

# Thermokinetics of Mercury (II) Cations' Sorption on the Carboxycationite

Elena Zauer

Volgograd State Technical University

**Abstract** Thermokinetics of sorption of mercury (II) acetate solution on the carboxylic acid cationite KB-4 in the sodium and hydrogen forms has been investigated by microcalorimetric method. The influence of the concentration of the sorbed ion in solution on sorption thermokinetics has been investigated. Total heat of sorption has been determined.

**Keywords** Microcalorimetry, Sorption, Mercury, Carboxylic acid cationite-4 KB

## 1. Introduction

Ion exchange processes are widely used in industry, in protection of the environment and in analytical chemistry due to their high selectivity, low energy cost and relative ease of ion exchange process.

The most commonly materials used for the ion exchange are ion exchange resins having a different nature and structure of the polymer matrix (including styrene) and containing various ionic groups capable of exchanging cations and anions from solutions. Efficient use of ion exchange material requires accurate data on the kinetics and mechanism of interaction of compounds extracted from an ion exchanger. Investigations of these issues were presented in a number of monographs and reviews [1-5]. To investigate the patterns and features of ion exchange processes different methods namely potentiometric titration, IR spectroscopy, atomic absorption spectrometry and X-ray fluorescence are used, the most informative one proved to be calorimetry. The first calorimetric studies of ion exchange processes were performed by the authors of [6, 7], which gave impetus to the widespread use of calorimetry for the study of sorption processes. At present, the thermal effects of sorption allows to study the influence of the type of an ion exchanger, its ionic form, nature and the amount of bridge forming fragment, the nature of the sorbed ions and co-ions on the kinetics and mechanism of the process.

A number of studies are known in which calorimetry method was used for investigation of the kinetics and mechanism of sorption of copper, nickel, cobalt, manganese and zinc on carboxylic cation exchangers type CB-2, CB-2e, CB-4, the KMT [8-13]. Continuing microcalorimetric

studies initiated in [13, 14], in the presented work the features of the sorption of mercury (II) acetate solutions of the carboxyl cation exchanger KB-4 in the hydrogen and sodium forms has been investigated.

## 2. Experimental

Cationite KB-4 in salt (Na) and hydrogen forms was prepared according to [15].

A solution of mercury (II) was prepared from its acetate and has been standardized by the method of acidimetric titration [16].

Determination of  $SE_{Hg}$  sorption capacity ( $mmol\ g^{-1}$ ) of the both forms of an ion exchanger was performed according to [2, pp. 114] as follows. A sample of cationite was mixed with mercuric acetate solution, after 3 days mercury (II) concentration has been determined by acidimetric titration. Calculation of the sorption capacity was carried out according to the formula

$$SC_{Hg} = \frac{(C_1 - C_2) \cdot V}{m},$$

where  $C_1$  and  $C_2$  are concentrations ( $mol\ L^{-1}$ ) of mercury in solution before and after sorption;  $V$  is the volume of solution (L);  $m$  is mass of the cationite sample (g).

Sorption kinetics was studied by microcalorimetric method [17] on the differential automatic calorimeter DAK-1-2M at 30°C. Weighed sample of 0.139 g of dry cation exchanger KB-4 was placed in a glass vial. An aliquot (0.35 mL), 0.5N solution of mercuric acetate (II) was poured into a glass vial with a bottom in the form of a thin-walled balloon. With the help of a special device, both vials were introduced into the calorimeter cell and thermostated. At the end of thermostating a thin-walled vial has been broken and thermokinetics curve of the sorption process has been registered by electronic recorder.

\* Corresponding author:

zea1@live.ru (Elena Zauer)

Published online at <http://journal.sapub.org/pc>

Copyright © 2014 Scientific & Academic Publishing. All Rights Reserved

Effect of the mercury concentration in solution on sorption kinetics were examined on C80 Setaram calorimeter at 30°C. Sodium form of cationite exchanger has been used.

