran) were taken on sulfonated ion-exchange resins of different contents of sulfonic groups, i.e. of a variable number of adsorption

sites. Three different models of adsorption by Langmuir were verified: (i) adsorption by one sulfonic group of a single molecule, without dissociation, (ii) adsorption by two sulfonic groups of a single molecule, with dissociation, and (iii) adsorption by two sulfonic groups of a single molecule, without dissociation. The method of the least squares was used to correlate the equations of adsorption isotherms with the results of measurements. The differentiation between the two assumed models (i) and (iii) correlating with the results of measurements could not be made on the basis of the analysis of the shape of the adsorption isotherm only. The present study aimed at describing investigations determining the number of sulfonic groups taking part in the adsorption of a molecule of alkene and alcohol on sulfonated copolymer Amberlyst 15. The concept of measuring adsorption on a series of sulfonated copolymers of a different number of sulfonic groups described in the above-mentioned study [1] was partly used in the methodology. However, as opposed to this methodology consisting in matching different adsorption models up with results of measurements, a simpler model of adsorption was suggested and its mathematical description was provided. Inverse gas chromatography was used in measurements.

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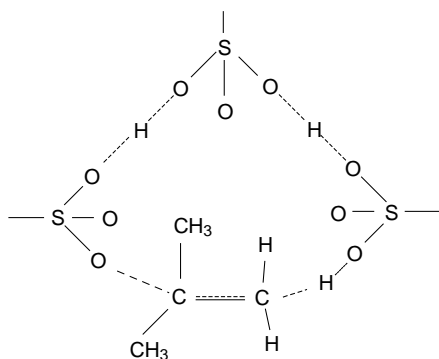


Fig. 1. Model of dual adsorption site of the one isobutene molecule by sulfonic group net of ion-exchange resin [3].

2. Theory

Two models can be used to describe the mechanism of adsorption of alkenes on sulfonated copolymer. The first model assumes the formation of two bonds between one molecule of alkene and two sulfonic groups [2]. The mechanism of the adsorption of isobutene according to the first model is shown on Fig. 1. Hydrogen from the first sulfonic group joins the methylene group and the *t*-butyl carbonium ion formed creates another bond between carbon and oxygen of the second sulfonic group. The formation of a single hydrogen bond between the double bond and hydrogen of the sulfonic group is assumed in the second model (Fig. 2) [3].

A one-center adsorption model of the mechanism of dehydration of alcohols on sulfonated copolymer Amberlyst 15 is suggested in the study [4]. It has been assumed that one molecule of alcohol can be adsorbed on one sulfonic group, and both products of parallel reactions of dehydration (ether and alkene) are produced as a result of different surface reactions of adsorbed molecules of alcohol. Sulfonic groups of copolymer are space-oriented to different directions (Fig. 3), and a molecule of alcohol forms a hydrogen bond between the hydroxyl group and the sulfonic group.

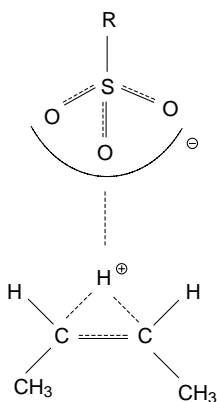


Fig. 2. Model of single adsorption site of the one isobutene molecule by sulfonic group of ion-exchange resin [1].

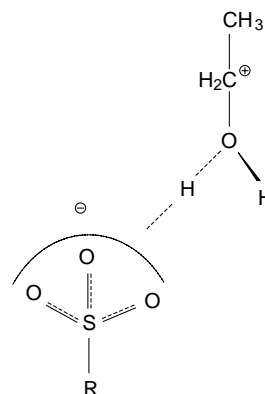
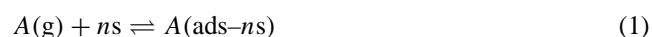


Fig. 3. Model of single adsorption site of the one alcohol molecule by sulfonic group of ion-exchange resin.

A different model of alcohol adsorption was suggested in the study [2]. The existence of the chain of sulfonic groups interconnected by hydrogen bonds was assumed in it. The chains make a network of proton donor and proton acceptor properties. A molecule of *tert*-butanol is adsorbed on two centers through the formation of the hydrogen bond with the hydroxyl group and the hydrogen bond between hydrogen of the methyl group and oxygen of the sulfonic group (Fig. 4).

