ADSORPTION EQUILIBRIA OF DIMETHYLFORMAMIDE–WATER VAPOUR MIXTURES OVER ACTIVE CHARCOAL

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Adsorption equilibria of dimethylformamide–water vapour mixtures were studied over active charcoal and the experimental results were compared with calculations of the adsorption equilibria using the Myers–Prausnitz and the Grant–Manes theory. Both theories assume that the adsorbed phase behaves as an ideal solution; as the assumption was not satisfied in the studied system, certain differences were found between the experimental data and the calculated values. Applications of the two theories of mixed-gas adsorption revealed that in the systems in which individual adsorption of all components of the adsorbate is described by the potential theory, the Grant–Manes theory is a special case of the more general Myers–Prausnitz theory.

One of the main problems in theories of mixed-gas adsorption is calculation of adsorption equilibria of mixtures from known adsorption equilibria of pure components. In applying various adsorption theories to the adsorption equilibria of pure substances over microporous adsorbents — among others over active charcoal — the potential theory of adsorption has proved itself to be very suitable. Several papers were published[1-3] in which this adsorption theory was extended to systems with several adsorbing components. However, treatments suggested in these papers cannot be applied to those cases where active charcoal is the adsorbent and water is one of the components of the adsorbate. This is because the potential theory of adsorption fails even for the very system water–active charcoal; there is no theory that would describe with a sufficient accuracy the adsorption equilibria of water vapours over active charcoal. The system studied by us, *i.e.* dimethylformamide–water–active charcoal, belongs to those systems in which water is a component of the adsorbate, too. So far there have been suggested only two theories that can be used to calculate adsorption equilibria in this system: that one of Myers and Prausnitz[4] and that one of Grant and Manes[5]. Both of them assume ideal behaviour of the mixture of adsorbed vapours; this assumption makes it possible — under certain conditions — to calculate adsorption equilibria of mixtures without any additional considerations concerning the nature of the adsorption process.

THEORETICAL

Myers and Prausnitz used classical Gibbs thermodynamics; for those systems to which the Gibbs adsorption thermodynamics may be applied they determined a basic condition which must be fulfilled in order to approximate the behaviour of the adsorbed phase by ideal behaviour. For the adsorption of n-component mixtures at a constant temperature, the following equation was derived by Gibbs:

$$-A \, d\pi + \sum_i N_i \, d\mu_i = 0 \, . \quad (T = \text{const}) \tag{1}$$

Here, A is the surface area of the adsorbent, π the spreading pressure, N_i and μ_i the mol number and the chemical potential of the i-th adsorbed component. At a constant temperature and a constant spreading pressure, (1) simplifies to

$$\sum_i N_i \, d\mu_i = 0 \, , \quad (T, \pi = \text{const}) \tag{2}$$

which is formally the same as the Gibbs–Duhem equation for three-dimensional fluids. In the systems for which the Gibbs adsorption thermodynamics holds, adsorbed solutions are thermodynamically analogous to three-dimensional solutions along the lines defined by

$$\pi = \text{const} \, . \tag{3}$$

Assuming ideal behaviour of adsorbed solutions,

$$f_i = x_i f_i^0(\pi) \, , \quad (T = \text{const}) \, , \tag{4}$$

where f_i is the equilibrium fugacity of the gaseous component over the adsorbent, and x_i its mole fraction in the adsorbed phase. With regard to (3), $f_i^0(\pi)$ is defined as the fugacity of the i-th component exhibiting at a given temperature T a spreading pressure π_i^0 which is the same as the spreading pressure π of the adsorbed solution. (The index ^{0} denotes here and further on the quantities related to the individual adsorption). At sufficiently low equilibrium pressures fugacity may be replaced by pressure and (4) can be written as

$$p_i = y_i p_\Sigma = x_i p_i^0(\pi) \, , \quad (T = \text{const}) \, , \tag{5}$$

where p_i is the partial pressure of the i-th component, y_i is its mole fraction in the gaseous phase, p_Σ is the total pressure; $p_i^0(\pi)$ is the equilibrium pressure of the pure i-th component at a given T and π. The dependence of the spreading pressure π_i^0 upon the equilibrium pressure p_i^0 can be calculated with the use of the individual isotherms, most accurately if the Kidnay–Myers formula[6] is used:

$$\pi_i^0 = \frac{RT}{A} \int_0^{N_i^0} \left(\frac{d \log p_i^0}{d \log N_i^0} \right) dN_i^0 \, ; \tag{6}$$

