ADSORPTION OF NOBLE GASES ON THE CARBON ADSORBENTS SUPERSORBON HS AND JADO

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Received September 30th, 1981

The isotherms, isosters and heats of adsorption of argon, krypton and xenon were measured on the active carbon Supersorbon HS and the carbon adsorbent Jado LD 1191 — in a temperature range 298 —473 K, using gas chromatography. Differences were observed in the adsorption behaviour of both types of adsorbents — which showed especially on the nonlinearity of adsorption isosters of all gases studied with the Jado LD 1191 adsorbent. It was found that both types of adsorbents possess good adsorption properties, which can be — for Supersorbon HS — utilized in the beds of the delaying lines of radioactive noble gases. The practical application of the Jado LD 1191 adsorbent for the same purposes is limited by the presence of inactive teflon support in the structure of this adsorbent.

The concentration of the radioactive isotopes of noble gases in the nuclear power plants effluents is, at present, most usually decreased by means of the methods based on dynamic adsorption of argon, krypton and xenon in the beds of delaying line units. The dominant position among the adsorbents has active carbon[1-4]. In our previous papers[5-7], a possibility was indicated of using the active carbon of Czechoslovak production for the separation of radioactive noble gases from the contamined effluents of nuclear power plants.

In these papers, the adsorption of krypton and xenon was evaluated by means of the dynamic adsorption coefficient — commonly applied in practice. Since the dynamic adsorption coefficient does not always provide a satisfactory criterion for proper selection of the adsorbent for the delaying line bed — in the present paper, the results are presented of a study of some other adsorption parameters describing the above mentioned adsorption systems, such as the adsorption isotherms, isosters and heats of adsorption. The gas chromatographic technique has been used because it enables not only to determine the characteristics of the adsorption process given above but it allows also to simulate the operation conditions of the delaying line beds.

EXPERIMENTAL

The adsorption of the noble gases was studied on two types of Czechoslovak adsorbents: commercial active carbon Supersorbon HS (grain size fraction 0·2—0·4 mm) and the carbon adsorbent Jado — the preparation and properties of which were described in papers[8,9]. For our study

we have chosen the LD 1191 sample of Jado, formed by teflon particles 0·3 mm in size, with their surface covered into the depth of 0·6 μm by the carbon adsorbent (6·2% wt.).

The gases used in the measurements — argon, krypton and xenon (Reinstgase, Technische Gase Leipzig, Betrieb Berlin) — were of spectral grade purity. Electrolytic hydrogen was used as carrier gas.

The study of the noble gas adsorption on the above mentioned adsorbents was based on evaluation of the chromatographic elution curves obtained by CHROM-4 gas chromatograph with thermal conductivity detector. The apparatus was equipped with a dosing system which permitted to introduce the gas samples quantitatively within a volume range $2 . 10^{-3}$—$1·5 . 10^{-1}$ ml (STP) — with an error less than 0·5%. The experimental system possessed also a facility for digital recording of the detector output. The adsorption beds were formed by chromatographic columns of 3 mm i.d., packed and activated by the standard procedure. The corresponding physical parameters are given in Table I. The elution curves — for each gas and adsorbent — were measured at the following temperatures: 298·15, 323·15, 373·15, 423·15 and 473·15 K. The linear flow rates of the carrier gas varied within 5—30 cm s^{-1} — dependent of the gas, the temperature and the bed parameters.

The isotherms, the isosters and the heats of adsorption were obtained from the chromatographic curves in a usual way — based on analysis of the descending parts of the curves[10]. In order to account for the effects which were not directly related with the adsorbent/adsorbate interaction, the descending part of the helium elution curve (obtained under comparable conditions) was subtracted from each analyzed curve.

Numerical calculations of all the above mentioned parameters were carried out on a Wang 2 200 calculator, using the programme described in paper[11].