Considering the issues mentioned above, a model of adsorption assuming that one molecule of alkene or alcohol can be adsorbed by one or more sulfonic groups interconnected by hydrogen bonds was suggested.

According to these assumptions, the adsorption through *n* sulfonic groups *s* of a single molecule of adsorbate A without dissociation proceeds in accordance with the reaction:



whose course can be shown by the equation:

$$\frac{c_A}{c_L} = \frac{(K_A p_A)^{1/n}}{[1 + (K_A p_A)^{1/n}]} \quad (2)$$

where c_A is the concentration of adsorbate adsorbed by sulfonic groups of copolymer (mmol/g), p_A the partial pressure

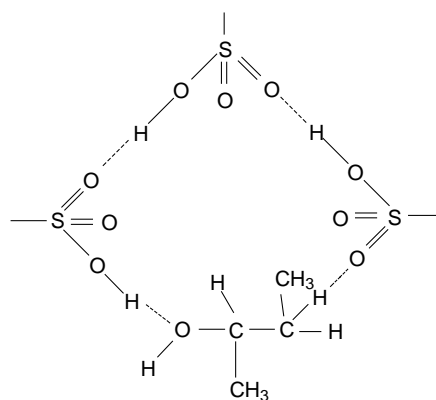


Fig. 4. Model of dual adsorption site of the one alcohol molecule by sulfonic group net of ion-exchange resin.

of adsorbate (kPa), K_A the constant of adsorbate adsorption (kPa^{-1}), c_L^0 the total ion-exchange capacity of sulfonated copolymer (mmol/g), c_L the ion-exchange capacity of sulfonated copolymer after partial neutralization (mmol/g).

The degree of neutralization of sulfonic groups x of copolymer is expressed by the following formula:

$$x = \frac{c_L}{c_L^0} \quad (3)$$

Changes of concentration of the adsorbate adsorbed by sulfonic groups in the function of the change of the partial pressure of the adsorbate for a series of copolymers of the different content of sulfonic groups can be expressed as the following function:

$$\frac{dc_A}{dp_A} = f(K_A, x^n) \quad (4)$$

The number of sulfonic groups n formed by the adsorption complex with one molecule of the adsorbate can be determined from this function after its differentiation in relation to dp_A and linear representation.

After the differentiation of Eq. (2) in relation to dp_A within the range of $p_A \rightarrow 0$ and the introduction of:

$$m = \frac{1}{n} \quad (5)$$

instead of n ,

$$dc_A = c_L (K_A p_A)^m dp_A = x c_L^0 K_A^m (p_A)^m dp_A \quad (6)$$

is obtained.

Assuming that $K_A^m = \text{constant}$ within the range of small partial pressures of alcohol:

$$\frac{dc_A}{m(p_A)^{m-1} dp_A} = K_A^m c_L^0 x \quad (7)$$

and after taking a logarithm of both members of the equation, for $m = 1$

$$\log c_A = m \log x + \log(K_A^m c_L^0) \quad (8)$$

is obtained, for $m = 2$

$$\log \left(\frac{c_A}{p_A} \right) = m \log x + \log(K_A^m c_L^0) \quad (9)$$

is obtained, and for $m = 3$

$$\log \left(\frac{c_A}{p_A^2} \right) = m \log x + \log(K_A^m c_L^0) \quad (10)$$

is obtained. Eqs. (8)–(10) are straight line equations, and the correctness of the adsorption model assumed can be determined by the slope of the straight line.

