# Solubility in the $KVO_3 + NH_4VO_3 + H_2O$ System

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The solubility of the potassium metavanadate and ammonium metavanadate in the $KVO_3 + NH_4VO_3 + H_2O$ system has been measured over a temperature range 293 K to 323 K. On the basis of the results, a section of the polytherm has been drawn. Additionally, the densities of the solutions have been measured. These results have led to the construction of the equilibrium diagram for the $KVO_3 + NH_4HCO_3 + KHCO_3 + NH_4VO_3 + H_2O$ system in the oblique projection according to Janecki. The optimum conditions for conducting the carbonization process of the $KVO_3$ ammonium solutions in order to obtain $KHCO_3$ are described.

## Introduction

Potassium carbonate is an important raw material in the production of high-quality optical, television, and lead glass. It is also used in the pharmaceutical, ceramics and catering industries. The industrial production of $K_2CO_3$ is mainly carried out according to the original Engel−Precht, formic, amine, and nepheline methods or the carbonization of KOH water solutions (Pozin, 1970; Trypuć, 1974; Pisarska and Gnot, 1995). KCl or $K_2SO_4$ salts are the essential compounds for the four above-mentioned methods.

Generating $K_2CO_3$ through the carbonization of the KCl-saturated water + ammonia solutions according to the Solvay method, where $Na_2CO_3$ is obtained from NaCl, is still impossible. The main reason is the low efficiency of the carbonization process in relation to potassium ion ($W_{K+}$). For example, for the solution carbonization degree $R = 90\%$ at 303 K, the efficiency $W_{K+}$ reaches only 16% (Trypuć and Koneczny, 1973). The introduction of carbamide to the carbonized ammonia brine solution causes an efficiency increase for the discussed conditions up to 22% (Trypuć, 1973).

This increase is mainly caused by the generation of the binary salt $NH_4Cl{\cdot}CO(NH_2)_2$, moving the reaction equilibrium to the side of products, that is, $KHCO_3$ (Trypuć, 1974, 1989; Rimsky, 1960).

Previous research points to the possibility of obtaining $KHCO_3$ by carbonization of water + ammonia solutions, where KCl will be substituted by $KVO_3$. Obtaining $K_2CO_3$ may be presented by the following reaction equations:

$$KVO_3 + NH_3 + CO_2 + H_2O \leftrightarrow NH_4VO_3 + KHCO_3 \qquad (1)$$

$$2KVO_3 + 2NH_3 + CO_2 + H_2O \leftrightarrow 2NH_4VO_3 + K_2CO_3 \qquad (2)$$

As a result of reactions 1 and 2, the sparingly soluble $NH_4VO_3$ salt (solubility at 293 K is 0.050 mol/dm$^3$) precipitates (Trypuć and Kiełkowska, 1996), and $KHCO_3$ or the mixture of $KHCO_3$ and $K_2CO_3$ remains in solution.

For obtaining $Na_2CO_3$ through the carbonization of NaCl ammonia brine, the situation is quite reverse. In this case $NaHCO_3$, the main reaction product (of a relatively high solubility at 293 K−1.20 mol/dm$^3$), precipitates, whereas in the solution $NaHCO_3$ is generated (Niederliński et al., 1978).

To decide on the reaction possibility course, eqs 1 and 2, an equilibrium diagram of the $KVO_3 + NH_4HCO_3 + NH_4VO_3 + KHCO_3 + H_2O$ system in the oblique projection according to Janecki has to be presented. To plot this curve, a knowledge of the reciprocal salt solubility in four three-component systems located on particular sides of the equilibrium diagram square—$KVO_3 + NH_4VO_3 + H_2O$, $KVO_3 + KHCO_3 + H_2O$, $KHCO_3 + NH_4HCO_3 + H_2O$, and $NH_4HCO_3 + NH_4VO_3 + H_2O$—is required.

