Study of Physico-Chemical Properties of Phosphorate Solutions

Israiljan Shamshidinov[1], *Asadjon* Kambarov[2], *Rikhsitilla* Najmiddinov[1], *Ilyos* Rustamov[1], *Ilkham* Usmanov[2], and *Murodjon* Samadiy[2*]

[1]Namangan Institute of Engineering and Construction, Namangan, Uzbekistan
[2]Yangiyer branch of Tashkent Chemical Technological Institute, Yangiyer, Uzbekistan

Abstract. The results of studies of the physicochemical properties of extraction phosphoric acids containing magnesium in the presence of ammonium nitrate are presented. A decrease in the heat of vaporization in the H_3PO_4-H_2O system was found in the range of acid concentrations of 20-30% and 37-45% P_2O_5. At an acid concentration of 20, 35% and 45% P_2O_5 there is a minimum electrical conductivity, while at a concentration of 30 and 40% P_2O_5, the electrical conductivity of solutions reaches a maximum value at temperatures of 25-45%, which is explained by structural changes occurring in the acid during dissociation and dimerization, depending on the concentration. The electrical conductivity of the H_3PO_4-H_2O system decreases with the introduction of magnesium sulfate and ammonium nitrate. The regularity of the thickening of magnesium-containing acid is substantiated.

1 Introduction

At present, due to the depletion of P_2O_5-rich deposits of phosphate raw materials, special attention is paid to the development of the technology for concentrated, single phosphorus fertilizers with the involvement of low-grade and high-magnesium phosphorites in industrial production [1].

The Republic has achieved high results in scientific research on the development and expansion of the range of concentrated phosphorus-containing fertilizers,ammophosphate, suprefos, PS-Agro, etc. Based on local phosphorites in the Central Kyzylkum.

However, there is no production of such a valuable, concentrated, single-phosphate fertilizer as double superphosphate in the country. Simple ammoniated superphosphate and enriched superphosphate are produced in small volumes, but this isn't enough to meet the needs of the agro-industrial complex for phosphate fertilizers for autumn ploughing. The lack of production is due, first of all, to the fact that the extraction of phosphoric acid is obtained from the phosphorites of Karatau and the Central Kyzylkum, which contain magnesium and thicken when concentrated.

The concentration of weak (21-32% P_2O_5) extractive phosphoric acid (EPA) above 50% P_2O_5 increases the efficiency of its transportability, which in turn allows the production of

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[*] Corresponding author: samadiy@inbox.ru

EPA to be concentrated near phosphorite deposits, and fertilizer production can be located in areas their consumption. In addition, concentrated EPA is the basis for the production of double superphosphate, defluorinated phosphates, polyphosphates and liquid complex fertilizers. EPA from high-quality raw materials is well evaporated to a concentration of 54% P_2O_5 and is used to obtain double superphosphate. EPA obtained from magnesium-containing raw materials, for example, from phosphorites of Karatau, Kyzylkum and Kingisepp, due to the content of magnesium impurities in it, thickens at a concentration of 37-38% P_2O_5 [2-3]. Claim [4], that the presence of more than 0.3% MgO in phosphate raw materials causes difficulties in concentrating EPA due to the formation of insoluble magnesium phosphate, leading to the formation of sludge. Other authors [5] believe that the thickening of the magnesium-containing EPA reduced to a concentration of 37-38% P_2O_5 occurs due to the formation of MgF_2 and SiO_2 as a result of the hydrolysis of $MgSiF_6$.

Authors [6] found that the evaporation of the system $MgO – H_3PO_4 – H_2SiF_6 – H_2O$ containing 25% P_2O_5, 1.0% MgO and 2% fluorine in the form of $H_2 SiF_6$ is possible up to a concentration of 62% and 67 % P_2O_5 and the acid is a fluid suspension (even at 67% P_2O_5 the viscosity is 1540 cps). In addition to SiO_2, $Mg(H_2PO_4)_2$, the presence of magnesium fluorometaphosphate, $MgPO_3F$, was found in solutions.

