



# Analysis of Adsorption, Ion Exchange, Thermodynamic Behaviour of Some Organic Cations on Dowex 50WX4-50/H<sup>+</sup> Cation Exchanger in Aqueous Solutions

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**Abstract:** The equilibrium adsorption, ion exchange characteristics of various concentrations of some organic cations from aqueous solutions onto dowex 50WEX/H<sup>+</sup> cation exchanger were studied at different temperatures in the range of 30-50 °C. The studied cations showed good adsorptive properties onto dowex 50WX4-5/H<sup>+</sup> at different concentrations and temperatures. Main adsorption behaviour was ion exchange between hydrogen ions and the organic cations as indicated from the linear relation between the initial concentration of the organic cations and the released hydrogen ions. It was found that the adsorption affinity of dowex 50WX4-50/H<sup>+</sup> towards the studied organic cations depends on the substituent type of the organic cations giving the following increasing order: 1-H < 2-OH < 3-OCH<sub>3</sub>. Thermodynamic parameters for the adsorption of the studied organic cations were evaluated and discussed. It was found that the adsorption 1-H organic cation was spontaneous, ordered, exothermic and favored with decreasing temperature. On the other hand the adsorption of both 2-OH and 3-OCH<sub>3</sub> organic cations was found to be spontaneous and disordered with enthalpy change varies significantly with increasing organic cation concentration, suggesting dipole-dipole adsorption forces as new active sites for adsorption under conditions of relatively high concentrations. Freundlich and Dubinin-Radushkevich adsorption isotherm models reasonably describe the adsorption of the studied organic cations onto dowex 50WX4-50/H<sup>+</sup> by segmented straight lines depending on the studied range of concentration, indicating the existence of two different sets of adsorption sites with substantial difference in energy of adsorption. According to Dubinin-Radushkevich adsorption isotherm model, physical-ion exchange mechanism was suggested for the adsorption of 1-H organic cation and both physical and chemical-ion exchange mechanisms were suggested for the adsorption of 2-OH and 3-OCH<sub>3</sub> organic cations depending on the studied range of concentration.

**Keywords:** Adsorption, Ion exchange, Thermodynamic, Organic cations, Isotherms, Aqueous solutions

## Introduction

The effect of organic pollutants on our environment is of great concern to scientists as well as to the general public. Some organic compounds and their degradation products may be carcinogen and toxic and consequently, they are important sources of water pollution and their treatment becomes a major problem for environmental manager. Conventional treatment methods for removal of organic pollutants from aqueous solution, like photochemical degradation, biological degradation, coagulation, chemical oxidation and adsorption have been investigated with varying success<sup>1,2</sup>. Between the mentioned methods, adsorption is one of the potential methods for removal of pollutants from water.

Different types of materials have been evaluated as adsorbents for various types of organics<sup>3-11</sup>. In recent years, synthetic polymeric ion exchangers have been emerging as an efficient adsorbent in industrial wastewater treatment due to its efficient removal, feasible regeneration for repeated use. The removals of organics by ion exchange resins may be accomplished by ion exchange and/or adsorption. Organics that are not ionized are not too well removed by ion exchange. Only organics that are substantially ionized can be removed by the mechanism of ion exchange<sup>12</sup>. As the first step in the ion exchange mechanism is the adsorption of ionic species onto the solution/solid interface, various adsorption isotherm models have been applied successfully to describe the adsorption processes that included ion exchange mechanism<sup>8,10,13</sup>. Different adsorption mechanisms may be found by studying the dependence of adsorption on various variables (pH, concentration of solutes, ionic strengths, and the type and topology of surfaces), and by interpreting the parameters of the determined adsorption isotherm. Also, thermodynamic parameters of adsorption from solutions provide a great deal of information concerning the type and mechanism of the adsorption process<sup>14</sup>.

1-Methyl-4[4<sup>\</sup> (-X)-styryl] pyridinium iodides are classified as donor-acceptor intermolecular charge transfer complexes and is belonged to class of organic compounds known as molecular rotors<sup>15</sup>. Recently, some of these organic salts have been used successfully as corrosion inhibitors for Al alloys<sup>16-18</sup> and mild steel<sup>19,20</sup> in aqueous acid solutions. In the present work the adsorption-ion exchange behavior of such compounds (where X: -H, -OH and -OCH<sub>3</sub>) by strong ion exchanger (Dowex 50WX4-50/H<sup>+</sup>) in aqueous solutions has been investigated as a function of the initial concentration and solution temperature. The distribution constant ( $K_d$ ) for the studied organic salts at various concentrations were evaluated at different temperatures. Thermodynamics of adsorption process has been studied and the change in standard enthalpy, free energy and entropy have been determined. Experimental data at equilibrium were fitted to various adsorption isotherm models to determine the best isotherm to correlate the experimental data.

## Experimental

The studied organic compounds are 1:1 electrolytes. The organic part being the cation while the inorganic part (I) being the anion. Their nomination and molecular formula are given in Table 1. The studied organic salts were synthesized purified and identified previously in our lab as described in the literature<sup>21</sup>.

Synthetic dowex 50WEX/H<sup>+</sup> cation exchanger was purchased from sigma-aldrich Company. The physical and chemical properties of dowex 50WEX/H<sup>+</sup> reported by the supplier are given in Table 2. The cation exchanger was treated three cycles with 1.0 mol L<sup>-1</sup> HCl solution and washed finally by de-ionized water several times till it becomes free from HCl as tested by AgNO<sub>3</sub> solution and methyl orange indicator. Then was dried in an oven at

50 °C and was kept over anhydrous CaCl<sub>2</sub> in a vacuum desiccator till its utilization. One mesh size of 500-600 μm ( $\bar{r}=1.275 \times 10^{-4}$  m) was used in this work with ion exchange capacity of 3.84 meq g<sup>-1</sup> of dry resin determined as described in the literature<sup>22</sup>.

**Table 1.** Names, structures and abbreviations of the studied organic salts

Name	Structure	Abbreviation
1-methyl-4[4'-(H) styryl] pyridinium Iodide		1-H
1-methyl-4[4'-(OH) styryl] pyridinium Iodide		2-OH
1-methyl-4[4'-(OCH <sub>3</sub> ) styryl] pyridinium Iodide		3-OCH <sub>3</sub>

**Table 2.** The physical and chemical properties of Dowex 50WEX/H<sup>+</sup>

Property	Specification
Functional group	-SO <sub>3</sub> H
Polymer type	Styrene divinylbenzene
Mobile ion	H <sup>+</sup>
Total capacity	1.2 meq/ml
Standard mesh size	16-50
Moisture retention	67%

### *Organic cations solutions*

The solutions of the studied organic salts were prepared by weighing fixed amount of each salt and then solvated with de-ionized water and completed to 100 mL by using measuring flask giving concentration in the range from  $5.0 \times 10^{-5}$  mol L<sup>-1</sup> to  $2.5 \times 10^{-3}$  mol L<sup>-1</sup>.