The position of particular lines separating the planes of salt cocrystallization depending on the degree of carbonization, the size of crystallization plane, and the location of ternary points in the equilibrium diagram is important for our future research work.

It is reported that $KVO_3$ may be obtained from KCl and $V_2O_5$ in the presence of water vapor or oxygen according to the following equations:

$$2KCl + V_2O_5 + H_2O_{(steam)} \rightarrow 2KVO_3 + 2HCl \qquad (3)$$

$$2KCl + V_2O_5 + 0.5O_2 \rightarrow 2KVO_3 + Cl_2 \qquad (4)$$

when the adequate course parameters, e.g., temperature, reaction time, components quantitative ratio, and granulometric composition, are provided (Fotiew et al., 1988).

There appears to be no literature data concerning the $KVO_3 + NH_4HCO_3 + NH_4VO_3 + KHCO_3 + H_2O$ system. Results for the $KVO_3 + NH_4VO_3 + H_2O$ system are very limited. Information on the solubility of pure $KVO_3$ in water is reported as 5.45 mass % at 293 K (Jacenko et al., 1974) and 9.7 mass % at 297 K (Pelch, 1961). The experimental data for the binary system $NH_4VO_3 + H_2O$ have been handled on the basis of the recently published results for the $NH_4HCO_3 + NH_4VO_3 + H_2O$ system (Trypuć and Kiełkowska, 1996). This system represents one side of the equilibrium diagram square $KVO_3 + NH_4HCO_3 + NH_4VO_3 + KHCO_3 + H_2O$ in its oblique projection according to Janecki.

This paper reports the solubility data for the three-component system of $KVO_3 + NH_4VO_3 + H_2O$ versus temperature.

## Experimental Section

The study of the reciprocal solubility of $KVO_3$ and $NH_4VO_3$ in water was performed in the temperature range 293 K to 323 K in order to determine the composition of the equilibrium solutions in the eutonic points saturated

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**Table 1. Solubility in the System $KVO_3 + NH_4VO_3 + H_2O$**

