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HYGROSCOPICITY OF FERTILISER MATERIALS

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The tendency of water-soluble substances to absorb, under certain conditions, water from the surrounding atmosphere, is called hygroscopicity. This phenomenon is very undesirable in most cases, encountered in the technical practice, since it results in increasing the water content and thus in the moistening of hygroscopic materials, which may eventually dissolve completely in the absorbed water. Virtually all the commercially produced fertilisers possess certain hygroscopic properties, which affect negatively the manufacturing process as well as the stages of fertiliser storage, handling and shipping. It is generally known that the increase in the moisture content of a fertiliser results in a decrease in its market value primarily due to the fact, that a higher water content is enhancing the caking tendency and reducing both the free-flowability and mechanical strength of granulated products. Hygroscopicity of fertilisers is thus a cause of considerable losses of energy and of increased operating costs as it reduces the overall efficiency of the granulation and drying operations and complicates all the so-called post-manufacture operations as well, e.g. by making it necessary to handle only bagged products.

The problems associated with hygroscopicity of substances, representing the essential fertiliser materials, have been studied for several decades. As early as at the end of the last century KORTRIGHT /1/ defined the hygroscopic point as the equality of the atmospheric water vapour pressure and vapour tension over the saturated solution of a salt at a given temperature. The hygroscopic points of numerous substances, forming the basis of fertilisers and of their most common binary mixtures, have been determined by the isothermal

method and published /2,3,4,5,6, and others/. A generally valid conclusion, drawn from the measurements /2,3/ is that the value of the hygroscopic point of a mixture of two salts is almost invariably lower than that of either of the pure components. Considering the complexity of the given systems, it has been generally accepted that it would be more advantageous to determine the values of hygroscopic points experimentally than by calculating. From the practical viewpoint, it has been also necessary to assess the rate, at which certain states are coming near to the respective equilibrium states.

The so-called critical moisture content was determined on the basis of measuring the time-dependence of the increase in weight of the examined substance /7/. This method has been further improved and modified /e.g. 8,9,10,11/ but the obtained results are neither reproducible accurately nor can they be interpreted adequately. The reason for this is that these methods are not based on more exact theoretical definitions of the essential variables and, moreover, the results depend largely upon experimental conditions, which have not been standardized sufficiently. A number of authors have conducted a direct determination of equilibrium water vapour pressure over a fertilizer sample using various types of tensimeters /6,12,13,14, and others/. An analysis of the obtained results has shown that a very fundamental condition is not fulfilled when adopting either the tensimetric or kinetic methods of measuring: the value of critical relative moisture content is not a constant and it has been confirmed experimentally that in many cases this value varies widely with varying content of water in the fertilizer. A number of authors have, therefore, orientated their work towards assessing the shape of the so-called sorption isotherms - that is to determining of the dependence of equilibrium water vapour pressure over a solid fertilizer sample on its water content /e.g. 7,10, 11,12,15/. The hitherto published knowledge in the field of hygroscopicity of fertilizers may be summed up as follows: Numerous data and various dependences have been published, aiming at elucidating and describing the studied phenomena

and processes. According to our opinion, however, no analysis has been presented yet, resulting in generally valid conclusions as to which of the variables or functions are essential for giving a true picture of the hygroscopic properties. Besides, there are not exact definitions available, relating to various terms adopted in the technical practice, as these are both measured and interpreted in different ways. This concerns e.g. such terms as critical point, hygroscopic point, critical moisture content, hygroscopic potential, or coefficient of hygroscopicity. Also the methods for the determination of the basic variables, characterizing hygroscopicity, have not yet been consolidated and standardized.

Extensive studies devoted to improving the physico-mechanical properties of fertilisers have been conducted in our Institute and among the various topics an analysis of equilibrium states in the processes of fertiliser moistening has been given due attention. A brief summary of results accomplished so far is the subject-matter of the presented paper.