3. Experimental

3.1. Materials

Amberlyst 15 resin (manufactured by Rohm and Haas) is a macroporous sulfonated copolymer of styrene–divinyl-

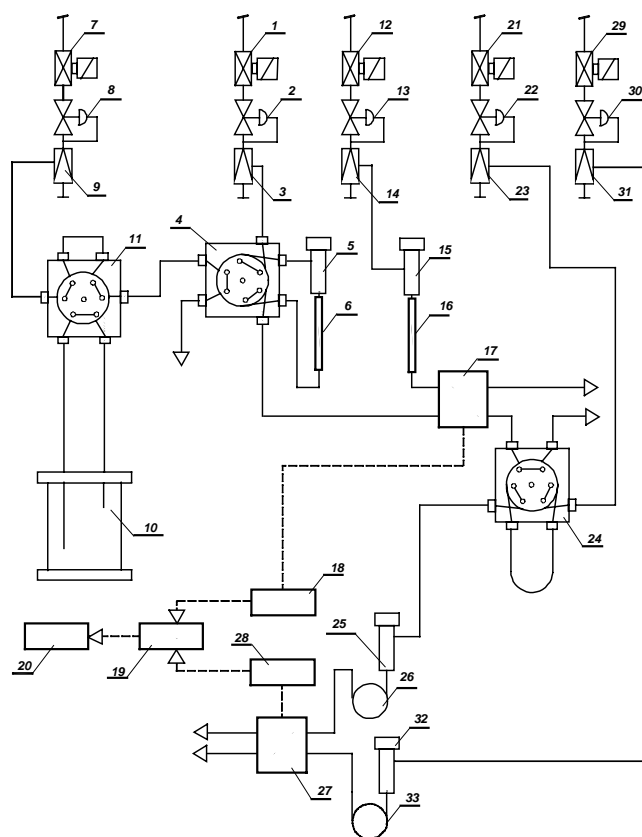


Fig. 5. Apparatus set for the determination of the adsorption model of alkenes and alcohols on sulfonic copolymer by inversion gas chromatography.

benzene (DVB) in H^+ form containing a matrix crosslinked with approximately 20% DVB. The exchange capacity was determined by titration as 4.8 mequiv SO_3H/g (grams of dry resin).

Propene, 1-butene and isobutene were from Merck-Schuchardt ('for synthesis' grade). 2-methyl-1-butene, 2-methyl-2-butene, 2-methyl-1-pentene, 2-methyl-2-pentene, 1-hexene, 2-methyl-2-hexene and 1-heptene were supplied by Aldrich. Methanol, ethanol, and *n*-propanol were supplied by POCh.

3.2. Apparatus

The determination of the number of adsorption sites by the adsorption of adsorbate (alkene or alcohol) on sulfonated styrene–divinylbenzene copolymer by inverse gas chromatography consists in saturating this copolymer with vapors of adsorbate under definite conditions (temperature, pressure), and, next, in removing its excess from the copolymer by blowing inert gas through its bed and the desorption of adsorbate adsorbed during the programmed increase in temperature. The experiments were performed in the apparatus presented in Fig. 5. The carrier gas of the measurement track flows through the electromagnetic valve 1, the flow stabilizer 2 and the needle valve 3. A six-port valve 4

serves to change over the flow of carrier gas and the flow of auxiliary gas, which contains vapors of alcohol. Both of these flows could be directed through the chamber of the injector 5 to the sorption pipe 6, in which the sample of sulfonic copolymer is placed. Auxiliary gas (electromagnetic valve 7, flow stabilizer 8 and needle valve 9) is saturated with vapors of alcohol in the reservoir for vaporizing 10. The reservoir for vaporizing is switched on in the auxiliary gas track by the six-port valve 11. The reference system is made by the parallel track of carrier gas (electromagnetic valve 12, flow stabilizer 13 and needle valve 14) and the chamber of the injector 15 with the sorption pipe 16, in which the reference sample of sulfonic copolymer is placed. From the sorption tubes (6, 16) the carrier gases of the measurement track and of the reference track are supplied by the thermal conductivity detector. The electric signal from detector is amplified in the amplifier 18, and is directed to the analog-to-digital converter 19 and the computer 20.

The chromatographic analysis is used to control whether during the desorption adsorbate process in desorbed gases, the possible products of the catalytic reaction (dehydration or isomerization) on the surface of sulfonated resin occur or not. To measure the desorbed adsorbate and possible products of the catalytic reaction by the gas chromatograph (electromagnetic valve 21, flow stabilizer 22 and needle valve 23), they are flown immediately (by four-port valve 24) to the sample injector 25 and the chromatography column 26. The six-port valve 24 with freezing capillary is used to improve the conditions of chromatography analysis in the case of considerably stretched desorption peaks. The sample injector 32 and the chromatographic column 33 serve as a system of reference of flame ionization detector. Electric signals from the electrometer 28 are directed to the analog-to-digital converter 19 and the computer 20.