N_i^0 is the adsorbed amount of the pure i-th component. By means of equation (6) the dependence of the spreading pressure on the extent of adsorption is obtained; as the adsorption isotherm yields the relation between the extent of adsorption and the equilibrium pressure, one can easily obtain the dependence of the equilibrium pressure on the spreading pressure. If this dependence is plotted for all components of the adsorbed mixture, the values of all pressures $p_i^0(\pi)$ can be obtained, for a certain value of the spreading pressure; also, the partial pressures p_i of various components can be easily calculated for each composition of the gaseous phase characterized by the mole fractions x_i. Thus, for a given value of the spreading pressure one can obtain the dependence of the composition of the adsorbed phase on the composition of the equilibrium gaseous phase. This dependence can be obtained even for another condition than that one of a constant spreading pressure as mentioned above. Under no other condition, however, the dependence of the composition of the gaseous phase on the composition of the equilibrium gaseous phase

is expressed through the simple Raoult's law. In the following section details of the calcula ... will be given which assumes a constant total pressure of all adsorbing components.

In order to obtain a full description of the equilibrium behaviour of an adsorption system, the degree of adsorption of the particular components must be determined. To calculate the total adsorbed amount N_Σ, Myers and Prausnitz derived the following equation

$$1/N_\Sigma = \sum_i x_i/N_i^0 \tag{7}$$

in which the degree of adsorption N_i^0 of the pure components and their mole fractions x_i in the adsorbed solution are related to a given value of the surface pressure. The values of adsorption of each component are then given by

$$N_i = x_i N_\Sigma . \tag{8}$$

In these calculations the spreading pressure plays a role of an important parameter of the adsorption equilibrium; its physical meaning — not very obvious especially in the case of microporous adsorbents — has been recently discussed[7]. The authors showed that for adsorbents of this type the product $A\pi$ does have a physical meaning despite the fact that their surface area A cannot be determined from adsorption data, and the spreading pressure π cannot acquire the meaning it has in some particular models. The product $A\pi$ in the case of microporous adsorbents may be regarded as a thermodynamical parameter, as its value hangs directly together with the change of the chemical potential of the adsorbent during adsorption. For this reason, the Myers–Prausnitz theory of mixed-gas adsorption may be applied to systems containing a microporous adsorbent; however, in all calculations the spreading pressure π must be replaced by the product $A\pi$. Grant and Manes started in their treatment from the potential theory. However, they used it only in calculating the individual isotherms. The adsorption equilibria of mixtures were determined under the assumption that the adsorbed phase behaved like an ideal solution and Raoult's law was considered along the lines defined by

$$W = \text{const} ; \tag{9}$$

$(W$ is the volume of the adsorbed phase). Thus Grant and Manes agree with Myers and Prausnitz in assuming ideal behaviour of the adsorbed phase; they differ, however, in the condition of validity of Raoult's law: condition (9) is confirmed in their paper but empirically. Assuming the validity of Raoult's law along the lines of constant volume of the adsorbed phase, it is necessary to replace (4) by

$$f_i = x_i f_i^0(W) , \quad (T = \text{const}) , \tag{10}$$

in which f_i^0 is the fugacity of the pure i-th component occupying at a given temperature the same volume W_i^0 as the adsorbed solution. The dependence of the adsorbed phase composition on the equilibrium gas phase composition can be thus found using an analogous procedure as that one of Myers and Prausnitz. Instead of the spreading pressure, however, one has to consider the volume of the adsorbed phase which is — because of the ideal behaviour assumption — given by

$$W = N_\Sigma \sum_i x_i v_i , \tag{11}$$

where v_i is the molar volume of the adsorbed component. By combining (11) and (8) one gets then the following expression for the extent of adsorption of a particular component N_i

