

## Calculation of adsorption equilibria of individual compounds on microporous adsorbents in a supercritical temperature range

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Experimental data on the adsorption of Ar, Kr, Xe, CH<sub>4</sub>, and CF<sub>3</sub>Cl on zeolite NaX and of CH<sub>4</sub> on PAU-10 carbon demonstrate that the linear temperature range dependences of the equilibrium matched standard values of  $\ln p_{i,st}$  and  $\ln \bar{c}_{i,st}$  which are used in the calculation of adsorption equilibria in a subcritical temperature range, remain unchanged up to temperatures  $T^* \cong T_{cr} + (100 \div 150)$ .

**Key words:** adsorption equilibrium, supercritical temperature range.

The use of the equilibrium matched standard states of components in adsorption and bulk phases<sup>1</sup> is an important point that considerably simplifies the calculation of adsorption equilibria on microporous adsorbents. The states chosen for this purpose are an adsorbate ( $\bar{c}_{i,st} = c_{i,0} = f(T)$ ) and the saturated vapor of an adsorbative ( $p_{i,st} = p_{i,s} = f(T)$ ) which are in equilibrium with each other. The linear dependences of  $\ln \bar{c}_{i,st}$  and  $\ln p_{i,st}$  on temperature and reverse temperature

$$\ln p_{i,st}(T) = A - B/T, \quad (1)$$

$$\ln \bar{c}_{i,st}(T) = \ln \bar{c}_{i,st}(T_0) - \alpha(T - T_0) \quad (2)$$

allow one to easily calculate the standard adsorption and pressure at different temperatures, and even to extrapolate these dependences from the vapor-adsorbate phase range, where they are valid, *i.e.*,  $T < T_{cr}$ , to the gas-adsorbate range, *i.e.*,  $T > T_{cr}$ . (In Eq. (1) A and B are determined by the dependence of the saturated vapor pressure  $p_{i,s}$  on temperature, where  $\alpha$  is the thermal adsorption coefficient).

In practical calculations, one should know to what temperatures the extrapolation can be used. The linearity of the adsorption isosteres in the supercritical temperature range has been experimentally established.<sup>2,3</sup>

We found the dependences of  $\ln \bar{c}_{i,st}$  on  $T$  for Ar, Kr, Xe, CH<sub>4</sub>, and CF<sub>3</sub>Cl adsorbed on NaX zeolite and for CH<sub>4</sub> adsorbed on PAU-10 carbon.

The dependence of  $\ln \bar{c}_{i,st}(T)$  for the Kr—NaX system is presented in Figure 1; the dependences for the other adsorption systems are similar. The values of  $\ln \bar{c}_{i,st}$  (Table 1) are determined as the intersection points of isosteres  $\log p = f(1/T)$  or their linear extension with the line  $\log p_{i,st}(1/T)$  drawn from  $T_b$  to  $T_{cr}$  or with its extension to the range  $T > T_{cr}$ , as shown in Figure 2 for the system CH<sub>4</sub>—PAU-10. The experimen-

tal isosteres of adsorption of Ar, Kr, Xe, CH<sub>4</sub>, and CH<sub>3</sub>Cl on NaX and of CH<sub>4</sub> on PAU-10 are presented in refs. 3—6 where gas adsorption was studied for a wide range of adsorption parameters ( $p$ ,  $T$ , and  $c$ ).

The analysis of the obtained  $\ln \bar{c}_{i,st}(T)$  dependences shows that they can be considered as linear for all of the systems up to the temperatures  $T^* \cong T_{cr} + 100 \div 150$ . The maximum deviation of points from the straight line  $\delta = \ln \bar{c}_{i,st} - \ln \bar{c}_{i,st}^{lin}$  does not exceed 0.5 %, if all of the points in the range  $T_b < T < T^*$  are used for the approximation. This proves the validity of the use of the equilibrium matched  $c_{i,st}$  and  $p_{i,st}$  values obtained by