Let the equilibrium state, which can be considered a basic quantitative measure of hygroscopicity, be such a value of relative atmospheric humidity, at which a given substance /i.e. a fertiliser/ does not exchange any water with the surrounding atmosphere, i.e. it does neither moisten nor dry. The higher is the value of this equilibrium humidity, the higher is the fertiliser quality as far as its hygroscopicity is concerned.

To analyze the dependences of the equilibrium moisture content on the basic physico-chemical parameters, let us first consider the simplest case, i.e. that of a two-component system equilibrium. One component in such a system is water /the only volatile component at the given constant temperature/ and the other one is a pure fertiliser salt. The diagramme /Fig.1/ demonstrates the dependence of water vapour pressure on the composition of the examined system at a constant temperature. The term P_1 designates the value of the pressure of pure water vapour at the given temperature. As the moisture content $/x_1/$ in the solid phase is increasing, three well defined regions can be distinguished:

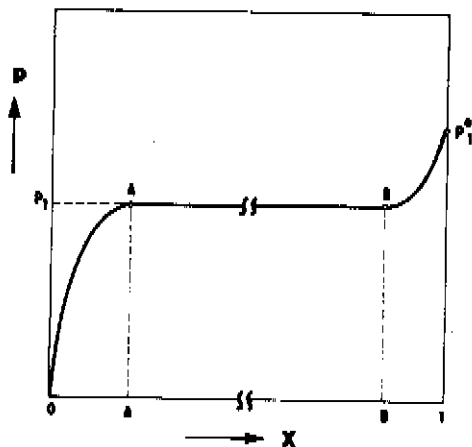


Fig. 1. Dependence of water vapour pressure on the composition of a salt-water system at constant temperature.

- Region /0;A/: a salt, initially completely dry, is absorbing water from the surrounding atmosphere and a saturated solution is formed consecutively /point A/. Water vapour pressure over the system is rising. The processes, taking place in the system, however, have not been described satisfactorily and we are still lacking adequate information concerning the mechanism, by which the water is combined with the solid salt.

Usually this region is described by sorption isotherms, i.e. by the dependences of the amount of absorbed water /as related to the amount of the salt/ on water vapour pressure of the surrounding atmosphere.

- Region /A;B/: this is a region, in which there exists a saturated solution and the water content in the system is further increasing, which brings about the dissolving of the solid salt until this is dissolved completely /point B/. Since a three-phase equilibrium exists during this process, the water vapour pressure in this region is equal to that over a saturated solution and is thus constant.

- Region /B;1/: represents only a further diluting of the once formed saturated solution and it is, therefore, no more interesting from the viewpoint of our studies.

Considering the basic condition for phase equilibria, it must hold for any point of the dependence that

$$f_1^{(g)} = f_1^{(c)} \quad (1)$$

where $f_1^{(g)}$ = fugacity of water in gaseous phase

and $f_1^{(c)}$ = fugacity of water in the condensed phase;

besides, $f_1^{(c)}$ is a function of water content in the solid phase: $f_1^{(c)} = f(x_1)$.

Taking pure water at a given temperature as the standard state, the condition for equilibrium may be expressed in terms of the corresponding activities:

$$a_1^{(g)} = a_1^{(c)} = \frac{f_1^{(g)}}{f_1^0} = \frac{f_1^{(c)}}{f_1^0} \quad (2)$$

where f_1^0 = fugacity of pure water under standard conditions.

Within the range of temperatures /0-50°C/, which are relevant when studying the problems of fertiliser hygroscopicity, the values of water vapour pressure are comparatively low, so that an ideal behaviour of the gaseous phase may be assumed and, therefore, it is possible to substitute pressure values for fugacities:

$$a_1^{(g)} = \frac{P_1^{(g)}}{P_1^0} \quad (3)$$

The conventionally used measure of atmospheric water vapour pressure is relative humidity φ , which is defined as

$$\varphi = \frac{P}{P_1^0} \cdot 100 \quad (4)$$

where P is the actual water vapour pressure in the air and P_1^0 is the pressure of saturated water vapour at the same given temperature.