RESULTS AND DISCUSSION

The adsorption isotherms of argon, krypton and xenon were measured (for the given adsorbent and temperature) in the noble gas partial pressure range 20—2 000 Pa —

TABLE I

Physical parameters of the adsorption beds

Adsorbent	Length of bed m	Weight of adsorbent g	External[a] porosity	Internal[b] porosity	Volume of pores ml g^{-1}
Supersorbon HS	1·194	4·175	0·407	0·307	0·62
Supersorbon HS	0·282	0·833	0·493	0·262	0·62
Jado LD 1191	2·442	1·206[c]	0·384	0·111	1·62

[a] The free volume between adsorbent grains in a unit bed volume; [b] the pore volume of adsorbent grains in a unit bed colume; [c] the weight of the carbon adsorption layer in a bed — related to total weight of the LD 1191 adsorbent 19·454 g.

which is comparable with the concentrations of the noble gas fission products in gaseous wastes of nuclear power plants. The experimental isotherms (*i.e.* the adsorbed amount a_i against partial pressure p_i) – which are shown for all the studied adsorption systems, both in tables and graphically elsewhere[12], were subjected to regression analysis. This analysis has indicated that the above parameters fit very well the Freundlich isotherm ($a_i = Ap_i^{1/n}$). The constants of this isotherm are presented in Tables II and III, including the standard deviations not exceeding the relative error in estimation of the adsorbed amount 5% at a 0·95 confidence level. From both tables it is evident that the numerical values of parameter $1/n$ are mostly close to one, which proves that the adsorption isotherms are within the investigated temperature and pressure ranges, practically linear. The adsorbed amounts – given in Tables II and III in the form of the Freundlich equation constants A – decrease in all the studied systems with the increasing temperature. For the given temperature, they increase in a sequence argon, krypton, xenon.

The comparison of both types of adsorbents – Supersorbon HS and Jado LD 1191 – shows better adsorption properties of Supersorbon HS at lower temperatures for krypton and xenon. With increasing temperature, the differences between the both adsorbents get smaller – the lighter the gas, the smaller are the differences.

TABLE II

Parameters of the Freundlich adsorption isotherm for argon, krypton and xenon, with Supersorbon HS. The upper values: parameters A (μmol g^{-1} Pa^{-1}), $1/n$; the lower values: their standard deviations

T, K	Ar		Kr		Xe	
	$A \cdot 10^5$	$1/n$	$A \cdot 10^5$	$1/n$	$A \cdot 10^5$	$1/n$
298·15	331·2	1·0009	2 532·2	0·9613	43 316	0·9166
	1·9	0·0019	2·7	0·00087	309	0·0026
323·15	228·3	0·9994	1 207·43	0·9708	16 267	0·9430
	3·7	0·00046	0·67	0·00022	97	0·0023
373·15	121·21	0·9993	414·78	0·9805	3 342	0·9557
	0·19	0·00053	0·53	0·0011	25	0·0025
423·15	74·63	0·9998	181·58	1·0021	11 45·5	0·9483
	0·16	0·00037	0·35	0·0017	3·7	0·0011
473·15	47·99	1·0007	116·86	0·9954	460·11	0·9776
	0·69	0·00066	0·12	0·00096	0·60	0·0009

TABLE III

Parameters of the Freundlich adsorption isotherm for argon, krypton and xenon, with Jado LD 1191. The upper values; parameters A (μmol g^{-1} Pa^{-1}), $1/n$; the lower values: their standard deviations

T, K	Ar		Kr		Xe	
	$A \cdot 10^5$	$1/n$	$A \cdot 10^5$	$1/n$	$A \cdot 10^5$	$1/n$
298·15	337·32	0·9999	1 124·7	0·9772	12 685	0·9416
	0·02	0·000027	2·5	0·00080	121	0·0041
323·15	262·60	1·0037	642·5	1·0071	6 216	0·9437
	0·55	0·0015	2·3	0·0025	4	0·0098
373·15	180·32	0·9998	284·7	1·0243	1 640·6	0·9647
	0·03	0·000014	1·6	0·0051	1·7	0·00056
423·15	153·00	1·0007	201·0	1·0155	606·1	0·9931
	0·23	0·0011	1·0	0·0047	1·8	0·0024
473·15	130·47	0·9997	134·23	1·0432	341·7	1·0127
	0·01	0·000024	0·97	0·0052	1·0	0·0029

