

# Microporous Adsorbent Sieve Effect on Thermodynamic Functions for State of Perturbation in Adsorbed Molecules

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**Abstract.** The correctness of the modified Polanyi–Dubinin potential theory application for the description of the thermodynamic state of polar molecules has been studied. It has been stated that the fundamental condition to obtain proper results is to include the influence of eventual molecular sieve effects. The values obtained for thermodynamic functions of perturbation determine the state of molecules only for those adsorbates for which the adsorption mechanism corresponds to the theory of volume filling of micropores.

**Key words:** Adsorption, carbon microporous adsorbent, sieve effect, thermodynamic functions.

## 1. Introduction

Many investigations [1–4] have shown the possibility of applying the modified Polanyi–Dubinin potential theory to the description of lower aliphatic alcohols and amines adsorbed on microporous carbon adsorbents. The basis for a development of the potential theory and its application for the description of polar substances adsorbed on microporous adsorbents was the statement that the state properties of the liquid phase of the adsorbate (modified liquid; state properties corresponding to the adsorbed layer) differ considerably from the state properties of the liquid phase of the adsorbative (the bulk liquid phase)[5–7].

The adsorption process can be considerably influenced not only by physical and chemical interactions but also by steric effects of differing types. For this reason, the values of thermodynamic functions of perturbation calculated after the modified Polanyi–Dubinin potential theory can be the result of differences between the state properties of the liquid phases of the adsorbate and the adsorbative. The values can depend also on steric effects accompanying adsorption of both the associating and standard substances.

The aim of this work is to determine the sieve effect influence on changes of the values of thermodynamic functions for the perturbation state of polar molecules adsorbed on microporous adsorbents.

## 2. Experimental

Adsorption measurements for spectrally pure benzene, argon, alcohols (methanol and ethanol), and for chemically pure aliphatic amines ( $\text{MeNH}_2$ ,  $\text{Me}_2\text{NH}$ ) have been carried out on carbon A prepared from chemically pure saccharose. The preparative method as well as

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the texture parameters have been given previously [8–10]. Adsorption isotherms have been determined within the temperature ranges 298.2–322.7 K for alcohols and 298.2–335.7 K for amines and benzene using the MacBain balance. The isotherm of argon adsorption has been measured with an isothermic–isobaric automatic apparatus at liquid nitrogen temperature. In the case of aliphatic amines, the adsorption occurs mainly irreversibly due to a chemisorption process [11]. Therefore, the adsorbent was presaturated with the amine studied (relative pressure of conditioning about 0.2 and temperature 298.2 K). After reaching the equilibrium