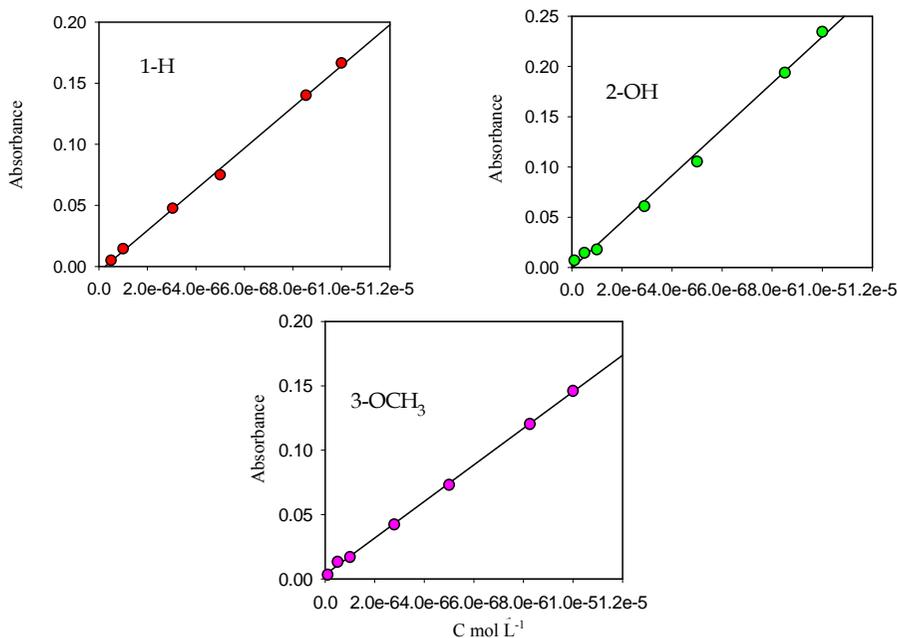
### *Batch method for adsorption-ion exchange equilibrium*

Fixed amount of resin was weighed and added into each of 250 mL glass flasks containing 100 mL of certain concentration for the studied organic cations. Then the solutions were stirred at constant speed and maintained at certain temperature. All systems were equilibrated for 24 h which is confirmed to be sufficient to reach adsorption equilibrium. It must be mentioned that a weight of 0.232 g of resin was used for all equilibrium experiments except otherwise stated.

### *Quantitative determination of the organic cations*

The concentration of the studied organic cations at equilibrium was determined by spectrophotometric method using Shimadzu, UV-VIS-Spectrophotometer model UV-1601. Standard solutions of each organic cation were prepared and the absorbance read at wavelength of 336, 372 and 369 nm for 1-H, 2-OH and 3-OCH<sub>3</sub>, respectively. The absorbance was then plotted versus the concentration to obtain the calibration curves as shown in Figure 1. The relation between the concentration and the absorbance is given by Beer-Lambert law<sup>23</sup>:

$$\text{Absorbance}_{(\lambda_{\max})} = aC \quad (1)$$



**Figure 1.** The relation between the absorbance and the concentration of the studied organic cations

When the relation between the concentration and the absorbance deviates from Beer-Lambert law, Eq. (1) can be written as:

$$\text{Absorbance}_{(\lambda_{\max})} = b + aC_{(\text{organic cation})} \quad (2)$$

By estimating the intercept ( $b$ ) and the slope ( $a$ ), the unknown concentration of the studied organic cations can be calculated as:

$$C_{(\text{organic cation})} = \frac{\text{Absorbance}_{(\lambda_{\max})} - b}{a} \quad (3)$$

When the  $b$  value becomes very small ( $b \ll 0.0$ ), Eq. (2) obeys scornfully Beer-Lambert law. The accuracy and precision of the method was estimated by calculating the standard deviation and the relative standard deviation of four different concentrations for each organic cation and the maximum deviation was  $< 5\%$ .

## Results and Discussion

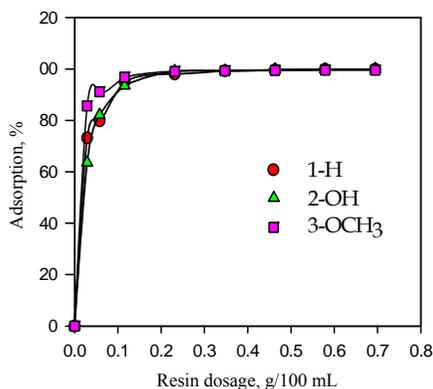
### *Effect of resin dosage on the adsorption %*

The adsorption % at equilibrium can be calculated as follows:

$$\text{adsorption \%} = \left( \frac{C_i - C_e}{C_i} \right) \times 100 \quad (4)$$

Where  $C_i$  is the initial concentration and  $C_e$  is the concentration at equilibrium. Figure 2 shows the adsorption % of the studied organic cations as a function of resin dosage. The resin dosage was varied from 0.029 to 0.694 and equilibrated for 24 h. It is clear that the adsorption % of the studied organic cations increases up to optimum dosage (0.232 g) beyond which the adsorption efficiency does not change. It may be concluded that by increasing

the adsorbent dose the adsorption% increases but adsorption density decreases<sup>24</sup>. The decrease in adsorption density can be attributed to the fact that some of the adsorption sites remain unsaturated during the adsorption process; whereas the number of available adsorption sites increases by an increase in adsorbent and this results in an increase in the adsorption %. As expected, the equilibrium concentration decreases with increasing adsorbent doses for a given initial concentration, because for a fixed initial solute concentration, increasing the adsorbent doses provides a greater surface area or adsorption sites<sup>24,25</sup>.



**Figure 2.** Effect of resin (Dowex 50WEX/H<sup>+</sup>) dosage on the adsorption % of the studied organic cations at 30 °C

### Effect of initial concentration

#### *Effect of initial concentration on the amount of hydrogen released ( $\Delta C_{H^+}$ )*

As dowex 50WEX/H<sup>+</sup> is a strong cation exchanger containing numerous fixed anionic groups, the ion exchange mechanism may play a key role in the adsorption. This was confirmed by monitoring the hydrogen ion released ( $\Delta C_{H^+}$ , mol L<sup>-1</sup>) corresponding to the organic cations uptake for various initial concentrations when stirred with 0.232 g of resin at 30 °C. The  $\Delta C_{H^+}$  was determined by monitoring the natural pH before dowex 50WEX/H<sup>+</sup> addition and the final pH after equilibrium reaction (24 h) with the exchanger.