In addition, by studying the $MgSO_4 – H_3PO_4 – H_2O$ system at a temperature of 20-80°C in the P_2O_5 concentration range from 0 to 80%, the authors of [7], found the presence of mono, penta, hexa and heptahydrate magnesium sulfate and established the absence of mono magnesium phosphate compounds. These data are confirmed by other authors [8], when studying the $MgSO_4 – H_2SO_4 – H_3PO_4 – H_2O$ system at a temperature of 60°C in the sulfuric acid concentration range from 0 to 60 wt. % and phosphoric acid from 0 to 75 wt. %. Authors [5], the formation of magnesium sulfate hydrates during the evaporation of the $MgO – H_2SO_4 – H_3PO_4 – H_2O$ system containing 25% P_2O_5, 1% MgO and 2.4% H_2SO_4 to a concentration of 53.4 % P_2O_5.

In addition, by studying the properties of real (industrial) EPA solutions from Karatau phosphorites, depending on the ratio of impurity compounds of magnesium, iron, aluminium, sulfuric acid, and others [9-11], it was found that EPA thickens as it is concentrated due to the presence of magnesium in the acid. In the form of magnesium sulfate hydrates. EPA (21% P_2O_5) from Karatau phosphorites contains 1.5-2.0% MgO (sometimes higher), i.e. 4.5-6.0% $MgSO_4$ or 9.0-12.0% $MgSO_4·7H_2O$ in dissolved form, and with an increase in concentration to 37-38% P_2O_5, the content of this salt reaches 16-21%. The solution is supersaturated with magnesium sulfate hydrates. When cooled, they crystallize and associate water molecules (this property is inherent in all crystalline hydrates), as a result of which the solution thickens. Other impurities present (calcium sulfate, iron and aluminium phosphates, sodium and potassium silicofluorides), especially sulfuric acid, enhance the thickening processes.

To eliminate thickening, i.e. improvement of rheological properties [12], a chemical reagent, ammonium nitrate, was used, and the solubility of magnesium compounds in a solution of this reagent was studied. For the first time [13], a method was developed for obtaining purified ammonium phosphates with a preliminary concentration of magnesium-containing EPA to a P_2O_5 content of 50-55% and its further ammonization. It was assumed that ammonium nitrate ions and molecules destroy the hydration shell of magnesium sulfate etc., and also prevent the association of water around crystalline hydrates, thereby the acid acquires fluidity and does not thicken even when cooled to minus 30-32°C.

2 Materials and methods

In solution, it is difficult to study with analytical accuracy the effect of ammonium nitrate on the dehydration of magnesium sulfate from heptahydrate to monohydrate or anhydrous.

Therefore, we studied the process of dehydration of $MgSO_4{\cdot}7H_2O$ in the system H_3PO_4 – $MgSO_4$ – H_2O in the presence of ammonium nitrate by changing the saturation vapour pressure, the heat of vaporization and electrical conductivity depending on the concentration of the components. To do this, we prepared phosphate solutions (PS) containing the components H_3PO_4, $MgSO_4{\cdot}7H_2O$, NH_4NO_3 and H_2O, the compositions of which are shown in Table 1.

Table 1. The composition of phosphate solutions.

Model solutions	Components	Content, wt. %						
FK-1	H_3PO_4	27.6	34.5	41.4	48.3	55.2	62.1	69.0
	(P_2O_5)	20.0	25.0	30.0	35.0	40.0	45.0	50.0
	H_2O	72.5	65.5	58.6	51.7	44.8	37.9	31.0
FK-2	H_3PO_4	27.6	34.5	41.4	48.3	55.2	62.1	65.3
	(P_2O_5)	20.0	25.0	30.0	35.0	40.0	45.0	47.3
	$MgSO_4{\cdot}7H_2O$	10.0	12.5	15.0	17.5	20.0	22.5	23.6
	H_2O	62.4	53.0	43.6	34.2	24.8	15.4	11.1
FK-3	H_3PO_4	27.6	34.5	41.4	48.3	55.2	62.1	63.7
	(P_2O_5)	20.0	25.0	30.0	35.0	40.0	45.0	46.2
	$MgSO_4{\cdot}7H_2O$	10.0	12.5	15.0	17.5	20.0	22.5	23.2
	NH_4NO_3 _	1.0	1.25	1.5	1.75	2.0	2.25	2.3
	H_2O	61.4	51.75	42.1	32.45	22.8	13.15	10.8

The boiling point of the systems at different pressures was determined by the dynamic method [14, 15].