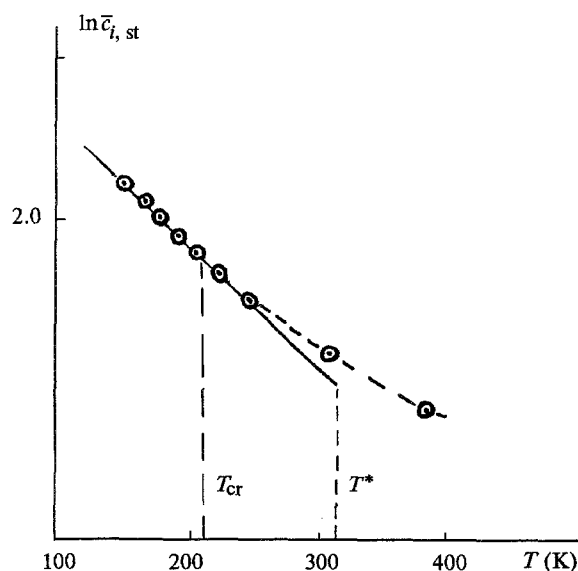


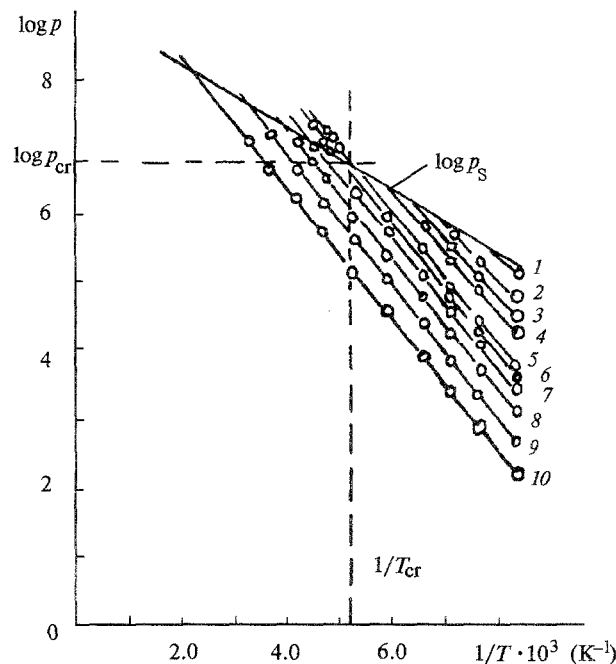
Fig. 1. Temperature dependence of  $\ln \bar{c}_{i,st}$  for the Kr—NaX system.

**Table 1.** Temperature dependences of  $\ln c_{i,st}$  (mmol g<sup>-1</sup>) in different systems

$T/K$	$\ln \bar{c}_{i,st}$	$\delta$	$T/K$	$\ln \bar{c}_{i,st}$	$\delta$
Kr—NaX			CH <sub>4</sub> —NaX		
148.8	2.054	0	143.5	2.054	0
163.9	2.028	0	171.2	2.002	0
177.0	2.002	0	177.9	1.988	0
191.9	1.974	0	187.3	1.974	0
204.5	1.946	0	195.3	1.960	0
222.7	1.917	0	201.6	1.946	0
248.8	1.872	0	224.2	1.902	0
307.7	1.792	+0.03	251.3	1.856	0
386.1	1.705	+0.09	289.9	1.792	+0.01
526.3	1.609	+0.26	349.7	1.705	+0.04
793.7	1.504	+0.62	454.6	1.609	+0.14
CH <sub>4</sub> —PAU-10			Xe—NaX		
131.4	2.434	0	168.9	1.758	0
142.0	2.416	0	221.2	1.705	0
153.4	2.398	0	243.9	1.668	0
162.6	2.380	0	256.4	1.649	0
180.8	2.357	0	265.3	1.639	0
191.6	2.335	0	280.1	1.619	0
211.0	2.303	0	290.7	1.609	0
251.3	2.251	+0.01	311.5	1.589	+0.01
296.7	2.197	+0.04	359.7	1.548	+0.04
425.5	2.079	+0.13	435.7	1.504	+0.09
CF <sub>3</sub> Cl—NaX			Ar—NaX		
222.2	1.435	0	123.2	2.303	0
254.8	1.386	0	138.9	2.277	0
280.5	1.348	0	160.0	2.251	+0.01
291.6	1.335	0	180.2	2.197	-0.02
300.3	1.322	0	248.8	2.079	-0.02
317.0	1.308	+0.01	392.2	1.946	+0.09
357.8	1.253	+0.01	694.4	1.792	+0.41
385.4	1.224	+0.02			
434.8	1.163	+0.03			
507.6	1.099	+0.07			
704.2	0.916	+0.17			