The degree of filling of the ion exchanger by ion absorbed (%) has been calculated by the formula

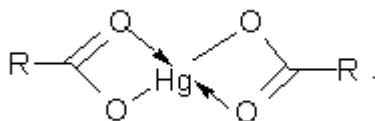
$$\% = \frac{n_{\text{sorp.}}}{m \cdot SC_{\text{Hg}}},$$

where  $n_{\text{sorp.}}$  is the amount of absorbed mercury (in mmol). Quantity of mercury sorbed was determined as the difference between its concentration in the solution before and after calorimetry has been completed, using acidimetric titration method.

### 3. Results and Discussion

Cationite KB-4 under investigation refers to complex forming ionites on which the sorption of transition metal ions is due to the simultaneous formation of an ionic bond with an oxygen atom of hydroxyl group and coordination to carbonyl oxygen [2].

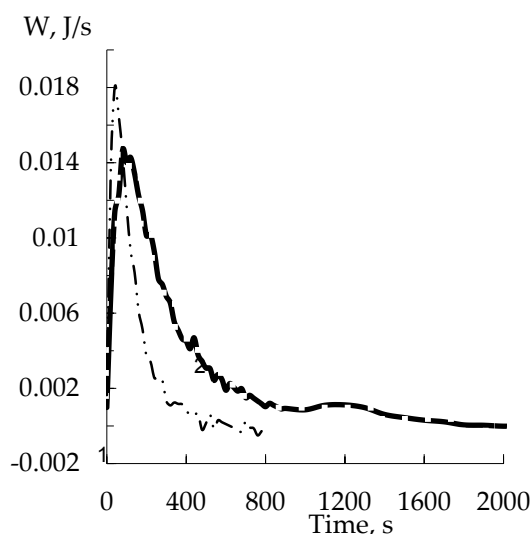
Furthermore, the authors of [18] on studying the mechanism of sorption of mercury on the carboxyl cationite SG-1 by the method of potentiometric titration have found that mercury, regardless of its concentration in the solution is characterized by the formation of complexes with two carboxyl groups of the ionite



According to [19] the formation of complexes of this composition occurs with maximum evolution of heat. It should also be noted that the formation of structures similar to those under consideration, requires energy loss associated with deformation of the polymer network [8].

The Figure 1 shows the curves of thermokinetics mercury sorption on weakly acidic cation exchanger KB-4 in the salt ( $\text{Na}^+$ ) (curve 1) and hydrogen (curve 2) forms. All sorption processes studied are exothermic. The nature of the curves is similar as on 2 or 3 min. after start a decrease in the sorption heat flux intensity has been observed. The initial increase of the intensity of heat evolution can be explain by the fact that sorption mainly occurs due to the functional groups located on the surface of the ion exchanger pellet. The subsequent decrease of the intensity of heat evolution may be due to the necessity of deep diffusion of sorbed ions into pellets of cationite associated with certain energy loss [8, 9].

Decreasing of the heat evolution of the hydrogen form cationite exchanger (curve 2) is much slower than that of the sodium form (curve 1). Duration sorption on the cation exchanger of the sodium and hydrogen forms is different viz. 800 s and 2100 s respectively.



**Figure 1.** Thermokinetics sorption curves of mercury (II) on sodium (1) and hydrogen (2) forms the cation exchanger KB-4

**Table 1.** Influence of the form of cation exchanger KB-4 on the sorption capacity (SC), the degree of filling and total thermal effect sorption of mercury (II)

Form Exchanger	$SC_{\text{Hg}}$ , mmol/g	The degree of filling of the ion exchanger, %	Total thermal effect	
			J/g*	kJ/mol**
$\text{Na}^+$	3,86	24,0	18.4	19.8
$\text{H}^+$	3,67	27,1	38.9	39.5

\* Per 1 g of cation exchanger; \*\* Based on 1 mol of sorbed ions.

Total thermal effects (Table) are also different, namely whereas the values of the sorption capacity and the degree of filling of the phase sorbed ion exchanger are similar the total heat effect for sodium form is about half less than that of hydrogen one (19.8 kJ/mol and 39.5 kJ/mol respectively).

The quantity of calorimetric thermal effect measured is determined not only by the formation ion-coordination bond of mercury ion with two adjacent functional groups (i.e., the actual exchange reaction), but also by the energy loss of the system due to the desolvation of metal ions and functional groups as well as by the change of position of functional groups and by the polymer mesh deformation [9]. The nature of co-ions may also influence on the power of the sorption process [20]. As follows from numerous studies mentioned above the contribution of each of these components to the total thermal effect of the sorption process varies depending on many factors.

