

CALCULATION OF ADSORPTION ISOTHERMS OF NaF FROM AQUEOUS SOLUTIONS BY THE SAMPLES OF ALUMINUM OXIDE

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Abstract In the paper the constants of adsorption equilibrium have been applied for calculation of adsorption isotherms of fluoride ions from model aqueous solutions with initial concentrations from $5 \cdot 10^{-4}$ to 0,50mmol/l. As fluorine adsorbents the aluminum oxihydroxides obtained by calcination at 200 and 800°C (A200 and A800) the electrochemical dimensional machining products of aluminum alloy have been used.

Comparison is given of theoretically calculated and experimentally obtained adsorption isotherms in the system $\text{Al}_2\text{O}_3 - \text{H}_2\text{O} - \text{NaF}$. It has been shown a satisfactory correlation of experimental and theoretically calculated values of isotherms of fluorine adsorption on studied samples.

Keywords: adsorption, adsorption isotherms, constants of equilibrium, fluorine, aluminum oxihydroxides, activity coefficient.

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1. INTRODUCTION

The isotherm of adsorption equilibrium calculation is very important from the theoretical viewpoint and for practical application of an adsorption method in water purification technology. Knowing the isotherm form and equilibrium constant, one can estimate the dose of adsorbent and the method of its application – in a static or dynamic mode, as well as to conclude, what is the mechanism of capture of adsorbate on the adsorbent surface. To calculate the isotherm, we first should determine the constant of adsorption equilibrium.

The constant of adsorption equilibrium (K_a) is widely used for calculation of many thermodynamic functions of an adsorption process – standard diminution of mole adsorption energy ($-\Delta F^0$), standard adsorption enthalpy (ΔH^0) and standard adsorption entropy (ΔS^0) [1-4].

There are a lot of references for these calculations presented in the literature with well-known models of adsorption application: Freundlich, Langmuir, Dubinin-Radushkevich, Riedlich-Peterson adsorption models and others [5-10].

However, not always the experimental data can be linearized with these equations. Therefore, the authors have based the calculation of the constant on the ratio of the

concentration of adsorbed substance on the solid surface to its concentration in the equilibrium solution [11-13].

2. RESULTS AND DISCUSSION

The method for calculation of the apparent adsorption equilibrium constant, which has been used at adsorption of non-polar low-molecular organic molecules from aqueous solutions on activated carbon [14], can be also applied for description of adsorption equilibrium of other systems, in particular at fluoride ions adsorption on pore aluminum oxide sorbents [15].

We deal in our investigation with a binary solution where water is a solvent (component 1) and NaF molecules – are a solute (component 2). For the constant calculation the following formula has been used [14,15]:

$$K_{a2} = \frac{\Theta_2}{\left[1 - \Theta_2 \left(\frac{v_2^0 - v_1^0}{v_2^0}\right)\right] \cdot C_2 \cdot v_2^0} \cdot \frac{\gamma_{a2}}{\gamma_2} \quad (1)$$

In equation (1) Θ_2 – the NaF molecules surface covering degree which is equal to $\frac{a_2 \cdot v_2^0}{v_m}$ where a_2 – the adsorption value, mmol/g, v_1^0 and v_2^0 – mole volumes of water and adsorbed NaF equal 0.0180 and 0.0217 cm³/mmol, respectively, v_m – the sorbent maximum adsorption pore volume cm³/g, C_2 – NaF solution equilibrium concentration, mmol/l, γ_2 and γ_{a2} – the NaF molecules activity coefficients in the equilibrium bulk solution and in the adsorption layer, respectively. Substituting numerical values of mole volumes of the water and sodium fluoride into equation (1) and expressing NaF bulk concentration in mmol/cm³ we obtain:

$$K_{a2} = \frac{4.6 \cdot 10^4 \cdot \Theta_2 \cdot \gamma_{a2}}{(1 - 0.172 \cdot \Theta_2) \cdot C_2 \cdot \gamma_2} \quad (2)$$

At the constant K_{a2} calculation it has been accepted that the relation of activity coefficients γ_{a2}/γ_2 in rather dilute solutions is equal to 1. In that case if the experimental adsorption data are presented in coordinates $\lg \frac{\Theta_2}{(1 - 0.172 \cdot \Theta_2) \cdot C_2}$ versus Θ_2 one can get linear extrapolation dependence and the intercept is numerically equal to adsorption constant logarithm ($\lg K_{a2}$).