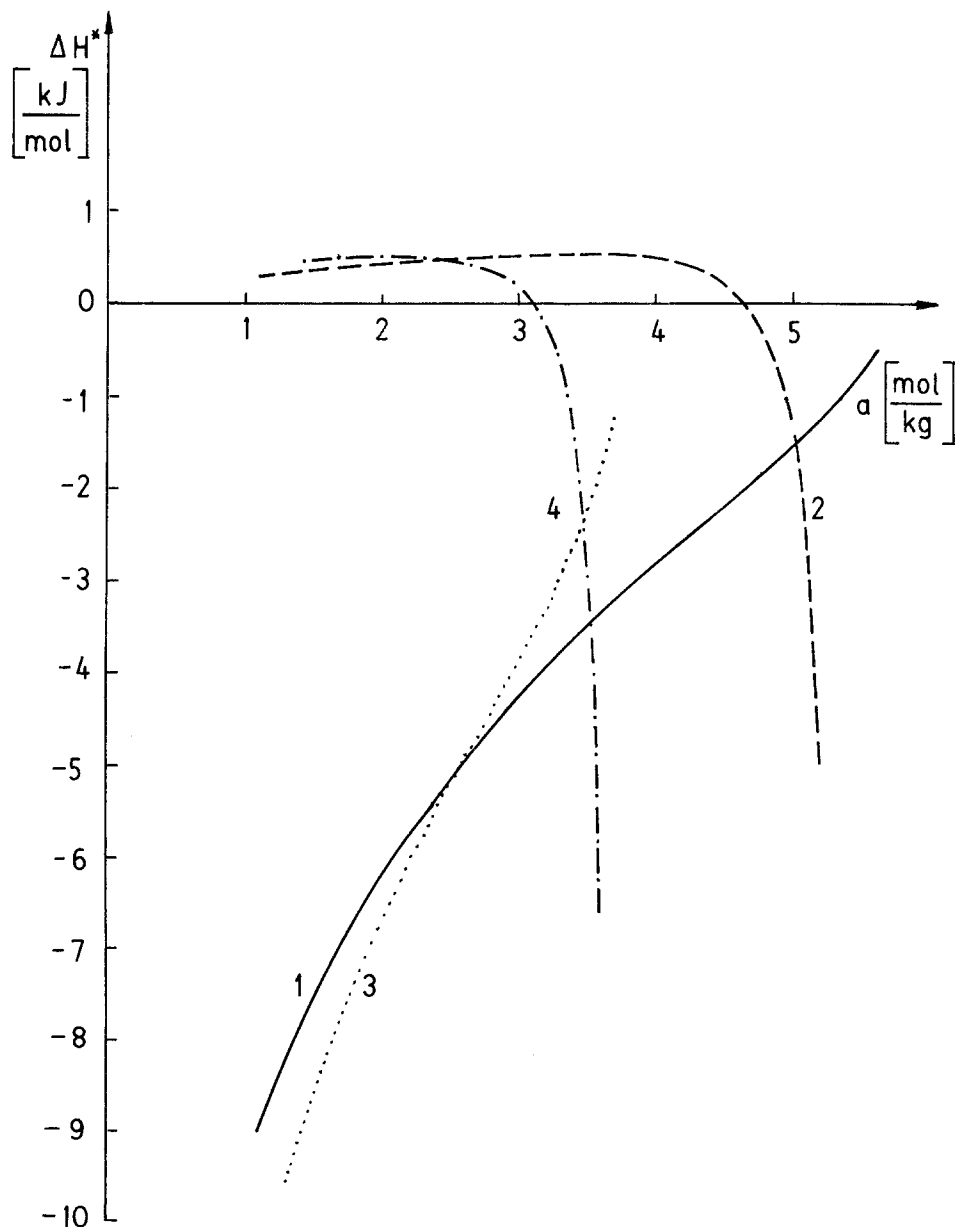


Fig. 1. Values of the differential molar enthalpy of perturbation for alcohols: 1 – for  $\text{CH}_3\text{OH}$  relative to argon; 2 – for  $\text{CH}_3\text{OH}$  relative to benzene; 3 – for  $\text{C}_2\text{H}_5\text{OH}$  relative to argon; 4 – for  $\text{C}_2\text{H}_5\text{OH}$  relative to benzene.