$$N_i = x_i W / \sum_i x_i v_i . \tag{12}$$

The two above described theories differ only in that the validity of Raoult's law is considered along different lines. It will be proved in the following that this difference vanishes, if the potential theory is valid for the individual adsorption of all components of the adsorbate. In the potential theory of adsorption of pure substances two basic postulates are formulated whose validity, however, has been confirmed so far only by extensive experimental data. These postulates operate with two variables which hang together directly with parameters of the adsorption equilibrium: the adsorption potential ε_i^0

$$\varepsilon_i^0 = RT \ln (p_{s,i}/p_i^0) \, , \tag{13}$$

$(p_{s,i}$ is the saturated vapour pressure of the i-th component at a given temperature and the index ^{0} at ε_i^0 indicates individual adsorption); the second variable is the volume of the adsorbed phase — mentioned earlier — which is given in the case of adsorption of a pure component by

$$W_i^0 = N_i^0 v_i \, . \tag{14}$$

Both these postulates can then be formulated together in the following way: if any equilibrium dependence of the extent of adsorption on pressure and temperature, as obtained by studying individual adsorptions of various substances over the same adsorbent, is transformed into the $\varepsilon_i^0/\beta_i - W_i^0$ coordinates, the resulting "characteristic curve" is temperature independent. The shape of this curve is determined unambiguously by the adsorbent; the influence of the adsorbate on the extent of adsorption is described by the affinity coefficient β_i the value of which is a constant for each substance. The affinity coefficient may be approximated by the ratio of the molar volume of a given adsorbate v_i to that one of the standard adsorbate v_s:

$$\beta_i = v_i/v_s \, . \tag{15}$$

Usually, benzene is used as the standard adsorbate. It can be shown that the Grant–Manes theory is in fact a special case of the more general Myers–Prausnitz theory: it must hold for the marginal points of the lines determined by (3)

$$\pi_i^0 = \pi_j^0 \, . \tag{16}$$

The spreading pressures π_i^0 and π_j^0 of two arbitrary components of the adsorbing mixture can be expressed by means of (6). This results in

$$(RT/A) \int_0^{N_i^0} (\mathrm{d} \log p_i^0/\mathrm{d} \log N_i^0) \, \mathrm{d} N_i^0 = (RT/A) \int_0^{N_j^0} (\mathrm{d} \log p_j^0/\mathrm{d} \log N_j^0) \, \mathrm{d} N_j^0 \, . \tag{17}$$

Using (13) and (14) this equation can be rewritten by means of the variables ε_i^0, W_i^0, ε_j^0, W_j^0. The resulting equation is then multiplied by v_s, and this results in (upon taking into consideration (15))

$$\frac{1}{A} \int_0^{W_i^0} \frac{\mathrm{d}(\varepsilon_i^0/\beta_i)}{\mathrm{d} \log W_i^0} \, \mathrm{d} W_i^0 = \frac{1}{A} \int_0^{W_j^0} \frac{\mathrm{d}(\varepsilon_j^0/\beta_j)}{\mathrm{d} \log W_j^0} \, \mathrm{d} W_j^0 \, . \tag{18}$$

Assuming the validity of the potential theory for all components of the adsorbate, and assuming that the adsorbent surface area A is the same, equation (18) can hold only if

$$W_i^0 = W_j^0 \, , \tag{19}$$

as the derivatives of the characteristic curve under the integral sign are the same. The integration limits N_i^0 and N_j^0 in (17) are related to certain pressures p_i^0 and p_j^0; the same pressures must correspond, of course, to the integration limits W_i^0 and W_j^0 in equation (18). In view of the fact that Raoult's law represents a linear dependence of the partial pressure p_i of the i-th component on its mole fraction x_i, the lines given by equations (3) and (9) are identical. The validity of Raoult's law along the lines of constant volume of the adsorbed phase thus follows from the validity of this law along the lines of constant spreading pressure and from the validity of the potential theory for all components of the adsorbate.

Equations (7) and (12) used in calculations of the extent of adsorption of the particular components are equivalent, though they were derived in both theories of mixed adsorption by different procedures. The ratio W/N_i^0 can be substituted into (12) for the molar volume v_i and a simple rearrangement leads then to equation (7).