The adsorption equilibrium constant for the oxyhydroxide aluminum sample A200 has been calculated in such a way [14].

However for more concentrated NaF solutions (more than 0,01 mol/l) it is necessary to take into account the activity coefficients both in the adsorption layer γ_{f2} and in the equilibrium bulk solution γ_2 and to use activities instead of concentrations.

Knowing the adsorption constant K_{a2} value we can make estimation of adsorption isotherms, i.e. to find the adsorption sodium fluoride dependence on its equilibrium concentration in solution (C_2) it is enough to get a functional dependence of γ_{f2} on surface covering degree Θ_2 .

The adsorption isotherms calculation are carried out as follows: fixed values of Θ_2 (or that is the same – adsorption values, a_2) are defined and for these values the equilibrium NaF concentrations in bulk solution (C_2) (or its activities) are computed from equation (2). Calculated adsorption values are determined for any Θ_2 from the expression $\hat{r}_{2calc.} = \Theta_2 a_m$, where a_m – the maximum adsorption, mmol/g which is calculated from the relation:

$$v_a = a_m \cdot v_2^0 \quad (3)$$

Then the isotherm is constructed in coordinates a_2 vs C_2 (or a_2 vs $C_2 \cdot \gamma_2$) and compared with experimental determined adsorption values a_{2exp} for corresponding equilibrium NaF concentrations or activities in solution.

It is known [14] that the coefficient γ_{a2} includes 3 items: γ_{c2} , γ_{a2-2} , and γ_{a2-H2O} , which characterize different types of interactions in the adsorption layer and can be presented as their sum:

$$RT \ln \gamma_{a2} = RT \ln \gamma_{C2} + RT \ln \gamma_{a2-2} + RT \ln \gamma_{a2-H2O} \quad (4)$$

The term γ_{c2} reflects the influence of NaF concentration growth in equilibrium solution on its content in the adsorption layer of the sorbent. The second term γ_{a2-2} is responsible for interaction between the adsorbed substance molecules and the term γ_{a2-H2O} notes the degree of interaction of adsorbed substance molecules with water in the adsorption layer.

Taking into account that in the system NaF-H₂O there is no association of NaF molecules (i.e there is no interaction between NaF molecules in adsorption layer) we can accept that $\gamma_{a2-2} = 1$ and $\lg \gamma_{a2-2} = 0$. On the other hand it is known [16] that sodium fluoride do not hydrolyze in water and therefore we can suppose the coefficient $\gamma_{a2-H2O} = 1$ and hence, $\lg \gamma_{a2-H2O} = 0$ as well. Thus, the activity coefficient γ_{a2} will mainly be defined by γ_{C2} that allows the term γ_{a2} to be substituted for γ_{C2} in equation (2) and makes concentration (activity) computation from the following expression:

$$C_2 \cdot \gamma_2 = \frac{4.6 \cdot 10^4 \cdot \Theta_2 \cdot \gamma_{C2}}{(1 - 0.172 \cdot \Theta_2) \cdot K_{a2}} \quad (5)$$

The maximum γ_{c2} value takes place at $\Theta_2 = 1$ when the total sorbent surface is occupied with NaF molecules (H₂O molecules are absent). Since in that case the adsorption layer is at equilibrium with saturated NaF solution, $\lg \gamma_{c2}$ will be determined by adsorption equilibrium constant K_{a2} (at $\Theta_2 = 1$) and NaF solubility in water at corresponding temperature C_{sNaF} (C_{sNaF} – saturated NaF solution concentration i.e. maximum solubility of NaF salt in water, mol/kg of water).

$$\lg \gamma_{C2\Theta_2=1} = \lg \frac{K_{a2} \cdot C_{sNaF}}{C_{sNaF} + C_{H_2O}} = \lg \frac{K_{a2}}{56,5}, \quad (6)$$

since $C_{sNaF} = 1$ mol/kg [17] and $C_{H_2O} = 55.5$ mol/kg.