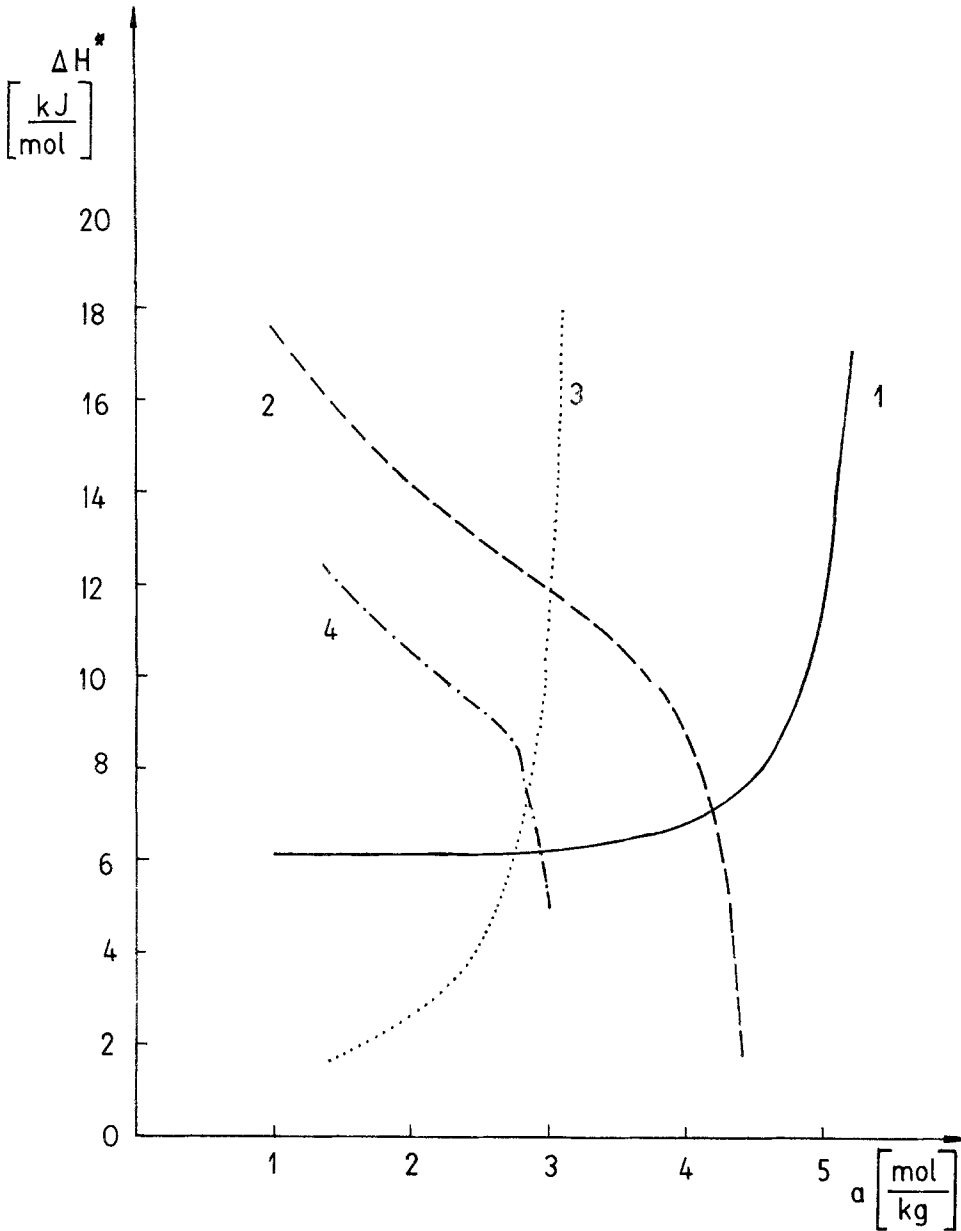


Fig. 2. Values of the differential molar enthalpy of perturbation for amines: 1 – for  $\text{MeNH}_2$  relative to argon; 2 – for  $\text{MeNH}_2$  relative to benzene; 3 – for  $\text{Me}_2\text{NH}$  relative to argon; 4 – for  $\text{Me}_2\text{NH}$  relative to benzene.

state, the sample was desorbed at a pressure of 1 mPa and a temperature of 335.7 K to constant mass. The experimental results (isotherms) for the examined adsorbates have been presented previously [1, 12, 13]. The application of the equations presented previously [3, 4] requires us to use a defined adsorption model because direct calculations of perturbation functions are impossible until now. The indirect comparative calculations are based on the second fundamental postulate of the affinity of the characteristic curves [14]

$$\left(\frac{A}{A_0}\right)_w = \beta \quad (1)$$

where  $A$  and  $A_0$  are the differential molar work of adsorption for the substance under examination and a standard, respectively; and  $\beta$  is the affinity coefficient. The standard used most frequently was benzene.