Grant and Manes showed that if the potential theory holds for the individual adsorption of all components, the assumption of validity of Raoult's law along the lines of constant volume of the adsorbed phase makes it possible to easily find simple relations for calculation of adsorption equilibria of mixtures. Only a minimum number of experimental data is required for this calculation, in the limiting case just the adsorption isotherm of one component. However, if experimental data on the individual adsorption of all components can be obtained (by measuring the adsorption isotherms of pure components at given temperatures and over the required pressure range), it is evident that the calculation of adsorption equilibria of mixtures can be done — using the above mentioned assumption — in an analogous way as in the Myers–Prausnitz theory, *i.e.* without using the potential theory. The Grant–Manes theory which, of course, acquires in this form an empirical character may be thus applied even to the system dimethylformamide–water–active charcoal as investigated in this study.

EXPERIMENTAL

Investigation of adsorption of the dimethylformamide–water vapour mixture was carried out over the industrial active charcoal Supersorbon HS-4 (Moravské chemické závody, Ostrava-Hrušov). This charcoal was produced by activating sawdust by zinc chloride at 650°C. Besides the adsorption of mixtures also the individual adsorption isotherms of dimethylformamide and water were measured over this active charcoal. Adsorption isotherms of vapours of these substances were obtained by the gravimetric method using quartz ballances of 5 mg/mm sensitivity. Extension of spirals and pressure on a U-shaped mercury manometer were measured by means of a cathetometer with a 0·01 mm accuracy. Vapour pressures of the adsorbate lower than 1 Torr were measured by means of a McLeod manometer. A detailed description of this vacuum adsorption arrangement was given elsewhere[8].

Measurement of the equilibrium values of mixed adsorption of dimethylformamide–water vapour was carried out in an apparatus in which a stream of carrier gas containing the vapours of both components passed through a stationary layer of the adsorbent. After an equilibrium was reached, the vapours trapped in the active charcoal sample were desorbed and their amount and composition was measured.

The schematics of the apparatus used is shown in Fig. 1. The carrier gas (nitrogen) of 2—3 atm pressure was divided into two streams and passed through the regulation valves 1 and 1′; these valves reduced its pressure and kept its flow rate constant. In order to remove traces of water vapour from it, the carrier gas passed through the column 2 (silica gel filling) and through the liquid nitrogen cooled traps 3 and 3′. Further parts of the apparatus through which the carried gas was led were located in the air-thermostat 13. One stream of nitrogen flowed through the valve 5 into the adsorption bed or, alternately, out of the apparatus. The second stream of nitrogen

carrier gas flowed through the coil 4 in which it was warmed up to the temperature of the thermostat and then passed through the U-shaped tube 6 in which it was saturated by vapours of both adsorbates. The valve 5 followed next: from it the saturated carrier gas either passed through the adsorption bed or, alternately, out of the apparatus. Two traps, 10 and 11, were connected with the tube 8 containing the adsorbent; they were used to trap the adsorbed vapours. The trap 10 was connected with a glass ampule which could be sealed off at the dashed line. The adsorbent 8 and the traps 10 and 11 could be evacuated; auxiliary active charcoal located in the bulb 12 and cooled by liquid nitrogen was used to evacuate the apparatus to high vacuum. The flow rate of the carrier gas was measured by means of a bubble flow meter connected with the apparatus.

Solution of dimethylformamide in water was introduced into the saturator 6 from the reservoir 9 constructed from two wide horizontal tubes. The reservoir was only half-filled in order to keep the solution level approximately constant during the measurements (the surface area of the solutions was rather large and their consumption rather small). Absorbed gases were released from this solution during the warming up of the thermostat and the trap 7 was used to collect them.
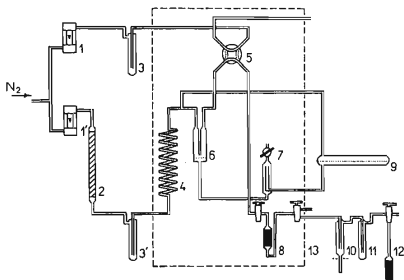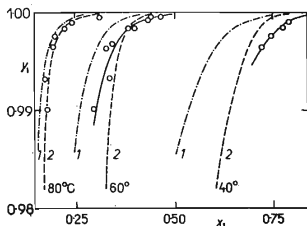

Fig. 1

The Apparatus Used in Measuring the Dimethylformamide–Water Mixed-Gas Adsorption over Active Charcoal

Fig. 2

Dependence of the Adsorbed Phase Composition (x) on the Equilibrium Gas-Phase Composition (y)

Dashed lines: Calculations using the Myers–Prausnitz (1) and the Grant–Manes (2) theory; x and y are mole fractions of water.