TABLE IV

Adsorption heats of argon, krypton and xenon, for Supersorbon HS and Jado LD 1191. The upper values: heats of adsorption (kJ mol^{-1}), the lower values: their standard deviations

a_i μmol g^{-1}	Supersorbon HS			Jado LD 1191		
	Ar	Kr	Xe	Ar	Kr	Xe
0·225	12·86	20·27	31·60	6·26	12·08	24·22
	0·22	0·67	0·65	0·29	0·69	0·71
0·450	12·86	20·08	31·29	6·34	11·95	23·88
	0·22	0·64	0·65	0·30	0·61	0·72
0·900	12·85	19·89	31·02	6·42	11·83	23·53
	0·22	0·61	0·65	0·32	0·54	0·73
1·335	12·86	19·78	30·86	6·47	11·75	23·33
	0·20	0·60	0·65	0·34	0·50	0·74

The differences become negligible at about 473 K with xenon and at about 323 K with krypton. Above this temperature, the adsorption parameters of Jado LD 1191 for krypton are clearly better. The amounts of the adsorbed argon are for the whole temperature range higher with Jado LD 1191 than with Supersorbon HS.

The adsorption isosters of argon, krypton and xenon for Supersorbon HS and Jado LD 1191 (Fig. 1–6) were derived from the isotherms for the adsorbed amounts a_i = 0·225; 0·450; 0·900 and 1·335 μmol g^{-1}. The adsorption heats were then obtained in a usual way using the Clausius–Clapeyron equation. In the above figures it can be seen that the isosters of Supersorbon HS are within the investigated temperature range linear. The derived adsorption heats are presented in Table IV. In the case of the Jado LD 1191 adsorbent, the adsorption isosters exhibit a nonlinear course with all the studied gases, which indicates that the adsorption heats are dependent on the temperature. For this reason, two different approaches were chosen for calculation of the adsorption heats. In the first case, the "average" adsorption heats were evaluated considering the whole temperature range of the isosters. In the second case, the isosters were divided and treated separately, as can be seen in Figs 4–6. The adsorption heats were then calculated for two separate temperature

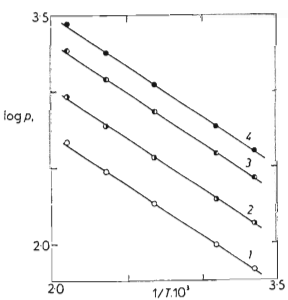

FIG. 1

Adsorption isosters of argon, with Supersorbon HS — for values a_i: *1* 0·225 μmol g^{-1}; *2* 0·450 μmol g^{-1}; *3* 0·900 μmol g^{-1}; *4* 1·335 μmol g^{-1}

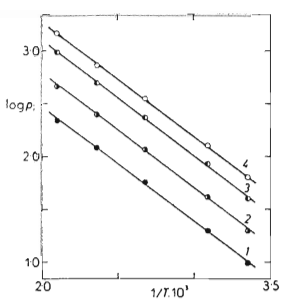

FIG. 2

Adsorption isosters of krypton, with Supersorbon HS — denotation of the isosters as in Fig. 1

regions (298·15–373·15 K; 373·15–473·15 K). The values of the "average" adsorption heats of argon, krypton and xenon for the Jado LD 1191 adsorbent are also given in Table IV.