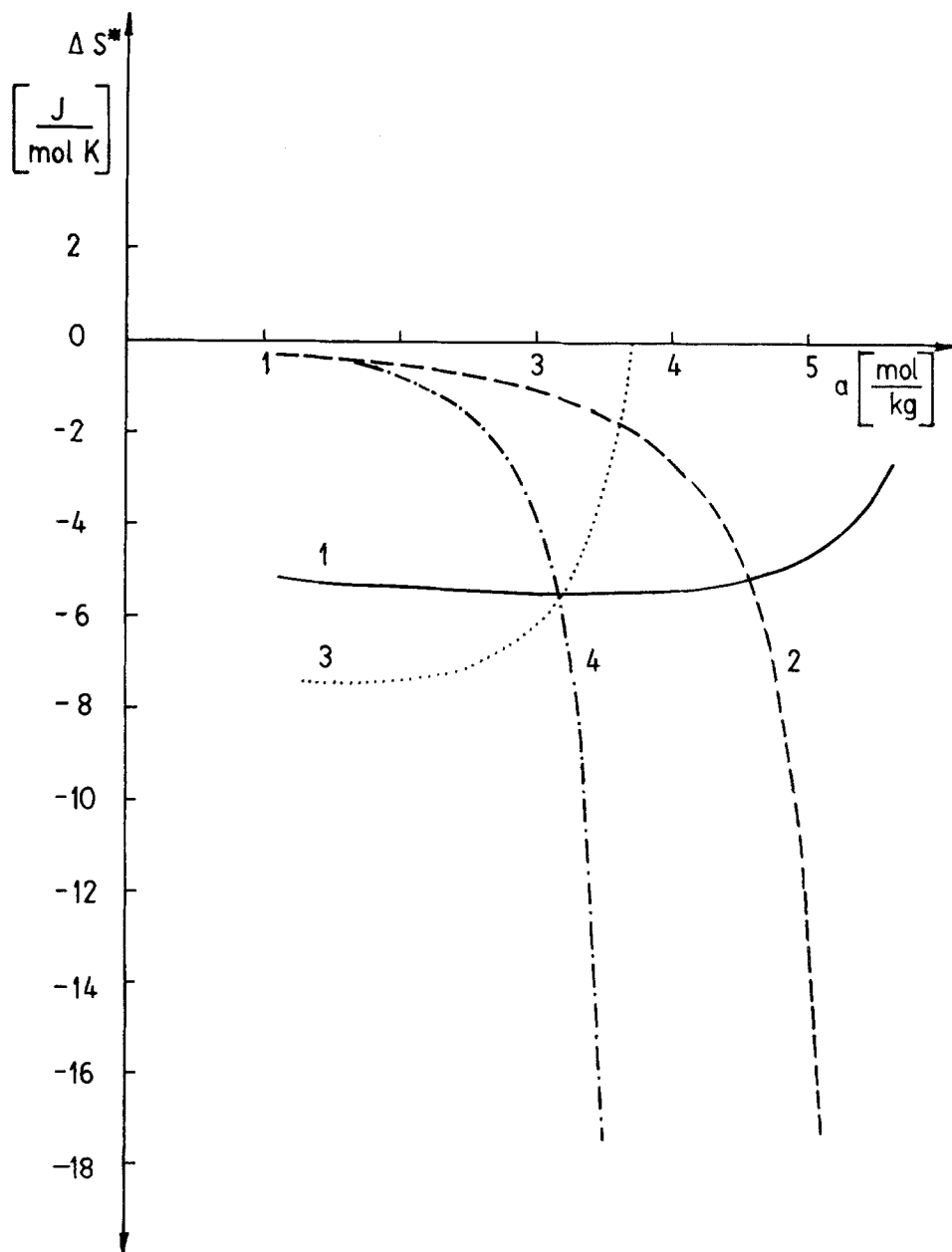


Fig. 3. Values of the differential molar entropy of perturbation for alcohols: 1 – for  $\text{CH}_3\text{OH}$  relative to argon; 2 – for  $\text{CH}_3\text{OH}$  relative to benzene; 3 – for  $\text{C}_2\text{H}_5\text{OH}$  relative to argon; 4 – for  $\text{C}_2\text{H}_5\text{OH}$  relative to benzene.

The values of fundamental thermodynamic functions of adsorption for the polar substances examined in relation to the bulk liquid phase ( $\Delta Y$ ) have been obtained directly from the adsorption data, whereas those in relation to the liquid phase of the adsorbate ( $\Delta Y'$ ) have been obtained from the experimental data for benzene using Eq. (1) [3,4].

The calculated values of the fundamental thermodynamic functions of perturbation  $\Delta Y^*$  as well as the activity coefficient  $\gamma$  [3] are presented in Figures 1-6 (curves 2 and 4).