3.3. Calculations

The equilibrium pressure corresponding with the concentration of adsorbate in the gas phase during the thermal desorption can be determined by the following formula:

$$p_A = \frac{R \sum_i n f(S_i) \Delta T_i}{\sum_i V_i} \quad (11)$$

where R is the gas constant, ΔT_i the temperature range (K) where the thermal desorption peak appears, V_i the volume of the retention peak (cm^3), and $n f(S_i)$ the quantity of moles calculated on the basis of the surface of the peak from the calibration curve.

3.4. Procedure

A sorption tube of 4 mm in internal diameter and 10 cm in length contained 5 g of Amberlyst 15. Amberlyst 15 was used in acidic form after being neutralized by KOH solution. The content of acidic groups was determined by titration in aqueous solution. In the experiments Amberlyst 15

of the contents: 0.89; 1.75; 2.68; 3.55, 4.45 mequiv $\text{SO}_3\text{H/g}$, respectively, was used. Before the measurements of adsorption were made, the bed was dried in a vacuum at 115°C for 12 h, and, then, just before the measurement in a chromatographic column, in a flow of helium $10\text{ cm}^3/\text{min}$ at 115°C for 24 h. The vapors of adsorbate were passed through the bed until the same concentration of adsorbate was achieved in the carrier gas at the inlet and the outlet of the sorption tube. After removing the vapors of adsorbate from the sorption tube, the quantity of adsorbate adsorbed was determined by heating the sorption tube at $25^\circ\text{C}/\text{min}$ up to 140°C and maintaining the final temperature for 40 min. A gas chromatograph N504 was provided with a thermal conductivity detector, the temperature of the detector 150°C , the flow of the carrier gas (helium) $120\text{ cm}^3/\text{min}$. A gas chromatograph N505 used to check the presence of products of catalytic reactions of alcohols on sulfonated copolymer in the carrier gas flowing out of the adsorption tube was equipped with a flame ionization detector.

To analyze the composition of the mixture leaving the sorption tube in the second gas chromatograph, the following conditions were used in the experiments:

- adsorption alcohols: column 2.5 m (internal diameter 3 mm) packed with Porapak Q, temperature of column 160°C , temperature of injector 180°C , temperature of flame ionization detection (FID) system 200°C , flow of carrier gas (helium) $55\text{ cm}^3/\text{min}$;
- adsorption C_4 alkenes: column 3.5 m (internal diameter 3 mm) packed with 10% (w/w) *n*-octane on Porasil C 80–100 mesh, temperature of column 25°C , temperature of injector 40°C , FID temperature 120°C , flow of carrier gas (helium) $40\text{ cm}^3/\text{min}$;
- adsorption C_5 alkenes: column 12 m (internal diameter 3 mm) packed with 23% (w/w) Triton X-305 on Chromosorb A 80–100 mesh, temperature of column 40°C , temperature of injector 60°C , FID temperature 120°C , flow of carrier gas (helium) $50\text{ cm}^3/\text{min}$;
- adsorption C_6 alkenes: column 6 m (internal diameter 3 mm) packed with 20% (w/w) Triton X-305 and 5% (w/w) Ucon LB 550X on Chromosorb W AW 80–100 mesh, temperature of column 60°C , temperature of injector 60°C , FID temperature 120°C , flow of carrier gas (helium) $60\text{ cm}^3/\text{min}$,
- adsorption C_7 alkenes: column 6 m (internal diameter 3 mm) packed with 15% (w/w) Triton X-305 and 8% (w/w) Ucon LB 550X on Chromosorb W AW 80–100 mesh, temperature of column 90°C , temperature of injector 90°C , FID temperature 140°C , flow of carrier gas (helium) $60\text{ cm}^3/\text{min}$.