3 Results and Discussion

The dependence of the vapour pressure of the studied systems on temperature obeys the Clausius-Claiperon equation:

$$lg\,P = -\frac{A}{T} + B \tag{1}$$

Based on the experimental data, plots lgP – 1/ T and P – f (T) were built, and the value of tg was determined from the angle of inclination of the direct abscissa axis since lg P has a linear dependence on 1/T.

The heat of vaporization was determined by the equation:

$$\Delta H = -2.3 \cdot R \cdot tg\alpha \tag{2}$$

Values A, B, ΔH are given in Table 2.

The results (Figure 1, curves 1) show a decrease in the heat of vaporization in the H_3PO_4 – H_2O system with an increase in concentration in the range of 20-30% and 37-45% P_2O_5. In the concentration ranges of phosphoric acid from 30% P_2O_5 to 37% P_2O_5 and from 45% P_2O_5 to 50% P_2O_5, the heat of vaporization increases sharply. The system has two minima of the heat of vaporization - at an acid concentration of 30% P_2O_5 (35.2 kJ/mol) and 45% P_2O_5 (46.92 kJ/mol) and three maxima - at 20% P_2O_5 (44.81 kJ/mol), at 35% P_2O_5 (49.72 kJ/mol) and at 50% P_2O_5 (61.39 kJ/mol).

According to Raoult's law, the saturated vapour pressure of a solution is always less than the saturated vapour pressure of a pure solvent, and a decrease in vapour pressure or an increase in the boiling point is proportional to the number of dissolved molecules in non-electrolyte solutions. According to the Arrhenius theory, it is known that in electrolyte solutions the change in saturated vapour pressure and other physical and chemical properties is proportional to the change in the number of dissociated ions. It is known that water molecules have physical and chemical effects on the molecules and ions of the dissolved substance.

Table 2. Thermodynamic data of phosphate solutions.

Model solutions	**Concentration acids, % P_2O_5**	**Vapour pressure**	**– ΔN, kJ/mol**
FK-1	20	$\log P = -2343.5/T + 9.0989$	44.81
	25	$\log P = -1987.1/T + 8.0894$	37.98
	30	$\log P = -1841.1/T + 7.5166$	35.21
	35	$\log P = -2600.0/T + 9.7610$	49.72
	40	$\log P = -2591.4/T + 9.6721$	49.56
	45	$\log P = -2453.4/T + 9.1226$	46.92
	50	$\log P = -3210.2/T + 11.2839$	61.39
FK-2	20	$\log P = -2247.2/T + 8.7652$	42.97
	25	$\log P = -2353.0/T + 9.0359$	44.99
	30	$\log P = -2526.9/T + 9.4949$	48.32
	35	$\log P = -2973.2/T + 10.8023$	56.86
	40	$\log P = -3337.9/T + 11.7181$	63.83
	45	$\log P = -3273.9/T + 11.2437$	62.61
	47.3	$\log P = -3023.2/T + 10.2779$	57.81
FK-3	20	$\log P = -2026.2/T + 8.0931$	38.73
	25	$\log P = -2170.2/T + 8.4321$	41.50
	30	$\log P = -2348.9/T + 8.9539$	44.90
	35	$\log P = -2848.9/T + 10.3919$	54.46
	40	$\log P = -2930.3/T + 10.4536$	56.04
	45	$\log P = -3183.8/T + 10.9143$	60.88
	46.2	$\log P = -3063.6/T + 10.4278$	58.59