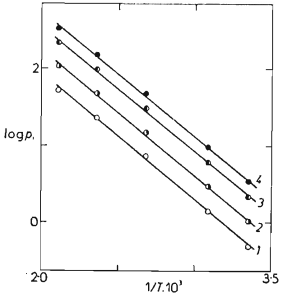

FIG. 3

Adsorption isosters of xenon, with Supersorbon HS — denotation of the isosters as in Fig. 1

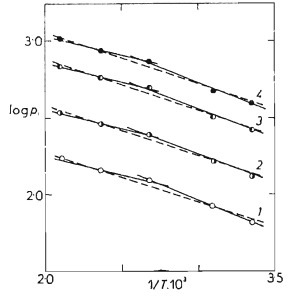

FIG. 4

Adsorption isosters of argon, with Jado 1191 — denotation of the isosters as in Fig. 1

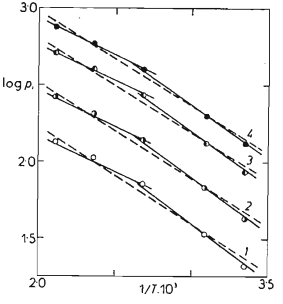

FIG. 5

Adsorption isosters of krypton, with Jado LD 1191 — denotation of the isosters as in Fig. 1

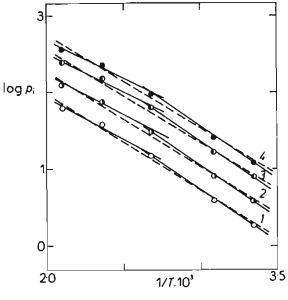

FIG. 6

Adsorption isosters of xenon, with Jado LD 1191 — denotation of the isosters as in Fig. 1

The adsorption heats determined for the individual temperature regions decrease with the increasing temperature. For the temperature range 298·15–373·15 K they are, for all the gases, by about 10% higher than the corresponding "average" adsorption heats. On the other hand, for the temperature range 373·15–473·15 K they are lower by about 20–25%. With both types of adsorbents, the dependence of adsorption heats on the adsorbed amount was found to be unsignificant.

The comparison of adsorption heats for both types of adsorbents shows that the adsorption heats on Supersorbon HS are substantially higher than the corresponding values for Jado LD 1191. The differences between both adsorbents decrease in the order: argon (100%), krypton (70%), xenon (30%). The adsorption heats determined on both adsorbents also indicate that the adsorption of the noble gases in the above mentioned cases has a physical character – without a more pronounced specific interaction with the surface of the adsorbents. One can therefore assume that the released adsorption heat will not considerably influence the temperature conditions of proper functioning of the delaying line adsorption beds.

The above presented results illustrate the differences in the adsorption behaviour of both types of adsorbents, resulting in the nonlinearity of the isosters and in better adsorption qualities of the Jado LD 1191 adsorbent with lighter gases – especially at higher temperatures. The results presented in this paper do not permit to explain unambiguously the case of the observed curving of the adsorption isosters. According to some sources describing this effect in literature – yet without deeper analysis[13–15] – it seems that the curving of the isosters is connected with uncomplete establishing of the adsorption equilibrium. Due to the internal structure of the Jado adsorbent[16], the noble gas probably diffuses at higher temperatures into the fundamental structural units. The kinetics of this process can consequently influence the equilibration rate of the adsorption process itself and in this way also the relevant adsorption parameters.

The exact explanation of the observed behaviour of the Jado LD 1191 adsorbent would require a more detailed study of the gas adsorption in this system – including thermodynamic measurements. Regardless to these facts, one can conclude that both types of adsorbents possess favourable properties for being potentially used in the beds of the delaying lines of radioactive noble gases. Unlike with Supersorbon HS, the presence of inactive support in bulk of the Jado LD 1191 adsorbent increases the demands on the total amount of the adsorbent (and thus also size of adsorption bed) required to achieve the requested decontamination efficiency of the bed. The range of practical utilization of the Jado LD 1191 adsorbent is therefore limited.

The authors would like to express their thanks to Dr J. Jansta and Dr F. P. Dousek, Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Prague, for providing the Jado LD 1191 sample and for information on its basic characteristics.

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Translated by Z. Dolejšek.