4. Results

Fig. 6 shows the effect of the change of the concentration of sulfonic groups on copolymer Amberlyst 15 on

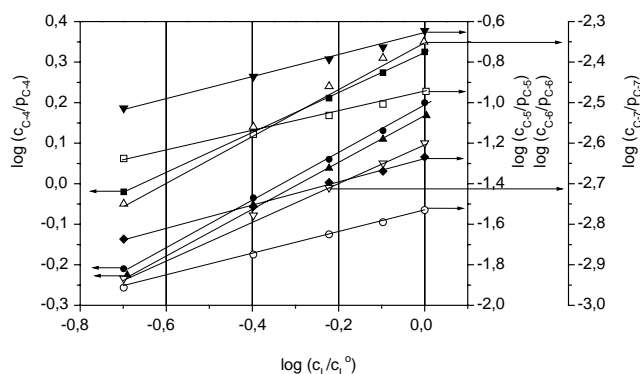


Fig. 6. Concentration of adsorbed alkene versus relative concentration of acidic groups of sulfonated copolymer Amberlyst 15 in logarithmic scale at temperature 298 K: (■) propene, $m = 0.49$; (●) 1-butene, $m = 0.57$; (▲) isobutene, $m = 0.52$; (▼) 2-methyl-1-butene, $m = 0.53$; (◆) 1-pentene, $m = 0.57$; (□) 2-methyl-1-pentene, $m = 0.49$; (○) 1-hexene, $m = 0.54$; (△) 2-methyl-2-hexene, $m = 0.56$; and (▽) 1-heptene, $m = 0.47$.

the quantity of propene, 1-butene, isobutene, 1-pentene, 2-methyl-1-butene, 1-hexene, 2-methyl-1-pentene, 1-heptene and 2-methyl-2-hexene adsorbed. In all the figures, the slope of the straight line coefficient (m) was from 0.47 to 0.57.

It can be assumed that the function describing the change of the quantity of alkenes adsorbed dependent on the content of sulfonic groups expressed by Eq. (9) is a straight line and Eq. (2) can be rearranged as follows:

$$\frac{c_{C-X}}{c_L} = \frac{(K_{C-X} p_{C-X})^{1/n}}{1 + (K_{C-X} p_{C-X})^{1/n}} \quad (12)$$

where $1.75 > n > 2.12$.

The equation describes the adsorption of one molecule of alkene by more than one sulfonic group, which shows that a number of sulfonic groups are involved in the adsorption of a molecule of alkene.

The numbers n determined (Eq. (1) of the adsorption) are not whole numbers. The molecule of alkene is adsorbed by sulfonic groups combined in chains of different length and variously space-oriented. The results of adsorption experiments excluded the correctness of a one-center adsorption model (Fig. 2). A two-center model can be assumed to be correct (Fig. 1), the more so because the value $n = 2$ is within the range of values experimentally determined.

From the present results of the measurements of sorption of such first-order alcohols as methanol, ethanol, n -propanol and n -butanol (Fig. 7), it follows that the slope of the straight line coefficient (m) of the function $\log c_{AN}$ from $\log(c_L/c_L^0)$ is close to 1. According to the present assumptions of the adsorption model of a molecule of alcohol by n sulfonic groups of copolymer, it is evident that the results of adsorption measurements are close to Eq. (8) and Eq. (2) assumes the following form:

$$\frac{c_{AN}}{c_L} = \frac{(K_{AN} p_{AN})}{1 + (K_{AN} p_{AN})} \quad (13)$$

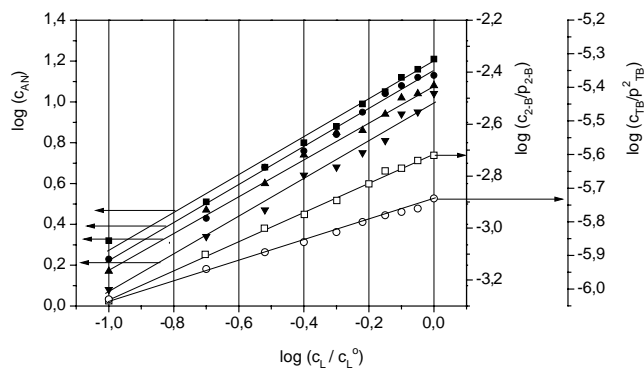


Fig. 7. Concentration of adsorbed methanol, ethanol, n -propanol and n -butanol, the ratio of concentration of 2-butanol to its partial pressure and the ratio of concentration of 2-butanol to its partial pressure versus relative concentration of acidic groups of sulfonated copolymer Amberlyst 15 in logarithmic scale, (■) methanol, $m = 0.921$; (●) ethanol, $m = 0.954$; (▲) n -propanol, $m = 0.906$; (▼) n -butanol, $m = 0.937$; (□) 2-butanol, $m = 0.570$; and (○) $tert$ -butanol, $m = 0.293$.