The plot of the initial concentration of each studied organic cation against  $\Delta C_{H^+}$  is presented by Figure 3 which showed straight lines passing through the origin with slope approximately of unity for all the studied organic cations. This observation proved that the adsorption of the studied organic cations by dowex 50WEX/H<sup>+</sup> occurred stoichiometrically by exchange of hydrogen ions as follows:



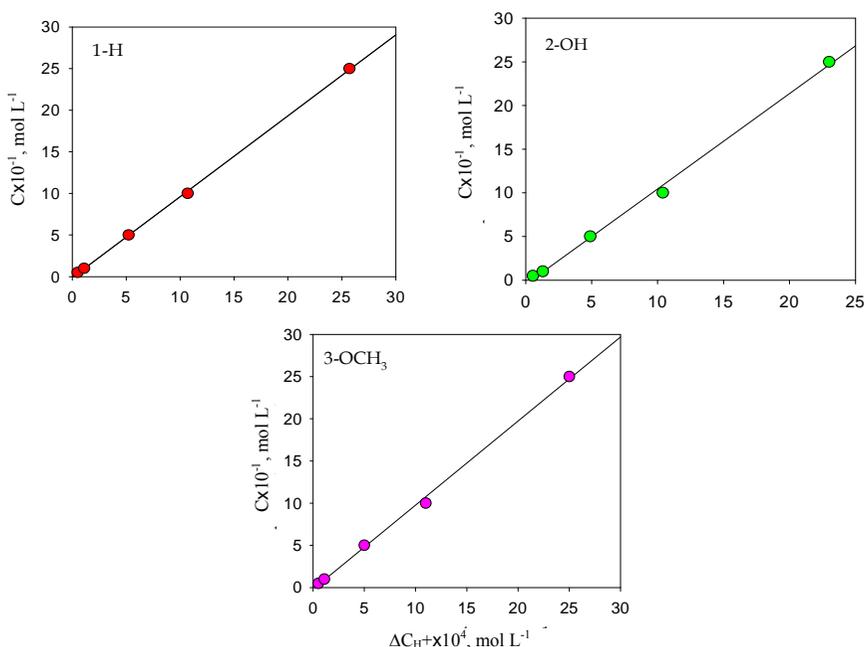
Similarly, Inbaraj *et al.*<sup>8</sup> proved that the basic brown 1 dye adsorption by the bacterial biopolymer poly(*c*-glutamic acid) occurred predominantly by ion exchange mechanism.

#### *Effect of initial concentration on the adsorption-ion exchange behavior*

The effect of initial concentration on the adsorption behavior of each of the organic cations on dowex 50WX4-50/H<sup>+</sup> cation exchanger in aqueous solutions was investigated at three different temperatures. For the adsorption equilibrium experiments done, from the difference

between the initial concentration ( $C_i$ ) of each organic cation and its equilibrium concentration ( $C_e$ ), the adsorbed amounts ( $q_e$ ) on the studied cation exchanger were calculated using the following equation:

$$q_e = (C_i - C_e) \times \frac{V}{m} \quad (6)$$



**Figure 3.** The relation between the initial concentration ( $C_i$ ) of the studied organic cations and the concentration of hydrogen ion released at equilibrium ( $\Delta C_{H^+}$ ) at 30 °C

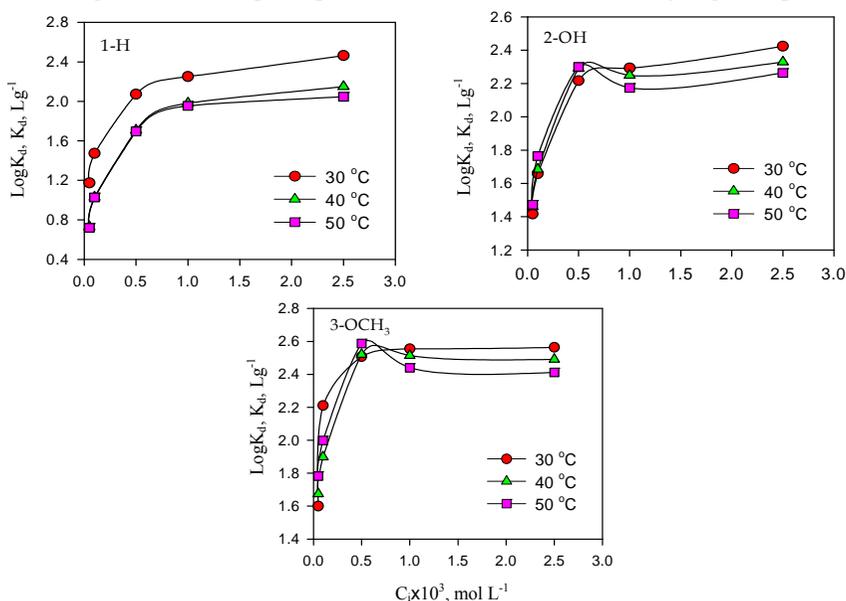
Where  $V$  is the total solution volume and  $m$  is the mass of the exchanger. The distribution coefficient ( $K_d$ ) of various concentrations of the organic cations between the aqueous phase and the solid phase at different temperatures can be calculated as below:

$$K_d = \frac{(C_i - C_e)}{C_e} \times \frac{V}{m} = \frac{q_e}{C_e} \quad (7)$$

The calculated  $K_d$  values for all systems at all temperatures were listed in Table 3. The distribution coefficient has been used in the literature<sup>26,27</sup> to indicate the adsorption affinity of a solid adsorbent towards a solute. The impact of the initial concentrations of the organic cations on their distribution coefficients in aqueous solutions at different temperatures is shown in Figure 4. As was shown from Figure 4, the adsorption capacity of dowex 50WEX/ $H^+$  is increased as the initial concentration was increased up to  $5.0 \times 10^{-4} \text{ mol L}^{-1}$ , after which it relatively becomes independent of the initial concentration. It was also seen from Table 3 that the solution temperature affected the  $K_d$  value in different ways as follows:

- For 1-H organic cation the  $K_d$  value decreases with the increase of temperature at all studied concentrations, indicating that the adsorption process is not favored with increasing temperature in the studied range.

- For both 2-OH and 3-OCH<sub>3</sub> organic cations the  $K_d$  value varies with temperature in two ways depending on the initial concentration:
- At concentrations  $\leq 5.0 \times 10^{-4}$  mol L<sup>-1</sup>, the  $K_d$  value increases with the rise in temperature indicating that the adsorption process is favored at relatively high temperatures;
- At concentrations  $> 5.0 \times 10^{-4}$  mol L<sup>-1</sup> the  $K_d$  values decrease with the rise in temperature indicating that the adsorption process is not favored at relatively high temperatures.