It obviously holds for any point /i/ in the first region /O;A/ of the diagramme /Fig.1/ that

$$\frac{P_1}{P_1^0} \cdot 100 = \mathcal{P}_i = a_1 \cdot 100 \quad (5)$$

The relative equilibrium water vapour pressure \mathcal{P}_i over a fertiliser is designated as the hygroscopic point. It follows clearly from the derived relation that the value of hygroscopic point depends on the content of water in the fertiliser salt. When the humidity of the surrounding atmosphere becomes higher than the hygroscopic point, the solid fertiliser salt will absorb water until the vapour pressure values are equalized at a new equilibrium value; the salt remains in the solid form but its water content has increased. It follows from the above considerations that the value of hygroscopic point is varying with the content of water in the fertiliser and, consequently, a hygroscopic point value does not characterize the hygroscopicity of a given fertiliser exactly unless its corresponding water content is given at the same time.

As stated earlier, the second region /A/B/ is that of a three-phase equilibrium of a system solid substance-saturated solution-gaseous phase /i.e. the surrounding atmosphere/. In this case Eq.(3) is converted to the following form:

$$a_1 = \frac{P_{\text{sat}}}{P_1^0} \quad (6)$$

where P_{sat} is water vapour pressure of a saturated solution at the given temperature. It is then possible to define the term critical relative humidity $\mathcal{P}_{\text{crit}}$ as

$$\mathcal{P}_{\text{crit}} = 100 \cdot a_1 = \frac{P_{\text{sat}}}{P_1^0} \cdot 100 \quad (7)$$

The value of thus defined parameter is constant for a given system at a given temperature. It is exactly defined on the basis of the thermodynamics and is of fundamental importance in technical practice as it indicates the maximum value of air humidity, at which a given salt may exist in the solid phase. It follows clearly from the above demonstrated relations that critical relative humidity $\mathcal{P}_{\text{crit}}$

represents the limiting value of hygroscopic point φ_1 .

This brief analysis of the equilibrium conditions makes it possible to draw a number of conclusions concerning both hygroscopicity of fertilisers and the possibilities as well as experimental methods for its determining. It is necessary to emphasize first that the value of hygroscopic points depends primarily on chemical composition of the examined substance but it is inevitably influenced by the physical conditions of the given material as well. The conditions of absorption may vary widely with the degree of crystal lattice development, its imperfections, unevenness of the surface, and particle size. In practice, these characteristic properties depend largely upon the respective manufacturing process, e.g. on the operational conditions of granulation, temperature and duration of drying, and the like. The physical state of a solid material is also causing that its sorption and desorption isotherms need not be identical and that hysteresis may occur. This phenomenon must be taken into consideration in the process of drying. It is very difficult to determine the sorption isotherms in the region, lying above the critical relative humidity and it is obvious that the result may be obtained more accurately and more readily by measuring the solution vapour pressure.

The simplest case of a two-component equilibrium /such as e.g. urea/ that enables to carry out an exact analysis of the equilibrium states is only rarely encountered among fertilisers. It stands to reason that in systems, comprising more components, the above given relations will be more complex. Two solid phases must be in equilibrium in a three-component system at a given temperature /i.e. two fertiliser salts and water/ if this has to have no degree of freedom in accordance with the Gibbs' law of phases. Eq.(7) holds even in this case but only when the concentration of the saturated solution and thus also the equilibrium solid phase does not change. If there is only a single solid phase present in a three-component system, then the concentration of the saturated solution and, consequently also its vapour pressure, may vary. To solve such cases exactly it is

necessary to know the corresponding diagrams of solubility.