On investigating the sorption of copper (II) by salt (Na) and hydrogen forms of carboxyl cationite KB-2e it was found [21] that in the case of a salt form sorption the process is endothermic, whereas in the case of hydrogen form it is exothermic. Explanation of the observed differences in sorption energies has been explained by different structural organization of salt and hydrogen forms of cation exchanger. The salt form, as noted in the work [21], has a fibrillar

structure with regular arrangement of functional groups, promoting the gradual sorption of metal ions from the periphery to the center of the granule. Hydrogen form has a globular structure characterized by the advancement of ions sorbed into the grain through interglobular space, leading to a uniform distribution all over the entire volume. As a result, energy losses for changing of the position of the polymer functional groups are less than that in the case of the hydrogen form.

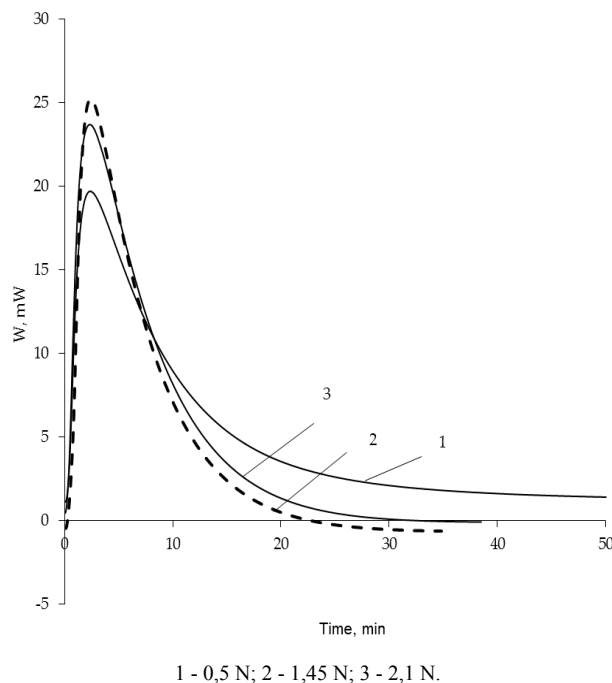
Apart from the above mentioned differences in the structure and organization of the salt form and the hydrogen form of an ion-exchanger, the nature of co-ions may influence on the heat effects as well. This effect is particularly evident in the case of using of  $H^+$  ionite and simultaneous presence of anions of weak acids (e.g., fluoride ions) in solution [20]. In [21] the effect of co-ions was reduced almost to a minimum as the sorption has been performed from copper nitrate solutions.

In the present study acetate ions appear as co-ions and in the case of using the hydrogen form of the  $H^+$  ionite an exchange on  $Hg^{2+}$  ion from solution yields the formation of a weak acetic acid, the latter reaction being an exothermic one ( $\Delta_f H^\circ = -487,0$  kJ/mol [22]). The same phenomenon was observed in [14] in the case of microcalorimetric study of the sorption of mercury on hydrogen form of cation exchanger KU-2-8 from acetate solutions.