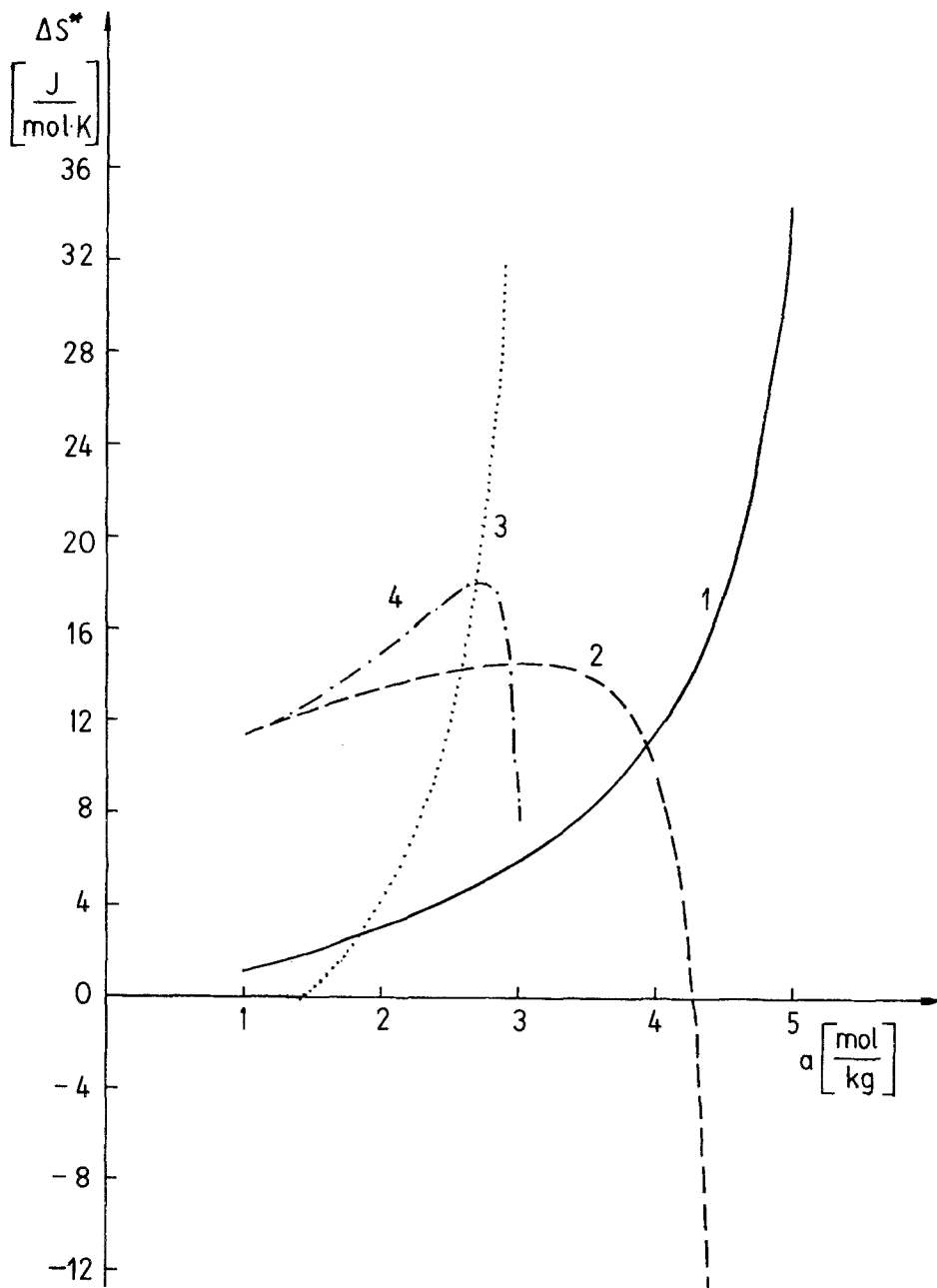


Fig. 4. Values of the differential molar entropy of perturbation for amines: 1 - for  $\text{MeNH}_2$  relative to argon; 2 - for  $\text{MeNH}_2$  relative to benzene; 3 - for  $\text{Me}_2\text{NH}$  relative to argon; 4 - for  $\text{Me}_2\text{NH}$  relative to benzene.