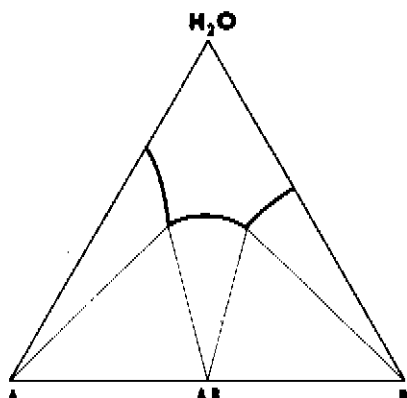


Fig. 2. Schematic diagram of three-component phase equilibrium in a system, in which an anhydrous double salt is formed.

Let us select from a number of possible systems such a system of salts A and B and water, in which the salts A and B can form an anhydrous double compound. The equilibrium diagram at constant temperature is shown schematically in Fig. 2. It follows from the diagram that when the component B is being added to the salt A, the total concentration of salts in the saturated solution is increasing, which necessarily results in a decrease in the solution vapour pressure. In all the three regions of the said system, where only one solid phase occurs in the equilibrium state, the variations in the ratio of the salts A and B will bring about changes in the composition of the saturated solution and thus also in the value of its water vapour pressure, so that they may be characterized by the changing values of hygroscopic points φ_1 . At the same time, there are two regions in the system, in which two solid phases are in equilibrium /A-AB or AB-B/ and these are characterized by the respective eutonic points, to which, logically, two different values of critical relative humidity φ_{crit} correspond. Even a very small increase in the humidity of the surrounding atmosphere above one of the φ_{crit} values will result in

that the system will start to absorb water from the atmosphere and one of the solid phases will be dissolving until it dissolves completely. There will be a shift of the system equilibrium and, ultimately, only one solid phase will be in equilibrium with the liquid. Almost generally the highest solubility of both salts is observed at the eutonic point, which explains the practical experience that φ_{crit} of a mixture of two salts is lower than φ_{crit} of either of the two components /e.g. urea-ammonium nitrate/. The mixing of salts, therefore, has almost always a deleterious effect on hygroscopic properties.

A number of three-component systems, encountered in the fertiliser practice, have been studied and some of the results will be discussed later. Though the individual cases often represent markedly different systems /occurrence of one or more hydrates, formation of mixed crystals, existence of several double salts and their hydrates/, the analysis of the obtained results has confirmed that the conclusions given briefly for the above example of a three-component system hold true universally.

The general definitions of critical relative humidity and of hygroscopic point may, therefore, be formulated as follows:

Critical relative humidity is that value of relative humidity, at which a maximum thermodynamically possible number of solid phases exists in equilibrium at a given temperature. Hygroscopic points of a system at a given temperature are all those values of equilibrium relative humidity, which do not meet the above given fundamental condition for critical relative humidity.

When the number of components in a system is increasing, its description is becoming extremely difficult and, in most cases, quite impossible. The commercially produced fertilisers usually represent a system comprising a rather high number of components. E.g. a conventional NPK fertiliser contains at least six components / NH_4^+ , Ca^{2+} , K^+ , H_2PO_4^- , HPO_4^{2-} , Cl^- /, which means that five or even more phases may

be in equilibrium at a constant temperature. Though the composition of the currently manufactured NPK fertilisers is varying only within a fairly narrow region of the whole system, any efforts to determine the exact values of critical relative humidity do not make any practical sense. It is recommended to characterize the hygroscopic properties of this type of fertilisers exclusively on the basis of hygroscopic points or by the shape of the entire sorption isotherm.

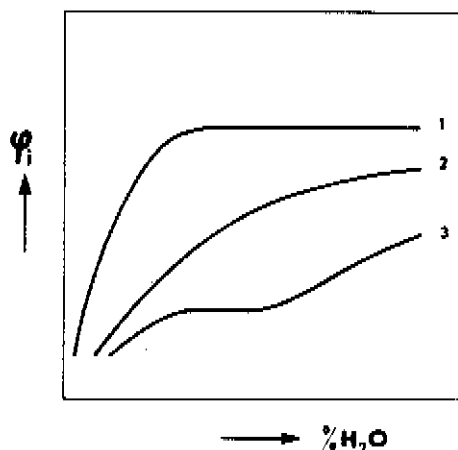


Fig.3. Sorption isotherms of some conventional NPK fertilisers.