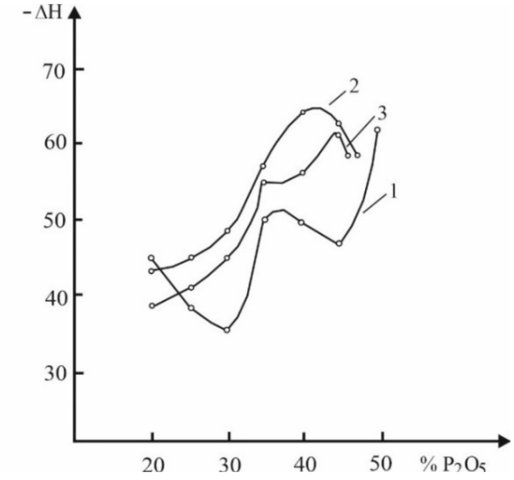

Fig. 1. Heat of vaporization of systems: 1- $H_3PO_4 - H_2O$; 2 - $H_3PO_4 - MgSO_4 \cdot 7H_2O - H_2O$; 3 - $H_3PO_4 - MgSO_4 \cdot 7H_2O - NH_4NO_3 - H_2O$.

Phosphoric acid dissociates into ions according to the following scheme:

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^- \quad (3)$$

$$H_2PO_4^- \rightleftarrows H^+ + HPO_4^{2-} \quad (4)$$

$$HPO_4^{2-} \rightleftarrows H^+ + PO_4^{3-} \quad (5)$$

(2.2) and (2.3) are suppressed by dissociated hydrogen ions (2.1), the dissociation constant of phosphoric acid in its 0.1-0.01 N solutions at 25°C is [16], pK 1 = 2.148±0.001; pK 2 = 7.199±0.002 and pK 3 = 12.35 ±0.02. Even though phosphoric acid is a relatively weak electrolyte, its concentrated aqueous solutions are characterized by the high activity of hydrogen ions [17, 18]. The degree of dissociation of H_3PO_4 passes through a minimum at a concentration of ~9 % and then increases due to the formation of the H_3PO_4 dimer, which is a stronger electrolyte [18].

It is known [19] that phosphoric acids with a concentration of more than 6.5% P_2O_5 partly form the $H_6P_2O_8$ dimer, which has more acidic properties than H_3PO_4. So, in a 10 M solution of H_3PO_4 with a concentration of 36% P_2O_5 is contained in g-ion/l: 3.755 H^+ ; 0.0598 $H_2PO_4^-$; 3.6955 $H_5P_2O_8^-$ and in mol/l: 0.6393 H_3PO_4 and 0.9596 $H_6P_2O_8$, as a result of the dissociation of the orthophosphoric acid monomer, only 1.6% of ions from their total amount are formed. Secondly, in solutions containing less than 50% H_3PO_4, phosphate anions bind with water more easily than with each other. And also hydrogen ions form hydronium ions in water:

$$H_3PO_4 + H_2O \rightleftarrows H_3O^+ + H_2PO_4^- \quad (6)$$

$$2H_3PO_4 \rightleftarrows H_6P_2O_8 \quad (7)$$

$$H_6P_2O_8 + H_2O \rightleftarrows H_3O^+ + H_5P_2O_8^- \quad (8)$$

These structural rearrangements are invariably reflected in changes in the physicochemical properties of phosphoric acid in the FK-1, FK-2, and FK-3 systems studied (Table 3).

As a result, it was found that phosphoric acid with a concentration of 20, 35 and 45% P_2O_5 has a minimum electrical conductivity, and at a concentration of 30 and 40% P_2O_5, the electrical conductivity of solutions reaches a maximum value at a temperature of 25-45°C (Figure 2). As the temperature rises, these characteristic points will mix to the right, i.e. in the direction of increasing the concentration of P_2O_5. So, the minima disappear at a concentration of P_2O_5 equal to 35%, and vice versa, at a concentration of 35-40% P_2O_5, the electrical conductivity of the solution has a maximum value (Figure 2). In addition, at a concentration of P_2O_5 equal to 50%, a maximum appears, which, with a decrease in temperature below 45°C, is weakly expressed.