extrapolation. If, as is the case in practical calculations, the linear dependence is determined only by points of the subcritical range, *i.e.*, in the range  $T_b < T < T_{cr}$ , and it is then extrapolated to the supercritical range, the maximum deviation of  $\delta$  at  $T^*$  increases to 3%. The values of the thermal adsorption coefficient obtained in this way (Table 2) agree well with the  $\alpha$  values calculated by the Dubinin—Nikolaev method.<sup>7</sup>

As the temperature increases above  $T^*$   $\ln \bar{c}_{i,st}$  increases, *i.e.*, the absolute value of  $\alpha$  decreases. Although the temperature range above  $T^*$  is of no concern for practical calculations, the character of the deviation of  $\ln \bar{c}_{i,st}$  from linearity is of interest from the theoretical viewpoint. This deviation cannot be explained by possible curvature of the adsorption isosteres corresponding to low filling in the range of high pressures and temperatures<sup>8</sup> or by non-linearity of the  $\ln p_{i,st}(T)$  dependence extrapolated to the range  $T > T_{cr}$ . It can rather

**Fig. 2.** Adsorption isosteres of CH<sub>4</sub> on PAU-10,  $\bar{c}_p$ , mmol g<sup>-1</sup>: 1, 11.4; 2, 11.2; 3, 11.0; 4, 10.8; 5, 10.5; 6, 10.3; 7, 10.0; 8, 9.5; 9, 9.0; and 10, 8.0.

be explained by the dependence of  $c_{i,st}$  on pressure, which increases exponentially as temperature increases linearly.

Since the density of the adsorbate decreases with temperature more slowly than the density of pure liquid,<sup>9</sup> for the adsorbate-adsorbent binary system the densities (concentrations) of adsorbate and adsorbent (at  $T > T_{cr}$ ) become equal at higher temperatures.

Thus, the analysis of the experimental data on the adsorption of Ar, Kr, Xe, CH<sub>4</sub>, and CF<sub>3</sub>Cl on NaX zeolite and of CH<sub>4</sub> on PAU-10 carbon obtained for a wide range of parameters ( $p$ ,  $T$ , and  $c$ ) shows that it is possible to extrapolate, with satisfactory accuracy, the linear  $\ln p_{i,st}(T)$  and  $\ln \bar{c}_{i,st}(T)$  dependences in the subcritical temperature range up to  $T^* \cong T_{cr} + 100 \div 150$ . It is also possible to extend the main equation of the micropore bulk filling theory<sup>10</sup> as well as the *a priori*

**Table 2.** Thermal adsorption coefficient

Adsorbate	Adsorbent	$T_b$ /K	$T_{cr}$ /K	$T^*$ /K	$-\alpha \cdot 10^3$ /K <sup>-1</sup>	$-\alpha_{calc} \cdot 10^3$ /K <sup>-1</sup>
Ar	NaX	87.3	150.8	250	1.60	1.43
Kr	NaX	115.8	209.4	310	1.83	1.50
Xe	NaX	165.0	289.7	390	1.33	1.22
CF <sub>3</sub> Cl	NaX	191.7	302.0	435	1.41	1.43
CH <sub>4</sub>	NaX	111.7	190.6	350	1.88	1.52
CH <sub>4</sub>	PAU-10	111.7	190.6	300	1.64	1.52

methods of calculation of adsorption equilibria of individual and binary fluids developed in previous works to this temperature range.<sup>1,11</sup>

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