According to our experience, the conventional NPK fertilisers give sorption isotherms of quite different shapes. Some examples are demonstrated in Fig.3. The curve 1 in Fig. 3 may be interpreted as follows: the values of hygroscopic point are rising steeply with increasing the water content in the fertiliser during the initial stage, which is a response to the formation of a saturated solution with comparatively high water vapour pressure. In many cases this may be due to the presence of a dilute acid, e.g. phosphoric acid. The case, characterized by the curve 2, is typical for a system, whose components are dissolving gradually, while a saturated solution with a low water vapour pressure is formed. A step-wise dependence of the hygroscopic point values on the content of water in the fertiliser is characterized by the curve 3. The system contains a small amount of

a readily soluble salt /or there occurs an eutonic point in it/ with a low water vapour pressure /e.g. calcium nitrate/, which is dissolving gradually. When it is completely removed from the solid phase, a next component of the system is being dissolved and equilibrium is established with a saturated solution at a different composition and at a higher vapour pressure.

The shapes of desorption isotherms are very similar to those of the sorption isotherms /16/.

A dynamic gravimetric method has been chosen for the measuring of fertilisers hygroscopicity as the most exact one. The selection of this method was based on both the theoretical analysis of the problem and on an evaluation of published information. A similar principle has been known /e.g. 17/ but the apparatus was developed in our laboratory.

An accurately weighed fertiliser sample /about 1 g/ is spread as a thin layer on a glass plate, which is suspended from the carrying arm of a tensometric balance. The examined sample is exposed in a standard stream of air, whose temperature and humidity are adjusted accurately at the desired values. The system is arranged so as to minimize the thickness of the layer, upon which the water vapour pressure gradient is being established. The tensometric measuring element consists of four tensometers fixed to a bearing plate by a special polymer-based adhesive and it is connected to a Wheatstone bridge, fed by steady current. The silicon tensometers are virtually ideal hysteresis-free transducers of a mechanical deformation to an electric signal. Since the measuring system is rather temperature-sensitive, the whole respective part of the apparatus is thermostated. The changes in the sample weight due to absorption of water bring about changes in the degree of deflection of the balance arm with the tensometers and thus also in the terminal voltage of the Wheatstone bridge. The corresponding output signal is continuously registered by an electronic compensating recorder. The apparatus enables to determine the complete course of both sorption and desorption isotherms or to measure the desired regions of these isotherms at temperatures ranging from -20 to $+80$ °C and at relative humidities 0.03 - 100 %.

The response of the apparatus is equal or better than that attained with analytical balance. The suggested and developed method is rather time-consuming (to determine a whole sorption isotherm may take 10-13 days) and the apparatus operation requires a skilled technician but the obtained results represent exact hygroscopic characteristics of the examined fertiliser.

A rapid, convenient method has been developed and used for the determination of the values of hygroscopic points of fertilisers. The apparatus design is fairly simple and it enables to measure directly the pressure of water vapour over a fertiliser sample. The sensing element is based on the principle of measuring the air water vapour pressure, which is in equilibrium with the tested fertiliser; vapour pressure over a lithium chloride solution is measured simultaneously and its value is equilibrated automatically with that over the fertiliser. Adequate amount of the fertiliser (about 200 g; weighing is not necessary) is placed into a vessel, whose head closure is fitted with the LiCl sensor. The whole apparatus is thermostated. When the required temperature is adjusted /30 min/, changes in the resistance of a platinum thermometer, which is a part of the sensing element, are registered by an electronic compensating recorder. Its scale is calibrated so, that it enables the direct reading of the values of relative humidity over the measured sample. The method gives reliable results within 30-100 % of relative humidity, the lower limit being due to the value of water vapour pressure of the LiCl solution. It can be applied for most of fertilisers except for those with a low water content (e.g. urea, ammonium sulphate), whose hygroscopic points are less than 30 %.