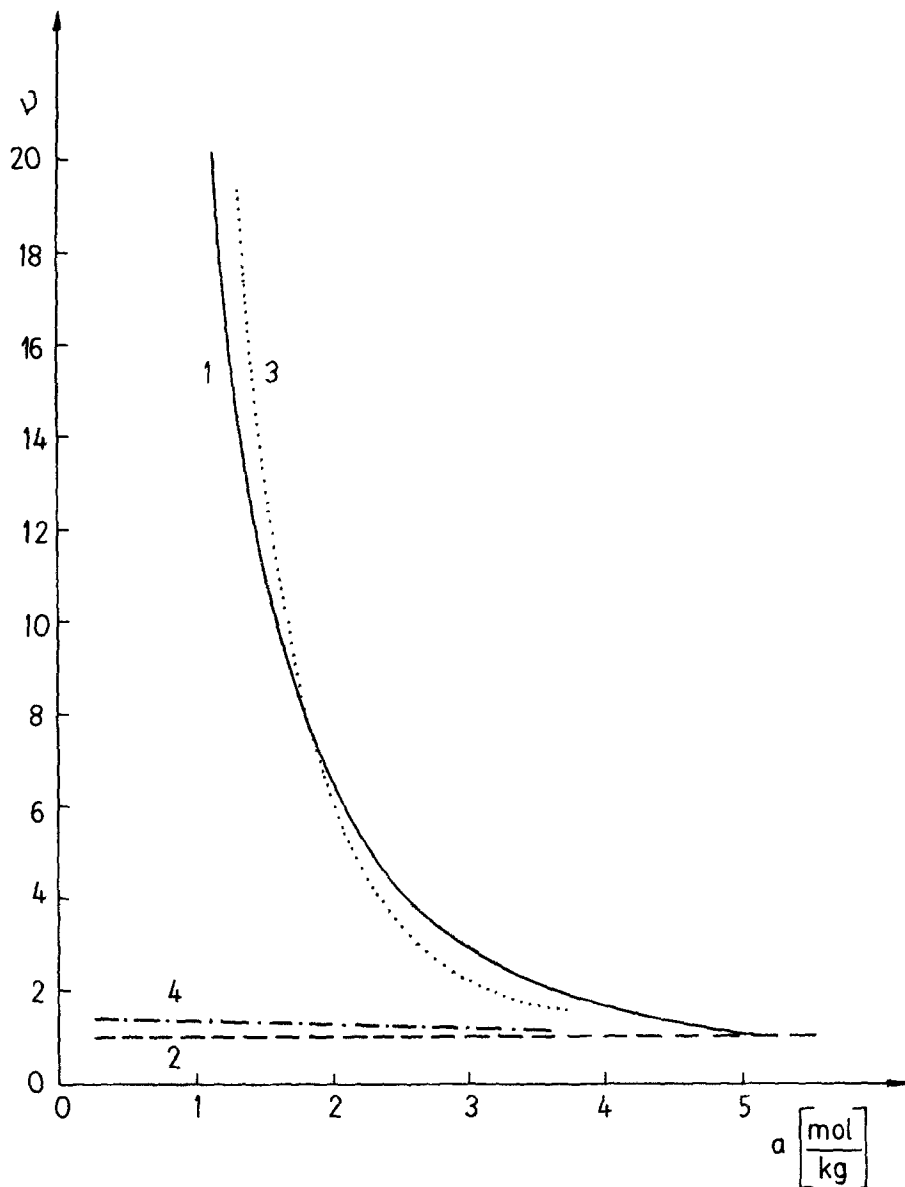


Fig. 5. Values of the activity coefficient  $\gamma$  for alcohols: 1 - for  $\text{CH}_3\text{OH}$  relative to argon; 2 - for  $\text{CH}_3\text{OH}$  relative to benzene; 3 - for  $\text{C}_2\text{H}_5\text{OH}$  relative to argon; 4 - for  $\text{C}_2\text{H}_5\text{OH}$  relative to benzene.