| | $c$/mol·dm$^3$ | | $X^a$ | | composition |
|---|---|---|---|---|---|
| $\rho$/g·cm$^{-3}$ | $KVO_3$ | $NH_4VO_3$ | $KVO_3$ | $NH_4VO_3$ | of the solid phase |
| | | | $T$ = 293 K | | |
| 1.064 | 0.604 | 0.000 | 1.000 | 0.000 | $KVO_3$ |
| 1.062 | 0.592 | 0.012 | 0.980 | 0.020 | $KVO_3$ |
| 1.062 | 0.578 | 0.026 | 0.957 | 0.043 | $KVO_3$ |
| 1.062 | 0.583 | 0.051 | 0.920 | 0.080 | $KVO_3$ |
| 1.063 | 0.568 | 0.089 | 0.864 | 0.136 | $KVO_3$ |
| 1.064 | 0.569 | 0.097 | 0.854 | 0.146 | $KVO_3$, $NH_4VO_3$ |
| 1.060 | 0.499 | 0.093 | 0.843 | 0.157 | $NH_4VO_3$ |
| 1.048 | 0.403 | 0.087 | 0.822 | 0.178 | $NH_4VO_3$ |
| 1.022 | 0.166 | 0.066 | 0.716 | 0.284 | $NH_4VO_3$ |
| 1.001 | 0.000 | 0.050 | 0.000 | 1.000 | $NH_4VO_3$ |
| | | | $T$ = 303 K | | |
| 1.085 | 0.842 | 0.000 | 1.000 | 0.000 | $KVO_3$ |
| 1.081 | 0.811 | 0.034 | 0.960 | 0.040 | $KVO_3$ |
| 1.082 | 0.780 | 0.090 | 0.897 | 0.103 | $KVO_3$ |
| 1.082 | 0.779 | 0.119 | 0.867 | 0.133 | $KVO_3$ |
| 1.083 | 0.778 | 0.144 | 0.844 | 0.156 | $KVO_3$, $NH_4VO_3$ |
| 1.075 | 0.714 | 0.138 | 0.838 | 0.162 | $NH_4VO_3$ |
| 1.049 | 0.415 | 0.112 | 0.788 | 0.212 | $NH_4VO_3$ |
| 1.021 | 0.170 | 0.095 | 0.641 | 0.359 | $NH_4VO_3$ |
| 1.002 | 0.000 | 0.074 | 0.000 | 1.000 | $NH_4VO_3$ |
| | | | $T$ = 313 K | | |
| 1.121 | 1.176 | 0.000 | 1.000 | 0.000 | $KVO_3$ |
| 1.119 | 1.171 | 0.035 | 0.971 | 0.029 | $KVO_3$ |
| 1.119 | 1.146 | 0.096 | 0.923 | 0.077 | $KVO_3$ |
| 1.118 | 1.137 | 0.118 | 0.906 | 0.094 | $KVO_3$ |
| 1.119 | 1.107 | 0.182 | 0.860 | 0.140 | $KVO_3$ |
| 1.120 | 1.085 | 0.222 | 0.830 | 0.170 | $KVO_3$, $NH_4VO_3$ |
| 1.110 | 1.011 | 0.215 | 0.825 | 0.175 | $NH_4VO_3$ |
| 1.077 | 0.690 | 0.183 | 0.790 | 0.210 | $NH_4VO_3$ |
| 1.042 | 0.364 | 0.149 | 0.710 | 0.290 | $NH_4VO_3$ |
| 1.019 | 0.171 | 0.127 | 0.574 | 0.426 | $NH_4VO_3$ |
| 1.002 | 0.000 | 0.105 | 0.000 | 1.000 | $NH_4VO_3$ |
| | | | $T$ = 323 K | | |
| 1.171 | 1.768 | 0.000 | 1.000 | 0.000 | $KVO_3$ |
| 1.169 | 1.760 | 0.038 | 0.979 | 0.021 | $KVO_3$ |
| 1.169 | 1.723 | 0.092 | 0.949 | 0.051 | $KVO_3$ |
| 1.167 | 1.687 | 0.140 | 0.923 | 0.077 | $KVO_3$ |
| 1.167 | 1.601 | 0.251 | 0.865 | 0.134 | $KVO_3$ |
| 1.166 | 1.571 | 0.303 | 0.838 | 0.162 | $KVO_3$ |
| 1.166 | 1.543 | 0.341 | 0.819 | 0.181 | $KVO_3$, $NH_4VO_3$ |
| 1.130 | 1.181 | 0.297 | 0.799 | 0.219 | $NH_4VO_3$ |
| 1.075 | 0.689 | 0.240 | 0.742 | 0.258 | $NH_4VO_3$ |
| 1.042 | 0.381 | 0.197 | 0.659 | 0.341 | $NH_4VO_3$ |
| 1.024 | 0.204 | 0.173 | 0.541 | 0.459 | $NH_4VO_3$ |
| 1.003 | 0.000 | 0.147 | 0.000 | 1.000 | $NH_4VO_3$ |

[a] $X$ is calculated in mole fraction.

toward $KVO_3$ and $NH_4VO_3$ and also to determine the composition of the solutions remaining in equilibrium with the $KVO_3$ precipitate and the $NH_4VO_3$ precipitate.

***Materials.*** $KVO_3$ (98%, Aldrich Chemical Co. Inc., Milwaukee, WI) and $NH_4VO_3$ (>99%; chloride maximum 0.002%, sulfate maximum 0.005%, phosphate maximum 0.005%, Aldrich Chemicals Co. Ltd., Gillingham, U.K.) were used without any further purification.

The experimental procedure is similar to that in the former paper by Trypuć and Kiełkowska (1996). The suitable mass portion of salts and volume of distilled water were placed into the Erlenmeyer flasks, each of 100 cm$^3$ capacity.