**Figure 4.** Variation of the distribution constant ( $K_d$ ) with the initial concentration of the studied organic cations ( $C_i$ ) at different temperatures

**Table 3.** The  $K_d$  values for the adsorption of various concentrations of the studied organic cations onto Dowex 50WEX/H<sup>+</sup> at different temperatures

$C_i$ mol L <sup>-1</sup>	$K_d, L g^{-1}$								
	1-H			2-OH			3-OCH <sub>3</sub>		
	30°	40°	50°	30°	40°	50°	30°	40°	50°
$5.0 \times 10^{-5}$	14.91	5.35	5.25	26.13	28.82	29.67	39.85	47.35	60.45
$1.0 \times 10^{-4}$	29.79	10.68	10.64	45.44	48.31	58.05	79.34	89.96	99.77
$5.0 \times 10^{-4}$	118.05	51.12	49.63	164.68	195.20	199.72	321.46	331.85	386.56
$1.0 \times 10^{-3}$	178.13	95.77	89.99	196.27	177.33	149.03	359.20	326.32	275.42
$2.5 \times 10^{-3}$	291.43	141.27	111.54	265.50	213.41	183.54	366.00	309.62	257.80
Mean value	126.46	60.84	53.41	139.60	132.61	124.00	233.17	221.02	216.00

However at all concentrations and temperatures the adsorption affinity of dowex 50WX4-50/H<sup>+</sup> towards the studied organic cations gives the following increasing order:



The above selectivity order was similar to that of increasing ionic size as indicated from the size of the substituent group. This suggest that the energy required for the dehydration of

the organic cations plays an important role in determining the selectivity series for the studied cations<sup>28</sup>, meaning that the cations which have the largest ionic size (low hydration energy) are more selected than those have the smallest ionic size (high hydration energy).

#### *Thermodynamic considerations*

$K_d$  value is related to the standard free energy of adsorption,  $\Delta G_{ads}^o$  by<sup>14</sup>:

$$\Delta G_{ads}^o = -RT \ln(C_{H_2O} K_d) \quad (8)$$

Where  $C_{H_2O}$  is the concentration of water molecules ( $g L^{-1}$ ) at the ion exchanger/electrolyte interface. The term  $C_{H_2O} K_d$  ( $g L^{-1} L g^{-1}$ ) is dimensionless. Equation (6) can be written as follows:

$$\ln K_d = -\ln C_{H_2O} - \frac{\Delta G_{ads}^o}{RT} \quad (9)$$

Thermodynamically,  $\Delta G_{ads}^o$  is related to the standard enthalpy ( $\Delta H_{ads}^o$ ) and entropy ( $\Delta S_{ads}^o$ ) of adsorption process by the famous equation:

$$\Delta G_{ads}^o = \Delta H_{ads}^o - T\Delta S_{ads}^o \quad (10)$$

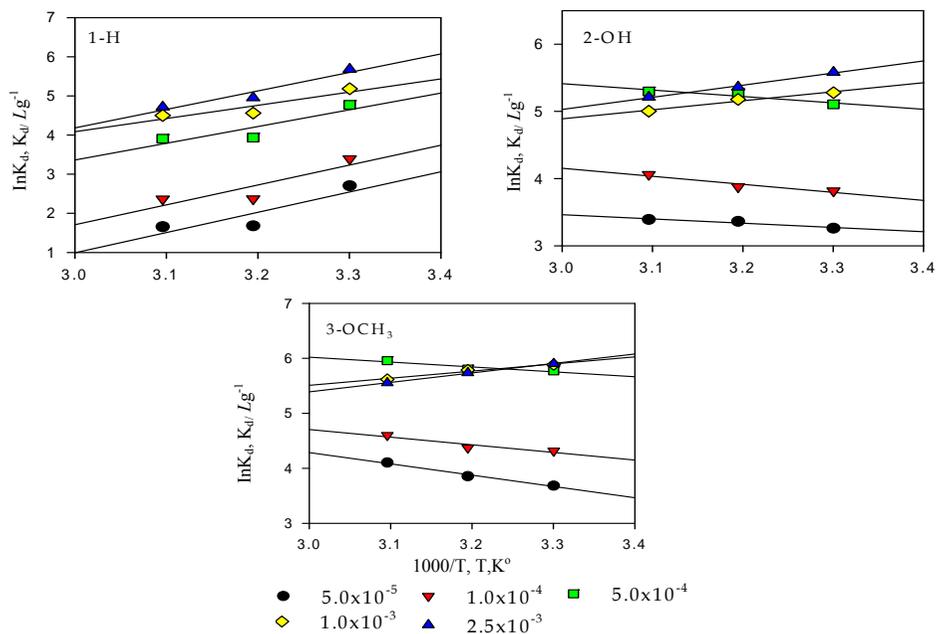
By coupling both Eqs. (9) and (10) the following equation can be written:

$$\ln K_d = (-\ln C_{H_2O} + \frac{\Delta S_{ads}^o}{R}) - \frac{\Delta H_{ads}^o}{RT} \quad (11)$$

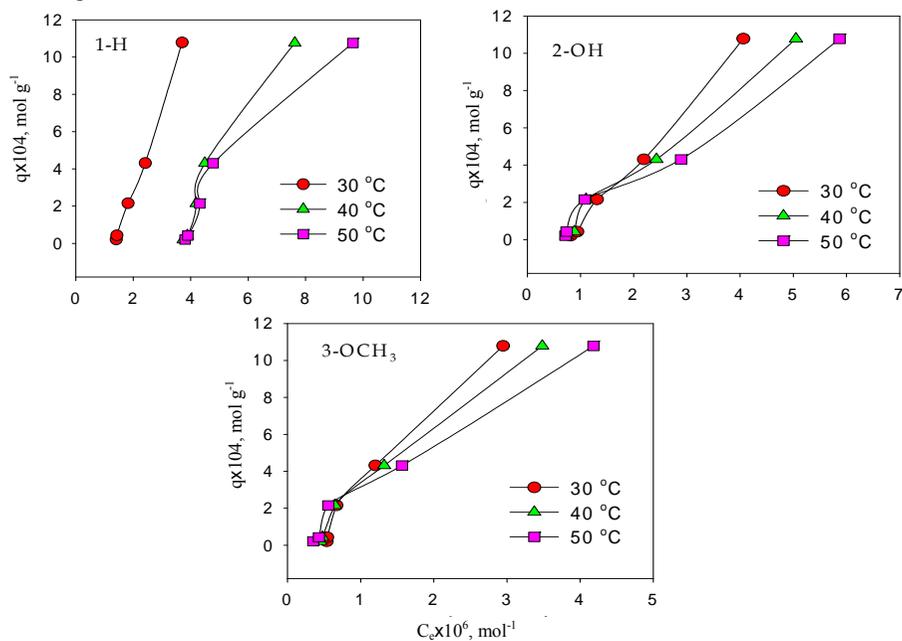
Figure 5 shows the linear relation between  $\ln K_d$  and  $\frac{1}{T}$  (Eq. 11). From the slope and intercept of the straight lines represented in Figure 5, the values of  $\Delta H_{ads}^o$  and  $\Delta S_{ads}^o$  for different systems were calculated in accordance to Eq. (11), respectively. The values of  $\Delta G_{ads}^o$  were also estimated by using Eq. (10). All estimated thermodynamic parameters ( $\Delta H_{ads}^o$ ,  $\Delta S_{ads}^o$  and  $\Delta G_{ads}^o$ ) for the adsorption of the studied organic cations on dowex 50WEX/ $H^+$  were listed in Table 4. The data in this table can be interpreted as follows:

- For  $\Delta H_{ads}^o$  - the high negative values of  $\Delta H_{ads}^o$  for the 1-H indicated exothermic adsorption process and reflecting high electrostatic attraction between the cations and the fixed ionic groups on the exchanger associated with ion exchange for the mobile  $H^+$  ions<sup>29</sup>. The  $\Delta H_{ads}^o$  data for both cations 2-OH and 3-OCH<sub>3</sub> showed that the sign of  $\Delta H_{ads}^o$  depends on the initial concentration of both of them:
  - i. At concentration  $\leq 5.0 \times 10^{-4} \text{ mol L}^{-1}$ : positive values for  $\Delta H_{ads}^o$  was recorded indicating endothermic adsorption under these conditions.
  - ii. At concentrations  $> 5.0 \times 10^{-4} \text{ mol L}^{-1}$ : negative values for  $\Delta H_{ads}^o$  was recorded indicating exothermic adsorption under these conditions.

The previous results may be related to the substituent type of the studied cations, *i.e.* the adsorption process may depend on the electronic effects of the substituent on the reaction center. In general, Hammett constant ( $\sigma$ ) measures the donor-acceptor property of a substituent.



**Figure 5.** Plots of  $\ln K_d$  against  $\frac{1}{T}$  for the adsorption of various concentrations of the studied organic cations onto Dowex 50WEX/H<sup>+</sup>.



**Figure 6.** Isotherms of the studied organic cations adsorbed onto Dowex 50WEX/H<sup>+</sup> at different temperatures

**Table 4.** Thermodynamic adsorption parameters of the studied organic cations onto Dowex 50WEX/H<sup>+</sup>.

C <sub>i</sub> mol L <sup>-1</sup>	$\Delta H_{ads}^{\circ}$ , kJ mol <sup>-1</sup>	$\Delta S_{ads}^{\circ}$ , kJ mol <sup>-1</sup> K <sup>-1</sup>			$\Delta G_{ads}^{\circ}$ , kJ mol <sup>-1</sup>		
		30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
1-H							
5.0×10 <sup>-5</sup>	-42.99	-0.063	-0.063	-0.063	-23.83	-23.18	-22.54
1.0×10 <sup>-4</sup>	-42.24	-0.055	-0.055	-0.055	-25.51	-24.96	-24.41
5.0×10 <sup>-4</sup>	-35.59	-0.021	-0.021	-0.022	-29.11	-28.88	-28.66
1.0×10 <sup>-3</sup>	-28.02	-0.007	-0.007	-0.007	-25.81	-25.74	-25.66
2.5×10 <sup>-3</sup>	-39.24	-0.026	-0.026	-0.026	-31.48	-31.20	-30.94
Mean value	37.62	-0.035	-0.035	-0.035	-27.15	-26.79	-26.44
2-OH							
5.0×10 <sup>-5</sup>	5.24	0.102	0.102	0.102	-25.64	-26.66	-27.67
1.0×10 <sup>-4</sup>	9.89	0.122	0.122	0.122	-26.99	-28.17	-29.39
5.0×10 <sup>-4</sup>	7.90	0.126	0.126	0.126	-30.31	-31.57	-32.80
1.0×10 <sup>-3</sup>	-11.14	0.065	0.065	0.065	-30.71	-31.33	-31.97
2.5×10 <sup>-3</sup>	-15.05	0.054	0.054	0.054	-31.44	-31.95	-32.49
Mean value	-0.63	0.094	0.094	0.094	-29.94	-29.94	-30.87
3-OCH <sub>3</sub>							
5.0×10 <sup>-5</sup>	17.13	0.144	0.144	0.144	-26.59	-28.04	-29.48
1.0×10 <sup>-4</sup>	11.56	0.131	0.131	0.131	-28.16	-29.47	-30.75
5.0×10 <sup>-4</sup>	7.40	0.130	0.130	0.130	-31.93	-33.23	-34.49
1.0×10 <sup>-3</sup>	-10.81	0.071	0.071	0.071	-32.29	-32.97	-33.68
2.5×10 <sup>-3</sup>	-14.22	0.060	0.060	0.060	-32.25	-32.25	-33.41
Mean value	2.21	0.107	0.107	0.107	-30.25	-31.19	-32.36

Those substituents which attract electrons from the reaction center are assigned positive  $\sigma$  values and those which are electron-donating have negative  $\sigma$  values<sup>30</sup>. So, as the negative value of  $\sigma$  increased the electron donor property of the substituent increases. The values of  $\sigma$  for 1-H, 2-OH and 3-OCH<sub>3</sub> are 0.00, -0.22 and -0.27, respectively. Inspection of  $\sigma$  values for the studied cations, it was expected that with increasing the donor property of the substituent (*i.e.* more negative values for Hammett constant) the cationic strength decreases and vice versa. The consequence of this is that the 1-H ( $\sigma = 0.00$ ) cation will be attracted strongly with the fixed group in the cation exchanger leading to release heat during the adsorption process (negative values for  $\Delta H_{ads}^{\circ}$ ). While in the case of 2-OH ( $\sigma = -0.22$ ) and 3-OCH<sub>3</sub> ( $\sigma = -0.27$ ) the cationic strength is lesser than 1-H, so the adsorption process of 2-OH and 3-OCH<sub>3</sub> requires high energy especially in the diluted solutions ( $\leq 5.0 \times 10^{-4}$  mol L<sup>-1</sup>) as a result the adsorption process becomes endothermic (positive  $\Delta H_{ads}^{\circ}$  values) with a magnitude similar to that observed in the case of ion exchange processes under diffusion control<sup>31,32</sup>. On the other hand, with increasing the concentration ( $> 5.0 \times 10^{-4}$  mol L<sup>-1</sup>) of 2-OH and 3-OCH<sub>3</sub> the adsorption process may occur in two stages:

#### Stage (1)

In the earlier contact with the exchanger, ion adsorption occurs on the strong bonded active sites.

*Stage (2)*

When the exchanger becomes near saturation, new adsorption sites may be created and the adsorption process continues under the electrostatic dipole-dipole interaction between the cations in the exchanger and those in the solution phase. The suggested dipole-dipole interaction was expected, because the studied cations can be considered as dipoles in which the pyridinium is the partially positive pole while the delocalized  $\pi$  electrons for the substituted phenyl ring is the partially negative pole.