The described method has been used to verify the results and conclusions based on the theoretical treatment of the problem. A number of two- and three-component systems as met in the commercially produced fertilisers were examined. The results of two measurements conducted according to the above described methods are discussed as illustrative examples.

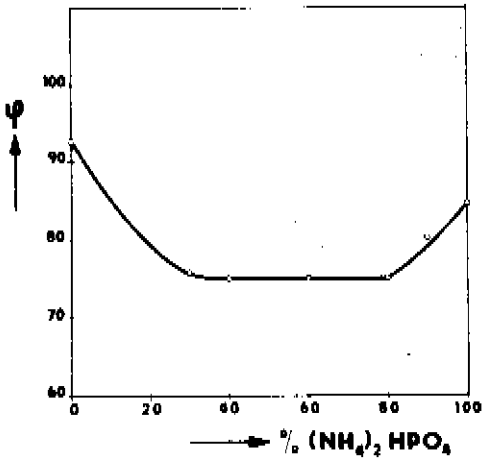


Fig.4. Relative equilibrium water vapour pressure over the system $\text{NH}_4\text{H}_2\text{PO}_4$ - $(\text{NH}_4)_2\text{HPO}_4$ at constant water content (20 % by weight) and 25 °C.

The diagram (Fig.4) demonstrates the results of equilibrium relative humidities of the system monoammonium phosphate - diammonium phosphate at a constant water content of 20 wt. % and at 25 °C. This is a simple example of a three-component equilibrium since no crystallohydrates, double salts or mixed crystals are formed. Either of the two pure salts exhibits a high value of critical relative humidity, i.e. 93.8 and 82.0 %, resp., at 25 °C. It can be seen in the diagram that when the two pure salts are mixed, the value of critical relative humidity will drop by 15-20 % relative, i.e. to a value close to 75 %. The value, determined with a commercial sample of the salts, trade-named "amofos", was 74.5 %, which conforms fairly well to theory. It has been proved experimentally that the values of critical relative humidity of most of the examined systems are lower than those of the individual pure salts because, like in the presented case, a saturated solution of two solid phases has the highest summary concentration of salts in the system.

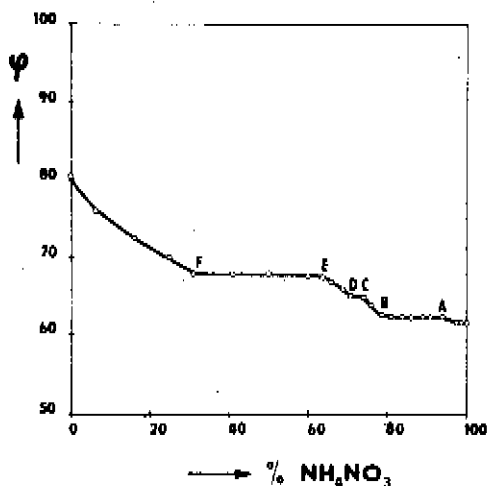


Fig.5. Relative equilibrium water vapour pressure over the system $(\text{NH}_4)_2\text{SO}_4\text{-NH}_4\text{NO}_3$ at constant water content (20 % by weight) and 25 °C.