The equation describes the adsorption of one molecule of alcohol by one sulfonic group, and therefore the adsorption of linear alcohols proceeds according to the one-center mechanism of sorption.

From the adsorption measurements of alcohols of higher order (2-butanol, $tert$ -butanol) on sulfonated copolymer Amberlyst 15, it follows that the number of sulfonic groups falling to one molecule of alcohol adsorbed is higher. The function describing the changes of the quantity of 2-butanol adsorbed in relation to the number of sulfonic groups (Fig. 7) described by the Eq. (9) is linear and of the slope of the straight line coefficient $m = 0.57$, which allows the Eq. (9) to be rearranged as follows:

$$\frac{c_{2-B}}{c_L} = \frac{(K_{2-B} p_{2-B})^{1/1.75}}{1 + (K_{2-B} p_{2-B})^{1/1.75}} \quad (14)$$

The equation describes the adsorption of one molecule of 2-butanol by more than one sulfonic group. The value determined, $n = 1.75$, is not a whole number and it can be assumed that the adsorption of 2-butanol proceeds according to two parallel mechanisms of adsorption: a one-center mechanism as in the case of alcohols of the first order, and a two-center mechanism as suggested in the study [2] (Fig. 4). By the adsorption Eq. (1), it is possible to describe the one-center adsorption ($n = 1$) and the two-center one ($n = 2$). The participation of these two mechanisms in the adsorption of 2-butanol is not identical, which accounts for the fact that the value n experimentally determined is not a whole number. It is possible that the branched molecule of 2-butanol adsorbed by a network of differently space-oriented sulfonic groups can additionally form bonds between the methyl group and oxygen of the sulfonic group as long as the space orientation of a molecule of alcohol and of sulfonic groups placed in its proximity makes it possible.

The dependence of the quantity of $tert$ -butanol alcohol adsorbed on the number of sulfonic groups included in copoly-

mer Amberlyst 15 is shown in Fig. 7, too. The straight line was obtained for the dependence $\log(c_{\text{TB}}/p_{\text{TB}}^2)$ versus $\log(c_{\text{L}}/c_{\text{L}}^0)$.

The slope of the straight line coefficient $m = 0.293$ and Eq. (2) can be written as:

$$\frac{c_{\text{TB}}}{c_{\text{L}}} = \frac{(K_{\text{TB}} p_{\text{TB}})^{1/3.41}}{1 + (K_{\text{TB}} p_{\text{TB}})^{1/3.41}} \quad (15)$$

From the equation it follows that three or more sulfonic groups take part in the adsorption of *tert*-butanol on sulfonated copolymer. It also confirms the correctness of the adsorption model of *tert*-butanol which was suggested in the study [2].

The present measurements show that the order of alcohol accounts for the number of sulfonic groups taking part in adsorption. The linear molecules of alcohol adsorbed form the hydrogen bond between the hydroxyl group and the sulfonic one, whereas adsorbed molecules of alcohols of the second order, and of the third order in particular, can form another bond between hydrogen of the methyl group and another sulfonic group.

5. Conclusions

The present study has shown that:

- (1) two sulfonic groups take part in the adsorption of an alkene molecule on sulfonated copolymer Amberlyst 15,
- (2) the adsorption of linear alcohols on sulfonated copolymer Amberlyst 15 proceeds according to the one-center mechanism of sorption, and
- (3) at least two sulfonic groups take part in the adsorption of alcohols of higher order (2-butanol, *tert*-butanol) on sulfonated copolymer Amberlyst 15.

6. Nomenclature

K	adsorption equilibrium constant (kPa^{-1})
p	partial pressure (kPa)

Subscripts

C-X	alkene
X	number of carbon atoms
AN	alcohol (methanol, ethanol, <i>n</i> -propanol, 1-butanol)
2-B	2-butanol
TB	<i>tert</i> -butanol

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