So, the resultant net heat of adsorption was negative with absolute values much less than those for 1-H cation in the studied range of concentration. Srivastava *et al.*<sup>33</sup> reported that the dependence of heat of adsorption with surface coverage is usually observed to display the adsorbent-adsorbate interaction followed by the adsorbate-adsorbate interaction. The adsorbent-adsorbate interaction takes place initially at lower  $q_e$  values resulting in high heats of adsorption. On the other hand, adsorbate-adsorbate interaction occurs with an increase in the surface coverage. Accordingly, the suggested dipole-dipole interaction is acceptable. However, according to the mean value of  $\Delta H_{ads}^o$  for the studied organic cations the following increasing order can be obtained:



- For  $\Delta S_{ads}^o$  - Table 4 recorded an increase in the mean value of  $\Delta S_{ads}^o$  for the studied cations as given in the following order:



This order is similar to that obtained for the mean value of  $\Delta H_{ads}^o$ . In general, the concept of entropy is associated with order-disorder changes. As the adsorption process occurred mainly through electrostatic interaction between the studied cations and the anionic group in the exchanger, it was expected that with increasing the cationic property the system becomes more ordered ( $\Delta S_{ads}^o$  value becomes more negative) under the so-called electrostriction effect<sup>34</sup>. So, negative  $\Delta S_{ads}^o$  values were recorded for 1-H cations which have the highest cationic property. Another factor can be taken into account is the so called "solvent replacement"<sup>35</sup>. In aqueous solution water molecules easily wets the exchanger, the studied cations must receive some heat and replace the water molecules then it could be adsorbed and exchanged by the mobile ion ( $H^+$ ). For the larger molar volume of both 2-OH and 3-OCH<sub>3</sub> than 1-H, the number of water molecule replaced by the two formers was larger than that by the latter one. So the solvent replacement in the case of 2-OH and 3-OCH<sub>3</sub> cations results in the increase of entropy. However, the entropy change is assumed to be temperature independent<sup>36,37</sup> and this is the case in the present study (Table 2).

- For  $\Delta G_{ads}^o$  - Table 4 recorded negative values of  $\Delta G_{ads}^o$  for all the studied systems, indicating the feasibility and spontaneity of the adsorption of the studied cations on dowex 50WEX/ $H^+$  at all investigated concentrations and temperatures. Inspection of  $\Delta G_{ads}^o$  values, the following results can be obtained:
- At constant temperature, generally  $\Delta G_{ads}^o$  decreases with increasing the concentration of the organic cations, meaning that the adsorption process becomes more spontaneous with increasing concentration.
- At constant concentration,  $\Delta G_{ads}^o$  increases with rising temperature for all systems which have negative values for  $\Delta H_{ads}^o$ <sup>29,38</sup> except that recorded for both 2-OH and 3-OCH<sub>3</sub>

cations as they gave limited decrease in  $\Delta G_{ads}^o$  with rising temperature. The latter behaviour may be attributed to the contribution of entropy change with positive values.

- $\Delta G_{ads}^o$  Values decreases with rising temperature for all systems which have positive values for  $\Delta H_{ads}^o$ . It was recorded<sup>26,39</sup> that the endothermic processes become more spontaneous with rising temperature.

In the experimental range of concentration and solution temperature, the following increasing order of the absolute value of  $\Delta G_{ads}^o$  for the studied organic cations can be written:



The above order gives good consistency with the data obtained previously from various thermodynamic parameters

### *Adsorption isotherms*

The dynamic adsorptive separation of solute from solution onto an adsorbent depends upon a good description of the equilibrium separation between the two phases. Adsorption isotherms are the equilibrium relation between the concentration of the adsorbate on the solid phase and in the liquid phase at constant temperature. Thus the correlation of equilibrium data by either theoretical or empirical equations is essential to the practical design and operation of adsorption systems.

The adsorption isotherms of the studied cations on dowex 50WX4-50/H<sup>+</sup> in aqueous solutions at three different temperatures are presented in Figure 6. It was seen that, for all systems the adsorbed amount of each of the organic cation increases with the increase of its concentration in the solution phase at equilibrium. It is worthnoting that in the case of 1-H organic cation the amount adsorbed at equilibrium changes significantly with small changes in the concentration in solution phase at equilibrium. The equilibrium sorption data were analyzed by using various adsorption isotherm models. By far away, it was found to obey Freundlich and dubinin-radushkevich adsorption isotherm models.

### *Freundlich adsorption isotherm model (FAIM)*

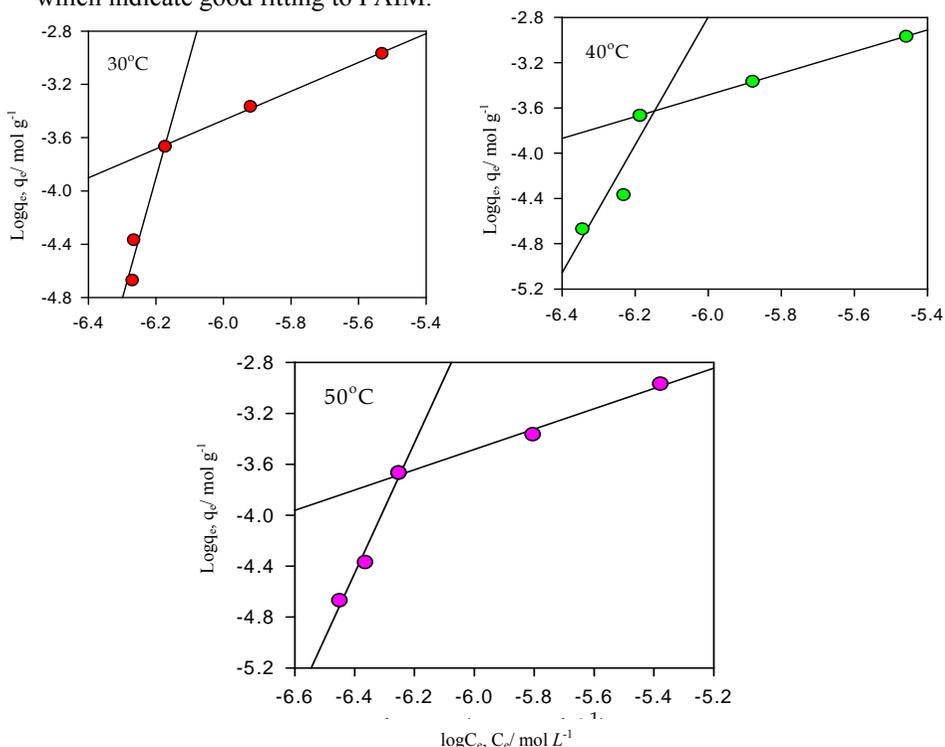
It is the most widely used empirical expression that account for the surface heterogeneity, exponential distribution of active sites of adsorbent and their energies towards adsorbate. The linearized form of FAIM is given in the following form<sup>40</sup>:

$$\log q_e = \log K_F + n_F \log C_e \quad (12)$$

Where  $n_F$  is a characteristic constant related to adsorption intensity and  $K_F$  is roughly an indicator of the adsorption capacity.