### 3. Results and Discussion

The values of the thermodynamic functions of perturbation characterize differences between the state properties of a real adsorbate (assumed in the modified potential theory) and of the model form of the bulk liquid phase (assumed in the Polanyi–Dubinin potential theory [14]). Simultaneously, the values of these functions provide information about the association of polar substances occurring in the adsorption force field. This is correct when adsorption of both the studied and standard substances follows the mechanism in the theory of volume

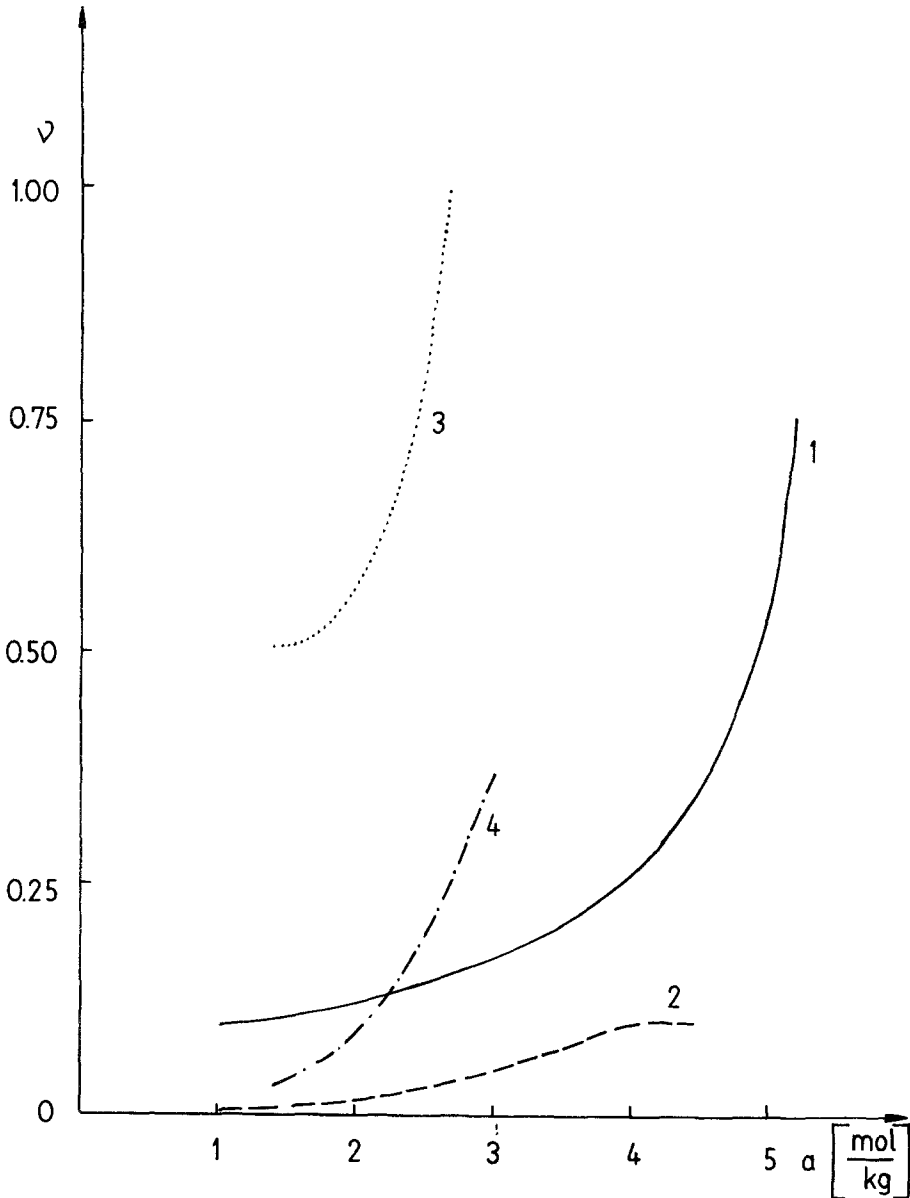


Fig. 6. Values of the activity coefficient  $\gamma$  for amines: 1 – for  $\text{MeNH}_2$  relative to argon; 2 – for  $\text{MeNH}_2$  relative to benzene; 3 – for  $\text{Me}_2\text{NH}$  relative to argon; 4 – for  $\text{Me}_2\text{NH}$  relative to benzene.