As the introduced solution entirely evaporated in the saturator, no enrichment of the carrier gas by the more volatile component (water) occurred and the mol fractions of dimethylformamide in the storage solution and in the vapour were the same. Active charcoal samples were weighted into the tube 8; in order to remove all adsorbed substances, they were evacuated up to 10^{-5} Torr at 350°C and then cooled down in the stream of nitrogen.

During the measurements of equilibrium adsorption values the carrier gas with vapours of both substances of the mixture was passing through the active charcoal sample until the adsorption equilibrium was established. This was indicated by an increase of the dimethylformamide vapour concentration in the carrier gas (after it passed through the adsorption bed) to the same value as that one in front of the adsorption bed. After the equilibrium was reached, desorption of both adsorbed substances was carried out: the traps 10 and 11 were first evacuated (the tube with the adsorbent was separated before that), and then the valve connecting the traps with the adsorbent was opened. The traps were cooled by liquid nitrogen and thus the dimethylformamide and water vapours condensed on their walls. After a short time the connection with the adsorbent was closed again, and the carrier gas was pumped away from the traps. Thus, the carrier gas was evacuated from the traps whose walls held trapped condensed vapours of dimethylformamide and water. The amount of these vapours pumped away together with the carrier gas was entirely negligible, as both dimethylformamide and water have practically zero vapour pressure at the liquid nitrogen temperature. The evacuation of the carrier gas from the traps was repeated several times; after removing almost all the carrier gas, when the rate of desorption of dimethylformamide and water from the active charcoal became sufficiently large, the temperature of the adsorbent was gradually increased up to 250°C. During several hours then all the adsorbed vapours de-
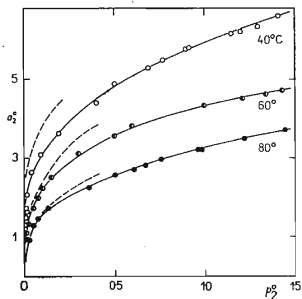

FIG. 3

Adsorption Isotherms of Dimethylformamide Vapour over Active Charcoal

Dashed lines: adsorption isotherms from mixtures with water vapour; a_2^0 (mmol/g) value of equilibrium adsorption; p_2^0 (Torr) equilibrium pressure.
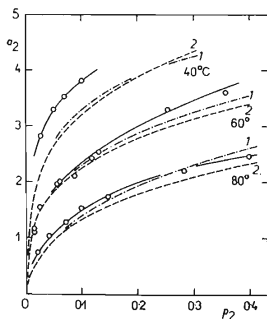
FIG. 4

Adsorption Isotherms of Dimethylformamide Vapour over Active Charcoal Obtained from Mixtures with Water Vapour

Dashed lines: calculations using the Myers–Prausnitz (1) and the Grant–Manes (2) theory; a_2 (mmol/g) value of equilibrium adsorption; p_2 (Torr) partial pressure.

sorbed and were collected in the traps. After the desorption was finished, the adsorbent was separated and only the ampule on the trap *10* was left immersed in liquid nitrogen. When all the desorbed substances were collected in it, the ampule was sealed off. The last operation was then the determination of the amount and composition of the desorbed vapours.

The analysis of the desorbed vapours (*i.e.* of aqueous solutions of dimethylformamide) was carried out by measuring their index of refraction using an immersion refractometer (Zeiss). The so called tempered prisms were used, and thus the amount of sample necessary to perform the analysis was but a few hundredths of cm^3. The prisms were tempered by a water ultrathermostat to $20° \pm 0.05°C$.