As $\lg\gamma_{C_2}$ changes from 0 at $\Theta_2 = 0$ to $\lg\gamma_{C_2} = \lg \frac{K_{a2}}{56,5}$ at $\Theta_2 = 1$, γ_{C_2} for any Θ_2 value can be estimated from interpolation dependence of γ_{C_2} on Θ_2 :

$$\gamma_{C_2} = \left(\frac{K_{a2}}{56,5} \right)^{\Theta_2}, \quad (7)$$

or

$$\lg\gamma_{C_2} = \Theta_2 \cdot \lg \gamma_{C_2\Theta_2=1}. \quad (8)$$

As to NaF activity coefficient in equilibrium bulk solution γ_2 , it can be calculated from a well-known equation [18, 19]:

$$\ln \gamma_{2\pm} = -0,5066 \cdot z^2 \cdot \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0,2I \right), \quad (9)$$

where I – ionic strength of the solution which for 1-1 electrolyte NaF is equal to molar solution concentration, mol/kg, z – atomic charge. The calculated data are shown in Table 1.

In Table 2 there are shown the calculated NaF adsorption isotherms on A200 sample with surface area $358\text{m}^2/\text{g}$ and sorption pore volume $0,457\text{cm}^3/\text{g}$ [20]. The equilibrium NaF solution concentration was calculated from equation (5) under the assumption that $\gamma_{a2}/\gamma_2 \neq 1$.

$K_{a2} = 3311$, $V_2^0 = 0.0217\text{cm}^3/\text{mmol}$, $S_{sp} = 358\text{m}^2/\text{g}$, a_m calc. = 36.0mmol NaF/g , a_2 calc. = $\theta_2 \cdot 36.0$ mmol NaF/g, $K_{a2} = 358$ at $\theta_2 = 1$.

The NaF adsorption isotherms on the sample of Al oxide A800 (surface area is $145,6\text{m}^2/\text{g}$ and sorption pore volume – $0,221\text{cm}^3/\text{g}$) calculated from equation (5) taking into account the NaF activity coefficients in adsorption layer and in equilibrium bulk solution (Table 1) are shown in Table 3 and Fig. 1.

$K_{a2} = 5937$, $V_2^0 = 0.0217\text{cm}^3/\text{mmol}$, $S_{sp} = 145.6\text{m}^2/\text{g}$, $v_m = 0.221\text{cm}^3/\text{g}$, a_m calc. = $v_m/v_2^0 = 10.18\text{mmol NaF/g}$, $K_{a2} = 367$ at $\theta_2 = 1$, a_2 calc. = $\theta_2 \cdot 10.18$ mmol/g.

As it is seen from the listed data in both cases there is a good agreement of calculated from equation (5) values of NaF adsorption – a_2 calc. with experimentally determined ones – a_2 exp. Discrepancies of calculated and experimental adsorption data do not exceed 12% for A200 and 8.5% for A800 oxides.

3. CONCLUSION

Experimental and theoretically calculated values of isotherms of fluorine adsorption on studied samples are in good agreement.

For adsorption equilibrium isotherm calculation in the system aluminum oxide – aqueous NaF solution is quite enough data of adsorption equilibrium constants and NaF solubility data.

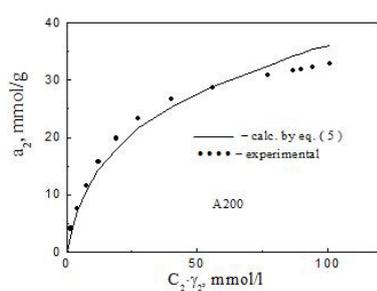
Table 1 Activity coefficients of NaF molecules in the equilibrium bulk solution in the system NaF – H₂O – Al₂O₃

A200			A800		
C ₂ , mmol/l	γ_2	NaF activity, mmol/l	C ₂ , mmol/l	γ_2	NaF activity, mmol/l
1.7	0.980	1.7	1.4	0.982	1.4
4.2	0.970	4.1	3.5	0.973	3.4
7.8	0.961	7.5	6.6	0.964	6.4
12.8	0.952	12.2	11.5	0.954	11.0
20.3	0.942	19.1	17.1	0.946	16.2
29.4	0.933	27.4	25.6	0.936	24.0
43.4	0.923	40.1	36.8	0.927	34.1
61.4	0.913	56.1	52.2	0.917	47.9
85.5	0.902	77.2	63.7	0.911	58.0
96.7	0.899	86.9	73.2	0.907	66.7
100.1	0.897	89.8	80.7	0.904	73.0
105.2	0.896	94.3	84.2	0.903	76.0
113.0	0.894	101.1	94.5	0.899	85.0
-	-	-	101.4	0.897	91.0