Figure 7 shows the logarithmic plots of the Freundlich expression for the adsorption of 1-H cations onto dowex 50WX4-5/H<sup>+</sup> at different temperatures. Similar Figures were obtained in the case of 2-OH and 3-CH<sub>3</sub> cations but are not shown. As was seen from Figure 7, two straight lines with different slopes are obtained indicating the existence of two different sets of adsorption sites with substantial different in energy of adsorption. Similar segmented Freundlich plots for the adsorption of some heavy metal cations on inorganic ion exchangers were reported in recent works<sup>41,42</sup>. The Freundlich isotherm parameters and the correlation coefficients of various systems were estimated and recorded in Table 5 and results can be discussed as below:

- In all studied systems, it was found that  $n_1 > n_2$  and  $K_{f1} > K_{f2}$  indicating that stronger binding sites are occupied first and then the binding strengths are decreased with increasing the degree of site occupation<sup>43</sup> and the latter increases with the increase of cation concentration in the solution phase.
- It was observed gradual decrease in  $n_2$  and  $K_{f2}$  values of all studied systems with the rise in temperature, indicating exothermic nature of adsorption process at higher level of concentrations and this result is in good agreement with that obtained from  $\Delta H_{ads}^\circ$  values at concentrations  $> 5.0 \times 10^{-4}$  mol L<sup>-1</sup>.
- The  $n$  values are in the range from 0.80 to 20.77. It was reported<sup>44</sup> that:
  - (i) when  $n > 1.00$  or becomes very large ( $n \gg 1.00$ ), the amount adsorbed at equilibrium changes significantly with the change in the solute concentration in the solution phase at equilibrium;
  - (ii) When  $n$  is less than unity, increased adsorption modifies the adsorbent in a manner that increases the adsorption capacity, such as forming new adsorption sites. In the present work,  $n_1$  and  $n_2$  values at all temperatures are referred to case (i) except that at temperature  $> 30^\circ\text{C}$ , it was found that  $n_2$  values for 3-OCH<sub>3</sub> cation are referred to case (ii). The latter result supports the suggested dipole-dipole interaction between the adsorbed molecules with increasing loading on the ion exchanger.
- The mean values of the correlation coefficients for the studied systems are  $\geq 0.93$  which indicate good fitting to FAIM.



**Figure 7.** FAIM for the adsorption of 3-OCH<sub>3</sub> organic cations onto Dowex 50WEX/H<sup>+</sup> at different temperatures

**Table 5.** FAIM parameters and correlation coefficients at different temperatures

t °C	$n_1$	$\log \frac{K_{f1}}{K_{f2}}$ mol g <sup>-1</sup>	$R_1^2$	$n_2$	$\log \frac{K_{f2}}{K_{f1}}$ mol g <sup>-1</sup>	$R_2^2$
1-H						
30°	7.98	42.16	0.94	2.27	9.35	1.00
40°	20.77	108.03	1.00	2.33	8.99	0.89
50°	18.13	93.61	0.99	1.75	5.82	0.90
Mean value	15.63	81.27	0.98	2.12	8.05	0.93
2-OH						
30°	4.90	25.15	1.00	1.42	4.70	1.00
40°	5.82	30.97	0.97	1.06	2.61	0.99
50°	5.08	26.64	0.95	0.930	1.88	0.97
Mean value	5.27	27.59	0.97	1.14	3.06	0.99
3-OCH <sub>3</sub>						
30°	9.08	52.41	0.93	1.08	3.02	1.00
40°	5.65	31.12	0.89	0.96	2.26	1.00
50°	5.13	28.37	0.98	0.80	1.30	0.99
Mean value	6.62	37.3	0.93	0.95	2.19	1.00

*Dubinin-Radushkevich adsorption isotherm model (D-RAIM)*

Another popular equation for the analysis of isotherms of a high degree of rectangularity is that proposed by Dubinin-Radushkevich<sup>45</sup> and the linear form can be written as:

$$\ln q_e = \ln K_s - B\varepsilon^2 \quad (13)$$

where  $\varepsilon$  is the *Polanyi adsorption potential* and can be correlated:

$$\varepsilon = RT \ln \left( 1 - \frac{1}{C_e} \right) \quad (14)$$

The constant  $B$  gives the energy  $E$  of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed by using the relationship:

$$E = \frac{1}{\sqrt{2B}} \quad (15)$$

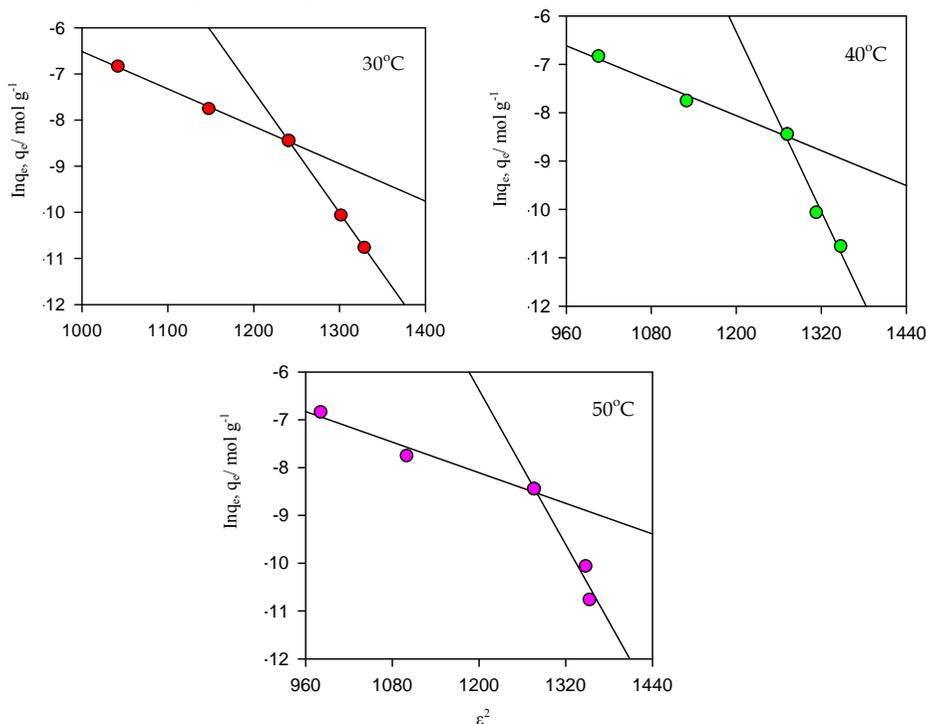
Figure 8 represent the plots of  $\ln q_e$  versus  $\varepsilon^2$  for 1-H cation at different temperatures. Similar Figures were obtained in the case of 2-OH and 3-OCH<sub>3</sub> cations but are not shown. All plots show two straight lines with different slopes, indicating that the energy of adsorption depends on the studied concentration range. All estimated D-R adsorption parameters ( $\ln K_{s1}$ ,  $\ln K_{s2}$ ,  $E_1$  and  $E_2$ ) and the correlation coefficients were tabulated in Table 6 and the obtained results were interpreted as follows:

- As can be seen, the obtained values for D-R adsorption capacity ( $\ln K_{s1}$  and  $\ln K_{s2}$ ) show similar trend as that discussed in the case of Freundlich adsorption capacity ( $K_{f1}$  and  $K_{f2}$ ). In all studied systems, it was found that  $E_1 < E_2$  indicating that the energy required to remove one organic cation from the bulk solution to the solid/solution interface depends on concentration range of the cations. This result was explained as that with increasing concentration, the bulk solution becomes rich with cations which experience dipole-dipole interactions with each others, so much energy must be required to transfer one molecule from the bulk solution to the solid/solution interface.