This property of phosphoric acid is observed for the first time and is explained by us by the structural changes that occur in the acid during its dissociation and dimerization depending on the concentration.

So, with an increase in the concentration of P_2O_5 to 30%, according to the Le Chatelier principle, the equilibrium in the process (2.1) should mix to the left, i.e. with an increase in the right side of the H_3PO_4 component, its hydration is accelerated and, accordingly, the number of dissociated (hydrated) ions increases. It is known [17] that dimerization occurs simultaneously (according to equation 2.5) and, obviously, its dissociation (according to equation 2.6).

Table 3. Electrical conductivity of phosphate solutions.

P_2O_5, %	**Electrical conductivity, χ, om $^{-1}$ sm $^{-1}$ at temperature, °C**									
	25	**30**	**35**	**40**	**45**	**50**	**55**	**60**	**65**	**70**
FK-1										
20	13.6	14.4	14.7	14.5	15.2	17.9	18.4	18.8	19.1	19.7
25	16.3	17.0	17.6	18.3	19.0	20.4	20.8	21.5	21.8	22.5
30	18.7	19.4	20.7	21.4	21.9	22.9	23.5	24.3	24.7	25.2
35	17.6	18.6	19.5	21.3	21.6	23.8	24.7	25.2	26.1	27.1
40	18.6	19.9	20.7	21.9	22.2	23.4	24.4	25.3	26.1	27.0
45	15.8	16.6	17.8	19.0	20.2	21.1	22.0	23.3	24.2	25.2
50	14.5	15.8	17.2	18.6	19.9	21.6	22.9	24.3	25.0	26.7
FK-2										
20	14.1	15.2	16.1	17.0	17.7	18.2	19.0	19.6	20.0	20.5
25	13.9	14.1	14.9	15.8	16.8	17.5	18.9	18.9	19.5	20.2
30	12.0	12.6	13.3	14.5	15.5	16.3	17.3	17.8	18.4	19.5
35	10.0	11.1	11.8	12.7	13.5	14.0	15.1	15.6	16.2	17.0
40	7.9	8.8	9.7	10.7	11.7	12.5	13.2	14.1	14.8	15.5
45	5.0	5.3	5.9	6.8	7.5	8.3	9.2	9.9	10.9	11.7
47.3	4.0	4.5	5.3	6.1	7.0	8.0	9.1	9.7	10.5	11.3
FK-3										
20	15.4	16.1	17.0	17.9	18.8	19.4	20.0	20.7	21.3	22.0
25	14.6	15.6	16.8	17.8	18.8	19.4	20.4	21.2	21.8	22.7
30	13.6	14.8	16.1	17.4	18.5	19.2	20.6	21.6	21.8	22.8
35	9.8	10.3	10.9	12.7	13.6	14.6	15.4	15.9	16.4	17.3
40	7.1	8.0	8.8	9.6	10.6	11.8	12.5	13.1	13.6	14.2
45	4.2	4.5	5.3	6.1	6.5	7.5	8.2	9.0	10.0	10.7
46.2	3.4	4.0	4.6	5.2	5.9	6.5	6.9	7.2	7.9	8.5

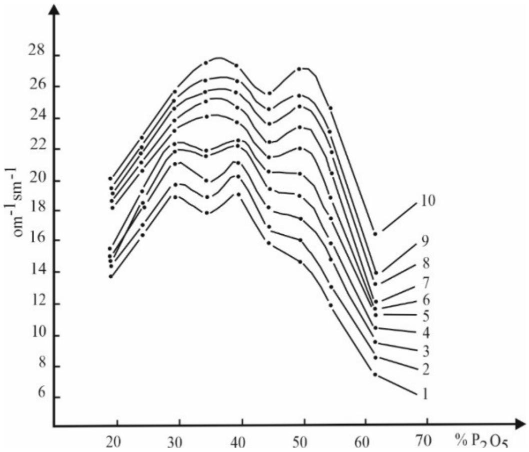

Fig. 2. Electrical conductivity of the $H_3PO_4 - H_2O$ system at temperatures: 25°C (1), 30°C (2), 35°C (3), 40°C (4), 45°C (5), 50°C (6), 55°C (7), 60°C (8), 65°C (9), 70°C (10).