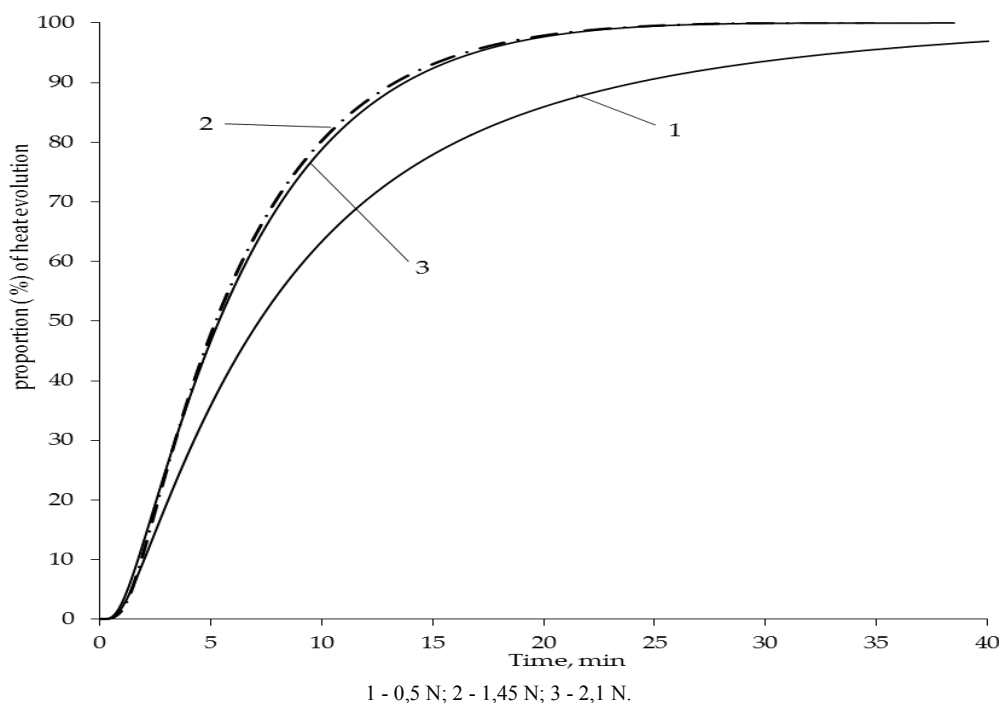
Figure 2 shows thermokinetics curves obtained from the results of research of mercury sorption on the salt (Na) cationite form of its acetate solutions of different concentrations. Nature of the curves is the same. However, sorption kinetics vary namely the enhancement of mercury content in solution increases the rate of sorption, and, as a

result, reduces its duration. For solutions with a low concentration of Hg an equilibrium state is reached approximately in 80 min time (curve 1) whereas for more concentrated solutions sorption time has been reduced up to 35-40 min (curves 2 and 3).

Based on the above presented thermokinetic curves we have calculated the proportion (%) of heat evolution. The results of these calculations are presented in Figure 3.



**Figure 2.** Thermokinetic sorption curves of Hg from solutions of different concentrations



**Figure 3.** Dependence of heat releasing on the mercury concentration in solution

The figure shows that the higher is the concentration of mercury in solution, the greater is the rate of sorption (curves 1 and 2). Thus for 10min time from the start of the sorption on the cationite from the solution at a concentration of 0.5N (curve 1) approximately 60% of the total amount of heat has been released, whereas about 80% of heat has been released during the sorption from a solution with a concentration of mercury equal to 1.45 N (curve 3). However, the figure also shows that there comes a point where no further increase in the concentration of mercury in solution does not lead to an increase in heat release rate (curve 3), and, consequently, the rate of sorption. This apparently is due to complete saturation of the cationite.

## 4. Conclusions

Thus thermokinetics of sorption of mercury (II) acetate solution on a hydrogen and a sodium cation forms of carboxyl cationite has been investigated by microcalorimetric method. It was shown that at close values of sorption capacity and the degree of filling of the ion exchanger heat evolution on the H-form is twice as much as that in the case of the Na-form. The influence of the concentration of metal sorbed on the rate and duration of sorption has been found.