- The magnitude of  $E$  gives information about the type of adsorption. If  $E$  value is between 8 and 16 kJ mol<sup>-1</sup> adsorption type can be explained by chemical-ionexchange mechanism<sup>46</sup> while if  $E$  value is lesser than 8 kJ mol<sup>-1</sup> adsorption type can be explained by physical adsorption mechanism<sup>47</sup>. On the bases of the obtained  $E$  values the mechanisms by which the studied cations are adsorbed on dowex 50WX4-5/H<sup>+</sup> may be illustrated as below:
- For 1-H cations both  $E_1$  and  $E_2$  values are lesser than 8 kJ mol<sup>-1</sup>, so physical-ion exchange mechanism may be suggested for its adsorption on dowex 50WX4-5/H<sup>+</sup> in the studied range of concentrations.
- For 2-OH and 3-CH<sub>3</sub> cations  $E_1$  values are lesser than 8 kJ mol<sup>-1</sup>, so physical adsorption mechanism was suggested for their adsorption on dowex 50WX4-5/H<sup>+</sup> at low concentrations. While chemical-ion exchange mechanism was suggested for their adsorption on dowex 50WX4-5/H<sup>+</sup> at relatively high concentrations, since  $E_2$  values are more than 8 kJ mol<sup>-1</sup>.
- The mean value of  $E_2$  for each studied organic cation was found to obey the following order:  
1-H < 2-OH < 3-OCH<sub>3</sub>

The above order is in good agreement with that obtained previously for  $\Delta H_{ads}^o$ .

- The mean values of the correlation coefficients for the studied systems are  $\geq 0.93$  which indicate good fitting to D-RAIM.



**Figure 8.** D-RAIM for the adsorption of 3-OCH<sub>3</sub> organic cations onto Dowex 50WEX/H<sup>+</sup> at different temperatures

**Table 6.** D-RAIM parameters and correlation coefficients at different temperatures

$t$ °C	$\ln K_{s1}$ $K_s, \text{ mol g}^{-1}$	$E_1$	$R_1^2$	$\ln K_{s2}$ $K_s, \text{ mol g}^{-1}$	$E_2$ $\text{kJ mol}^{-1}$	$R_2^2$
			1-H			
30°	43.84	3.26	0.94	6.98	6.00	0.89
40°	119.57	2.01	1.00	6.64	5.91	0.89
50°	103.04	2.23	0.99	2.99	7.04	0.90
Mean value	88.82	2.50	0.98	5.54	6.32	0.93
			2-OH			
30°	24.19	4.39	1.00	1.60	7.91	1.00
40°	30.78	4.02	0.98	-0.84	9.13	0.99
50°	25.97	4.30	0.95	-1.71	9.71	0.96
Mean value	26.98	4.24	0.98	-0.32	8.92	0.98
			3-OCH <sub>3</sub>			
30°	55.63	3.27	0.93	-0.29	9.13	1.00
40°	30.80	4.16	0.89	-1.19	9.71	1.00
50°	27.80	4.39	0.98	-2.33	10.66	0.99
Mean value	38.08	3.94	0.90	-1.27	9.83	1.00

## Conclusion

- The studied cations showed good adsorptive properties onto dowex 50WX4-50/H<sup>+</sup> at different concentrations and temperatures.
- Main adsorption behaviour was ion exchange between hydrogen ions and the organic cations as indicated from the linear relation between the initial concentration of the organic cations and the released hydrogen ions.
- It was found that the adsorption affinity of dowex 50WX4-50/H<sup>+</sup> towards the studied organic cations depends on the ionic size of the organic cations giving the following increasing order:

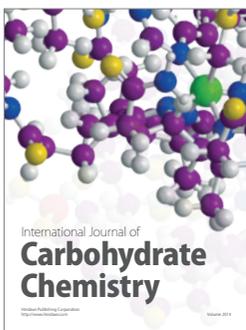
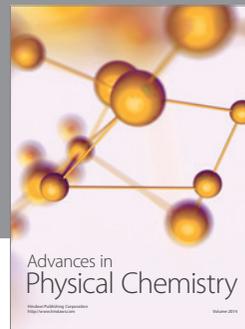
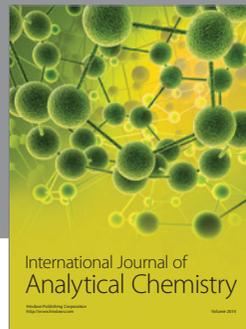
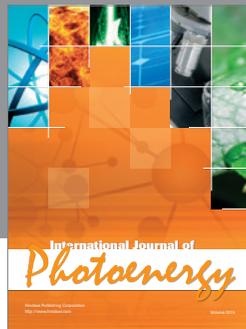
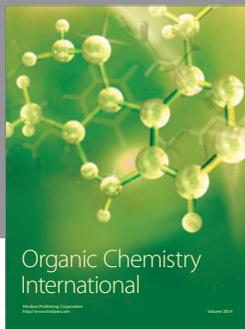
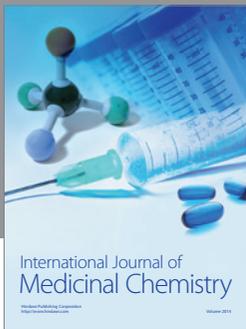


- Thermodynamic parameters for the adsorption of 1-H organic cation onto dowex 50WX4-50/H<sup>+</sup> revealed spontaneous, ordered and exothermic process which is favored with decreasing temperature.
- Thermodynamic parameters for the adsorption of 2-OH and 3-OCH<sub>3</sub> organic cations onto dowex 50WX4-50/H<sup>+</sup> revealed spontaneous, disordered process with enthalpy change varies significantly with increasing organic cation concentration, suggesting dipole-dipole adsorption forces as new active sites for adsorption under conditions of relatively high concentrations. However, their adsorption is favored with increasing temperature.
- FAIM and D-RAIM reasonably describe the adsorption of the studied organic cations onto dowex 50WX4-50/H<sup>+</sup> by segmented straight lines depending on the studied range of concentration, indicating the existence of two different sets of adsorption sites with substantial difference in energy of adsorption. According to D-RAIM, physical-ion exchange mechanism was suggested for the adsorption of 1-H organic cation and both physical and chemical-ion exchange mechanisms were suggested for the adsorption of 2-OH and 3-OCH<sub>3</sub> organic cations depending on the studied range of concentration.

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