Equilibrium is assumed to occur in the process (2.4) at a temperature of 25-45°C at a concentration of 30% P_2O_5, and temperatures above 45°C, it shifts towards an increase in the concentration of P_2O_5 (35-37%). With an increase in acid concentration to 35% P_2O_5 (25-45°C) and up to 45% P_2O_5 (above 45°C), process (2.5) prevails and process (2.6) accelerates and equilibrium occurs at a concentration of 40% P_2O_5 (25-45°C). With an increase in temperature, it will mix in the direction of increasing the concentration to 50% P_2O_5 and the process (2.5) ends.

With a further increase in the concentration of P_2O_5, the amount of “free water” in the system decreases and the equilibrium of reaction (2.6) will shift to the left side - associations, due to which dissociated ions and, accordingly, electrical conductivity decrease.

$H_3PO_4 – H_2O$ system decreases with the introduction of $MgSO_4·7H_2O$ and NH_4NO_3 salts into it (Figure 3, curves 2 and 3) since, with an increase in the concentration of substances in a solution (equivalently, the proportion of water in the system decreases), the degree of dissociation of molecules decreases and effective ions decrease. The lowest electrical conductivity is observed in the $H_3PO_4 – MgSO_4·7H_2O – H_2O$ system. The maximum values of the heats of vaporization (Figure 2.) and, accordingly, the minimum values of electrical conductivity (Figure 3. curve 2) in this system are explained by the presence of hydrated magnesium sulfate molecules and the association of water molecules around them. As a result, the proportion of “free water” in the system decreases.

The decrease in the heat of vaporization above the concentration of P_2O_5 40% is explained by the acceleration of the process of dehydration of magnesium sulfate heptane and its transition to less hydrated forms. Ammonium nitrate reduces the heat of vaporization of the $H_3PO_4 – MgSO_4 – H_2O$ system and increases its electrical conductivity, even though the content of components in the system increases.

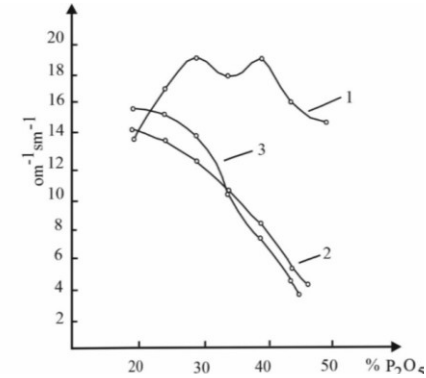

Fig. 3. Electrical conductivity of systems (at 25°C): 1 - H_3PO_4 - H_2O; 2 - H_3PO_4 - $MgSO_4·7H_2O$ - H_2O; 3 - H_3PO_4 - $MgSO_4·7H_2O$ - NH_4NO_3 - H_2O.

This indicates that ammonium nitrate and its ions have an effect (Coulomb - electrostatic forces) on magnesium sulfate hydrates, destroying their hydration shells with the formation of water molecules. The released water molecules dilute the system and increase the degree of dissociation of the molecules. Due to this, the electrical conductivity increases and the heat of vaporization of the system decreases.

4 Conclusions

By studying the thermodynamic, and electrochemical properties of concentrated phosphoric acid, changes in the physicochemical properties of the acid were established, which are determined by a change in the structure of phosphoric acid and the influence of other components of the system, associated, among other things, with hydration processes. The regularity of thickening (structuring) of magnesium-containing EPA as its concentration increases to 37-38% P_2O_5, associated with the formation of magnesium sulfate hydrates and their associates, is substantiated. The possibility of reducing the process of thickening of phosphoric acid, the content of magnesium salts, by introducing ammonium nitrate, which increases the solubility of magnesium salts and destroys magnesium sulfate hydrates and their associates, is shown.

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