The second example /Fig.5/ demonstrates a more complex case of a three-phase equilibrium, involving the occurrence of double salts and eutonic points, which, however, do not have the highest summary concentration of salts. The system is $\text{NH}_4\text{NO}_3\text{-(NH}_4)_2\text{SO}_4\text{-H}_2\text{O}$. From the known solubility data of the system /18/ and on the basis of a theoretical analysis, one may evaluate the dependence of the relative equilibrium humidity values on the increasing of the content of one of the salts:

- the lowest equilibrium relative humidity will be that of pure ammonium nitrate;
- the highest equilibrium relative humidity will be that of pure ammonium sulphate;
- two double salts /i.e. $3\text{NH}_4\text{NO}_3\cdot(\text{NH}_4)_2\text{SO}_4$ and $2\text{NH}_4\text{NO}_3\cdot(\text{NH}_4)_2\text{SO}_4$ and three eutonic points will occur in the system;
- three values of critical relative humidity must exist in the system in the regions where there are the equilibria of two solid phases;
- the values of these critical relative humidities will lie between those of pure ammonium nitrate and ammonium sulphate.

The diagram /Fig.5/, showing the curve of relative humidities as measured at a constant water content /20 % by weight/, at 25 °C justifies fully the above assumptions. When the content of $(\text{NH}_4)_2\text{SO}_4$ in the system is increasing, the value of the gaseous phase relative humidity is rising slowly until the region of the first eutonic point (equilibrium of two solid phases - NH_4NO_3 and $3\text{NH}_4\text{NO}_3 \cdot (\text{NH}_4)_2\text{SO}_4$) is reached. The value of the corresponding critical relative humidity is 62.6 %. (The constant value of relative humidity between points A and B.) When the content of ammonium sulphate is growing further, only the double salt is stable and the value of relative humidity is rising to point C. An equilibrium of two solid phases (i.e. of both the double salts) is established in the system at critical relative humidity 65 % /points C-D/. The value of relative humidity is increasing again within the region of stability of the second double salt $2\text{NH}_4\text{NO}_3 \cdot (\text{NH}_4)_2\text{SO}_4$. The third critical relative humidity at 68.1 % /points E-F/ corresponds to the equilibrium region of two solid phases, that is of the salts $2\text{NH}_4\text{NO}_3 \cdot (\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{SO}_4$. This is in accordance with the size of the corresponding area in the equilibrium solubility diagram, in which that isotherm covers the longest concentration range. As the content of ammonium sulphate is growing on, also the values of relative humidity are increasing once more since there is only one stable solid phase present in the system - i.e. ammonium sulphate. It follows clearly from the afore-said that the appraisal of the system behaviour, based on an analysis of the solubility diagram, has been fully confirmed experimentally. The lengths of the concentration segments, characterizing the critical relative humidities, correspond fully to the sizes of those areas of the triangular regions in the solubility diagram, in which two solid salts are present in an equilibrium.

A practical conclusion that may be drawn from the discussed example is that the addition of ammonium sulphate to ammonium nitrate will reduce the total concentration of salts in the saturated solution and thus increase the value of critical relative humidity. It explains also the known fact

that the hygroscopic properties of such a product are more favourable than those of pure ammonium nitrate. Such a case, however, is rather an exception in the fertiliser practice.

The presented theoretical analysis of the problem of hygroscopicity makes it possible to elucidate clearly certain phenomena, encountered when dealing with fertilisers, for which there has not been any explanation and which, therefore, have appeared as being less logical. It enables to give reasons for the growth of the values of hygroscopic points as observed when the content of water in a fertiliser is increasing, to explain the frequently found marked decrease in the value of critical relative humidity of mixtures of two salts, although their respective critical relative humidities may be comparatively high, as well as the possibility of the occurrence of several values of critical relative humidity in systems, in which double salts are formed, and other phenomena. It has been proved that the knowledge of solubility data enables to predict fairly accurately the hygroscopic characteristics of two- and three-component systems.

It is necessary to emphasize, however, that the presented analysis has been carried out exclusively for equilibrium conditions. The obtained experimental results are successively published, e.g. /19/. In view of the theoretical and practical aspects, it will be very desirable to study also the kinetic phenomena that play an important role in the evaluation of the hygroscopic characteristics of fertilisers and which would enable to assess the time allowed for the storage of a fertiliser under the given conditions, to appraise the actual effect of a number of fertiliser conditioning methods, and the like. These problems will be the subject-matter of our future research programme.

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