RESULTS

Measurements of the adsorption equilibria of dimethylformamide and water vapours were carried out at 40°, 60°, and 80°C. The total pressure of both components was kept constant at the particular temperature (29·5, 37·4, and 42·4 Torr at 40°, 60°, and 80°C, respectively). As the partial pressure of dimethylformamide vapours varied between 0·015 and 0·400 Torr, the changes in the partial pressure of water vapours were only small.

Figs 2, 3, 4, and Table I summarize the experimental results. The quantities that are related to the more volatile component of the adsorbate (water) are denoted by the index 1, those related to the less volatile component (dimethylformamide) by 2. The dependence of the composition of the adsorbed phase on the composition of the gaseous phase is shown in Fig. 2 as an *x–y* diagram. As can be seen, the dimethylformamide vapour adsorption from the mixture with water vapours is highly selective, *i.e.* a considerable enrichment of the adsorbed phase by dimethylformamide occurs. Fig. 2 shows the adsorption isotherms of pure dimethylformamide vapours, and Fig. 3 the adsorption isotherms of dimethylformamide vapours measured with water vapour present. The latter are also shown (as dashed lines without experimental points) Fig. 3; it is evident from this comparison that the dimethylformamide vapour adsorption from mixtures with water vapour is higher than the adsorption of the pure compound at the same equilibrium pressure. The experimental values of the water vapour adsorption were almost constant at the particular temperatures studied; they are shown in Table I together with the interval in which the dimethylformamide vapour adsorption was measured at each temperature.

TABLE I

Experimental and Calculated Values of Water Vapour Adsorption

Interval of calculated values N_1 (mmol/g) of water vapour adsorption corresponds to the experimental interval of N_2 (mmol/g) of dimethylformamide vapour adsorption.

°C	Experimental values		Calculated N_1	
	N_1	N_2	Grant–Manes	Myers–Prausnitz
40	10·18	2·81 – 3·82	7·10 – 7·91	5·15 – 5·29
60	1·26	1·09 – 3·59	0·89 – 1·83	0·80 – 1·28
80	0·41	0·77 – 2·46	0·24 – 0·53	0·26 – 0·48

The experimental data were compared with the results of the adsorption equilibria calculations carried out with the use of the Myers–Prausnitz and Grant–Manes theories. Both theories assume that Raoult's law is valid for adsorbed solutions along certain lines (constant π or W, respectively). The marginal points of these lines lie on the individual isotherms of dimethylformamide vapour and water vapour. If one calculates with the use of these isotherms the dependence of the volume W_1^0 and W_2^0, and of $A\pi_1^0$ and $A\pi_2^0$ on the equilibrium pressure p_1^0 and p_2^0, one can construct the dependence

$$p_1^0 = F(p_2^0) \quad (W_1^0 = \text{const}), \tag{20}$$

$$p_1^0 = G(p_2^0) \quad (A\pi_1^0 = \text{const}). \tag{21}$$

Equations (20) and (21) relate p_1^0 (water vapour pressure) to p_2^0 (dimethylformamide vapour pressure) in the marginal points of the lines defined by the condition of a constant volume W or a constant product $A\pi$. Further relations whose validity is obvious follow immediately

$$x_1 + x_2 = 1, \tag{22}$$

$$y_1 + y_2 = 1, \tag{23}$$

$$y_1 p_\Sigma = x_1 p_1^0, \tag{24}$$

$$y_2 p_\Sigma = x_2 p_2^0. \tag{25}$$

In this way a system of five equations ((20) or (21) and (22) through (25)) with seven variables is obtained. From those the total pressure p_Σ is determined by the experimental conditions, and another one (best of all y_1 or y_2) can be chosen. However, equations (20) and (21) are given in a graphical form only, and thus the entire problem must be solved graphically, too. For a given temperature a $x - y$ diagram can be thus obtained, i.e. the dependence of the composition of the adsorbed phase on the composition of the equilibrium vapour phase. The extent of adsorption of both components of the system under study is then calculated by means of equations (7) and (8) or (12).