## REFERENCES

- [1] F. Helfferich. Ion Exchange. McGraw Hill, New York, 1962.
- [2] K. M. Saldadze and V. D. Kopylova-Valova. Complex-Forming Ion Exchangers (Complexites). Khimiya, Moscow, 1980 [in Russian].
- [3] S. K. Sahni, J. Reedijk., 1984 Coordination chemistry of chelating resins and ion exchangers. Coordination Chemistry Reviews, 59(9), 1-139.
- [4] A.A. Zagorodni. Ion Exchange Materials: Properties and Applications. Elsevier. 2006.
- [5] Ion Exchangers (K. Dorfner, ed.), Walter de Gruyter, Berlin, 2011.
- [6] O. D. Bonner, J. R. Overton., 1961, The effect of temperature on ion-exchange equilibria. IV. The comparison of enthalpy changes calculated from equilibrium measurements and calorimetrically measured values. Journal of Physical Chemistry, 65, 1599-1602.
- [7] G. E. Boyd, F. Vaslow, S. Lindebaum., 1964, Calorimetric Determinations of the Heats of Ion-Exchange Reactions. I. Heats of Exchange of the Alkali Metal Cations in Various Cross-Linked Polystyrene Sulfonates. Journal of Physical Chemistry, 68, 590-597.
- [8] P. Yu. Kolobov, V. D. Kopylova, A. N. Amelin., 2003, A microcalorimetric study of the sorption of transition metal ions on a carboxylic cationite in various ionic forms." Russian Journal of Physical Chemistry A, 77(5), 811 – 813.
- [9] V. D. Kopylova, A. I. Val'dman, D. I. Val'dman, G. L. Vdovina, Eh. A. Sabanashvili, T. A. Munsh., 1990, Vliyanie prirody i kolichestva mostikoobrazovatelja na ehntalpiju i skorostj sorbcii ionov medi (II) karboksilqnym kationitom KB-2eh. Zhurnal fizicheskoi khimii, 64, 3007-3011 [in Russian].
- [10] V. D. Kopylova, A. N. Amelin, Yu. S. Peregudov, and A. V. Astapov., 2001, The enthalpy of interaction of copper (II) ions with KB-4 and ANKB-35 ionites and their low-molecular-weight analogues. Russian Journal of Physical Chemistry A, 75, 720-723.
- [11] V. D. Kopylova, A. I. Val'dman, D. I. Val'dman, N. V. Portnykh., 1989, Ehntalpija i kinetika sorbcii ionov 3d-metallov kapboksilqnymi kationitami. Zhurnal prikladnoj kximii, 62(7), 1539- 1545. [in Russian].
- [12] P. Yu. Kolobov, A.N. Amelin., 2003, Selektivnostj karboksilqnego kationita KB-2Eh po ionam perexodnyx metallov." Izvestija vuzov. Kximija i kximicheskaja tehnologija, 46(2), 160-161. [in Russian].
- [13] E. A. Zauer., 2008, A microcalorimetric study of the sorption of copper (II) on KB-4 carboxyl cationite." Russian Journal of Physical Chemistry A, Focus on Chemistry, 82, 1368-1370.
- [14] E. A. Zauer., 2007, A microcalorimetric study of mercury (II) sorption on KU-2-8 sulfocationite, Russian Journal of Physical Chemistry A, 81, 779-780.
- [15] Physicochemical Methods of Analysis: Practical Manual: Textbook for High School. Ed. by V. B. Aleskovskii (Khimiya, Leningrad, 1988) [in Russian].
- [16] G. Charlot. Les methodes de la chimie analytique; analyse quantitative minerale. Masson, Paris, 1961.
- [17] E. Calvet and H. Prat. Microcalorimetrie, Masson, Paris, 1956.
- [18] Eh. A. Chuveleva, P. P. Nazarov, K. V. Chmutov., 1970, Sorbcija rtuti i kalqcija na smole SG-1. Zhurnal fizicheskoi khimii, 44(5), 1242- 1245. [in Russian].
- [19] S. K. Sahni, R. Vanbennekorn, J. Reedijk., 1985, A spectral study of transition-metal complexes on a chelating ion-exchange resin containing aminophosphonic acid groups. Polyhedron, 4(9), 1643-1658.
- [20] S. V. Kertman, G. M. Kertman, Yu. A. Leikin, and A. N. Amelin., 1996, Effect of anion nature on the heat of cation-exchange sorption of transition metal ions. Russian Journal of Physical Chemistry A, 70(3), 483-486.
- [21] P. Yu. Kolobov. Kislotno-osnovnoe ravnovesie i sorbcija ionov perexodnyx metallov karboksilqnymkationoobmennik om KB-2eh s razlichnym kolichestvom kross-agenta. Dis. ... kand. xim. nauk. Voronezh, Voronezhskij gosudarstvennyj universitet. 2003. 126s. [in Russian].
- [22] V. A. Rabinovich and Z. Ya. Khavin. Concise Chemical Handbook Khimiya, St. Petersburg, 1994, p. 208. [in Russian].