filling of micropores proposed by Dubinin and coworkers [15,16]. Thus, for adsorption of alcohols on active carbons the values of the perturbation enthalpy  $\Delta H^*$  and perturbation entropy  $\Delta S^*$  obtained for the first stage of the adsorption process have been considerably higher than expected as a result of strong vertical adsorbate–adsorbent [17] interaction. Besides the specific interactions, different steric effects can also considerably influence the adsorption process. The carbon A used in this work is characterized by the finest micropores having sizes close to those of the molecules studied. For this carbon, a molecular-sieve effect

has been observed for benzene while it has not been present for argon. Generally, we see that:

$$\Delta Y^* = \Delta Y_{s.p.}^* + \Delta Y_{s.ef.}^* \quad (2)$$

$$\gamma = \gamma_{s.p.} \cdot \gamma_{s.ef.} \quad (3)$$

where:  $\Delta Y_{s.p.}^*$  and  $\gamma_{s.p.}$  are expressions connected with differences in state properties;  $\Delta Y_{s.ef.}^*$  and  $\gamma_{s.ef.}$  are expressions resulting from steric effects.

For this reason, the calculated values of the thermodynamic functions of perturbation and the activity coefficient (Figures 1–6, curves 2 and 4) are the result of both the differences between the state properties of adsorbate and adsorbant and the steric effects of the standard substance (benzene) adsorption. Figures 1–6 (curves 1 and 3) present new values of the activity coefficients  $\gamma$  and the thermodynamic functions of perturbation calculated in relation to argon as the standard substance. Generally it can be stated that a molecular-sieve effect causes a decrease of the values of the activity coefficients  $\gamma$ . In such systems, one clearly observes an overstating of the values of the perturbation enthalpy  $\Delta H^*$  and of the perturbation entropy  $\Delta S^*$  for low and average degrees of adsorption volume filling. When one includes the influence of the molecular-sieve effect (Figures 1–6, curves 1 and 3), the direction of changes in the fundamental thermodynamic functions of perturbation and in the activity coefficients becomes analogous to that for systems studied earlier [1, 3]. This conclusion refers only to alcohols (Figures 1–3) which have a degree of association which is lower in the adsorbed state and approaching that of the liquid phase of the adsorptive ( $\gamma = 1$ ) with filling of the adsorption space of the micropores. Similarly, the negative values of the thermodynamic functions of perturbation for the alcohols studied approximate progressively to the values characteristic for the liquid phase of the adsorptive ( $\Delta S^* = 0$ ;  $\Delta H^* = 0$ ).

Values which are quite different from those which might be expected have been observed for amines (Figures 4–6) where the thermodynamic functions of perturbation increase with the filling of the adsorption volume of active carbon. Only the changes in the value of the activity coefficient follow expectations. This proves that adsorption of aliphatic amines on the active carbon studied does not follow the Polanyi–Dubinin potential theory. In this case, the dimensions of the micropores are comparable to those of the adsorbed amine molecules and the direction of changes in the determined values of the thermodynamic functions of perturbation can only be a proof of the activated character of the adsorption process studied [18].

The above discussion leads to the following conclusions:

- Thermodynamic functions of perturbation determine the real state of molecules in the field of adsorption forces for polar adsorbates only when their adsorption mechanism follows the theory of volume filling of micropores.
- The fundamental condition for correct application of the modified Polanyi–Dubinin potential theory is the exclusion of any influence due to molecular-sieve effects.
- The occurrence of molecular-sieve effects for standard substances causes a decrease of the measured activity coefficients  $\gamma$  and an increase of the enthalpy  $\Delta H^*$  and entropy  $\Delta S^*$  of perturbation within the adsorption ranges where the assumptions of the Polanyi–Dubinin potential theory for the standard substance (argon) are satisfied.

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