The results of the calculations of the equilibrium values of mixed-gas adsorption of dimethylformamide–water vapours were compared with the experimental data. Fig. 2 shows the calculated $x - y$ diagrams, in Fig. 4 the adsorption isotherms of dimethylformamide vapour are shown; the calculated values of water vapour adsorption are then compared with the experimental data in Table I. Table I contains also the limiting values at which the calculated water vapour adsorption changed. These values are always related to the interval in which the dimethylformamide vapour adsorption was measured and which is given in Table I, too.

DISCUSSION

It is evident from comparison of the measured and calculated isotherms of dimethyl-formamide vapour in the studied system dimethylformamide–water–active charcoal that both theories of mixed-gas adsorption gave results which were close to, but still somewhat different with the experimental data. Largest deviations occur at 40°C and they decrease with increasing temperature. To a certain extent this holds for the comparison of the experimental and calculated values of water vapour adsorption, too However, as can be seen from Table I, the calculation with the use of the Grant–Manes. theory gave a better agreement with the experiment than that one using the Myers–Prausnitz theory. As a result, even the $x - y$ diagrams calculated by means of the Grant–Manes procedure are closer to the measured data.

Application of the Myers–Prausnitz theory to mixed-gas adsorption equilibria is justified from the thermodynamic point of view for systems to which the Gibbs adsorption thermodynamics may be applied. As mentioned in the theoretical part of this paper, this condition was satisfied for the system studied by us (see Bering, Myers, Serpinskij[7]). To thermodynamically justify the Grant–Manes theory, one must postulate – besides the validity of the Gibbs adsorption thermodynamics – also the validity of the potential theory for individual adsorption of all components of the adsorbate. In the system dimethylformamide–water–active charcoal, however, the potential theory does not describe the individual adsorption of one component (water) and, therefore, there is no coincidence of the lines defined by the condition of a constant spreading pressure and those defined by the condition of a constant volume of the adsorbed phase. Thus, the assumption of Grant and Manes about the validity of Raoult's law along the lines of constant volume of the adsorbed phase may be regarded as an empirical one only. With the use of it a slightly better agreement of the calculations with the experimental results was obtained; however, this is rather a result of a certain compensation of deviations from Raoult's law (non-ideal behaviour of the dimethylformamide–water surface solution) due to the shape of the lines along which Raoult's law was applied.

In both theories of mixed-gas adsorption employed in the reported calculations of adsorption equilibria the behaviour of the adsorbed solution is approximated by Raoult's law, though it is almost certain that this law described only approximately the behaviour of the dimethylformamide–water adsorbed solution. The three-dimensional solution of the two substances exhibits a substantial non-ideal behaviour; however, information on the behaviour of three-dimensional solutions cannot be simply extrapolated to adsorbed solutions. This is because the behaviour of adsorbed solutions is influenced considerably by the heterogeneity of the adsorbent surface and it is just this property which is a characteristics of the active charcoal surface.

The increase of the dimethylformamide vapour adsorption in the presence of water vapours indicates a strong interaction of the molecules of the two substances

in the adsorbed phase. One may thus assume that larger deviations from the ideal occur in the behaviour of the adsorbed dimethylformamide–water solution. This could then explain the differences between the calculations of adsorption equilibria and the direct measurements. In order to express the real behaviour of this solution one has to know the activity coefficients γ_i of both solutions

$$\gamma_i = p_i/x_i p_i^0(\pi) \,. \tag{26}$$

Myers and Prausnitz found that for various systems studied by them the activity coefficients of adsorbed solutions components were close to one. Although Grant and Manes did not determine values of the activity coefficients, it follows from the agreement between their theory and the measured adsorption equilibria that in their systems the activity coefficients were close to one, too. Myers and Prausnitz surmise that a possible explanation of this near-ideal behaviour of adsorbed solutions is that the corresponding three-dimensional solutions behave ideally.

However, according to Serpinskij[9] the ideal behaviour of adsorbed solutions is not a general phenomenon. In particular in those cases where the adsorbed components form rather nonideal three-dimensional solutions, the adsorbed solutions behave non-ideally, too. So far, however, no predictions concerning the values of the activity coefficients of the particular components of non-ideal adsorbed solutions can be made. Quoting the above mentioned author, only systematic studies of adsorbed solutions would make it possible to find rules that would allow to estimate values of the activity coefficients.

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