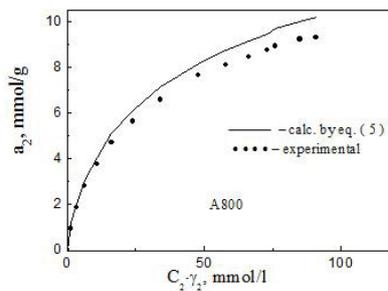
For NaF solutions concentrations more than 0.01mol/L at adsorption equilibrium constants calculation one should take into account the activity coefficients of NaF molecules in the adsorption layer and in the bulk equilibrium solution.

Table 2 Adsorption isotherms of NaF from aqueous solutions by the sample A200 at 20°C

θ_2	$\frac{\Theta_2}{(1-0.172 \cdot \Theta_2)}$	$\lg \gamma_{a2}$	γ_{a2}	$C_2 \cdot \gamma_2$, calc. by eq. (5), mmol/l	a_2 , calc., mmol/g	a_2 , ex- perim., mmol/g	Relative devia- tion, Δ , %
0.1	0.101	0.08	1.17	1.7	3.6	4.1	12.2
0.2	0.207	0.15	1.41	4.1	7.2	7.6	5.3
0.3	0.316	0.23	1.70	7.5	10.8	11.6	6.7
0.4	0.429	0.31	2.04	12.2	14.4	15.7	8.3
0.5	0.547	0.40	2.51	19.1	18.0	19.8	9.1
0.6	0.669	0.47	2.95	27.4	21.6	23.2	6.7
0.7	0.796	0.56	3.63	40.1	25.2	26.6	5.2
0.8	0.926	0.64	4.36	56.1	28.8	28.6	0.7
0.9	1.060	0.72	5.24	77.2	32.4	30.8	5.2
0.95	1.140	0.74	5.49	86.9	34.2	31.7	7.9
0.96	1.150	0.75	5.62	89.8	34.7	31.8	9.1
0.98	1.180	0.76	5.75	94.3	35.5	32.2	10.2
1.0	1.208	0.78	6.02	101.0	36.0	32.8	9.8



(a)



(b)

Fig. 1. Calculated and experimental adsorption isotherms of NaF on oxyhydroxides aluminum samples: (a) – A200, (b) – A800

Table 3 Adsorption isotherms of NaF from aqueous solutions by the sample A800 at 20°C

θ_2	$\frac{\Theta_2}{(1-0.172 \cdot \Theta_2)}$	$\lg \gamma_{c2}$	γ_{c2}	$C_2 \cdot \gamma_2$, calc. by eq. (5), mmol/l	a_2 , calc., mmol/g	a_2 , ex- perim., mmol/g	Relative devia- tion, Δ , %
0.1	0.101	0.081	1.20	1.4	1.2	0.94	8.5
0.2	0.207	0.162	1.45	3.4	2.04	1.88	8.5
0.3	0.316	0.243	1.75	6.4	3.05	2.82	8.2
0.4	0.429	0.324	2.11	11.0	4.07	3.76	8.2
0.5	0.547	0.405	2.54	16.2	5.09	4.70	8.3
0.6	0.669	0.486	3.06	24.0	6.10	5.64	8.2
0.7	0.796	0.567	3.69	34.1	7.13	6.58	8.4
0.8	0.926	0.648	4.45	47.9	8.14	7.66	6.3
0.86	1.00	0.697	4.98	58.0	8.75	8.10	8.0
0.9	1.065	0.729	5.36	66.4	9.16	8.46	8.3
0.93	1.107	0.753	5.66	73.0	9.46	8.74	8.2
0.95	1.136	0.769	5.87	76.0	9.67	8.93	8.3
0.98	1.178	0.794	6.22	85.0	9.97	9.21	8.2
1.00	1.207	0.810	6.46	91.0	10.18	9.3	9.5

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