The flasks, equipped with magnetic stirrers and closed with rubber stoppers, were placed in a thermostat. The solutions were constantly stirred for 168 h to achieve the saturation. The temperature was monitored using the mercury thermometer with an accuracy of ±0.1 K. After the set time limit, stirring was discontinued in order to sediment the precipitate.

The clear solution was sampled to the calibrated, at a given temperature, Ostwald pycnometer. To check the accuracy of determining the solution density, a densimeter DA-110 M by METTLER-TOLEDO (Switzerland) was employed. In the both cases the accuracy of density measurements was estimated to be within ±0.002 g·cm$^{-3}$.

The solution from the pycnometer was then sampled quantitatively to the graduated flask of 500 cm$^3$ capacity and filled with distilled water. The solution obtained was used to determine the concentration of potassium, metavanadate, and ammonium ions.

The concentration of potassium ions was determined using the balance method in the form of potassium tetraphenylborate (Furman, 1962). It was necessary to eliminate $NH_4^+$ ions before the final determination of the $K^+$ ions concentration because of the partial precipitation of the ammonium tetraphenylborate. The mean determination error was constant within 0.1%.

The concentration of metavanadate ions was determined by the manganometric method in the presence of $H_2SO_4$, after reducing the ions of vanadium(V) to vanadium(IV) employing the solution of iron ammonium sulfate (Mohr's salt) (Furman, 1962; Williams, 1985). The average relative error of the determination was less than 1%.

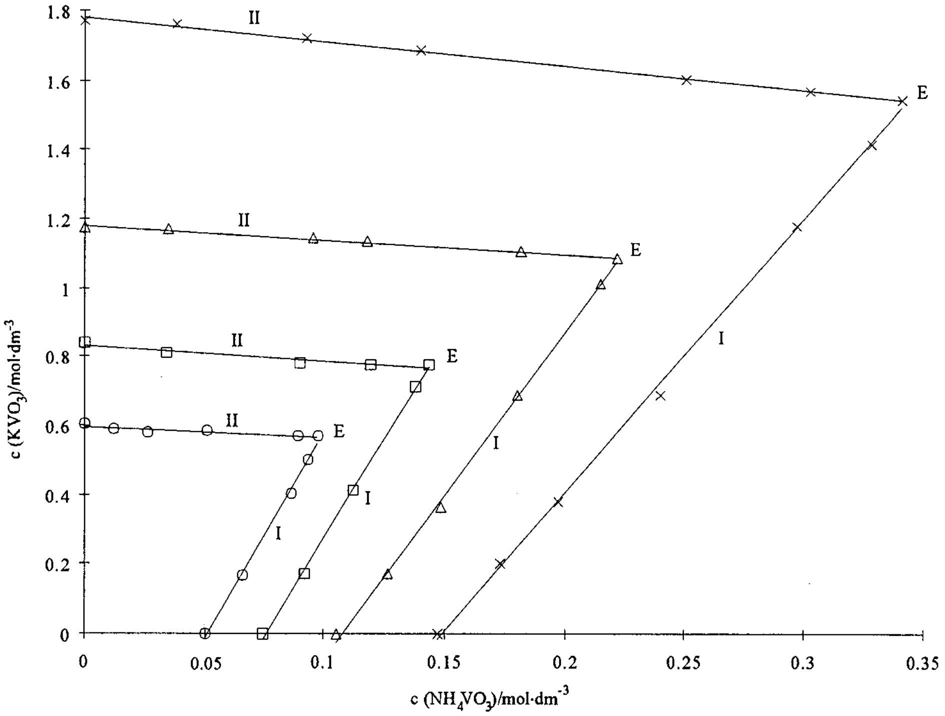

**Figure 1.** Solubility of $NH_4VO_3$ and $KVO_3$ in the $KVO_3 + NH_4VO_3 + H_2O$ system: (○) $T = 293$ K ; (□) $T = 303$ K ; (△) $T = 313$ K; (×) $T = 323$ K.

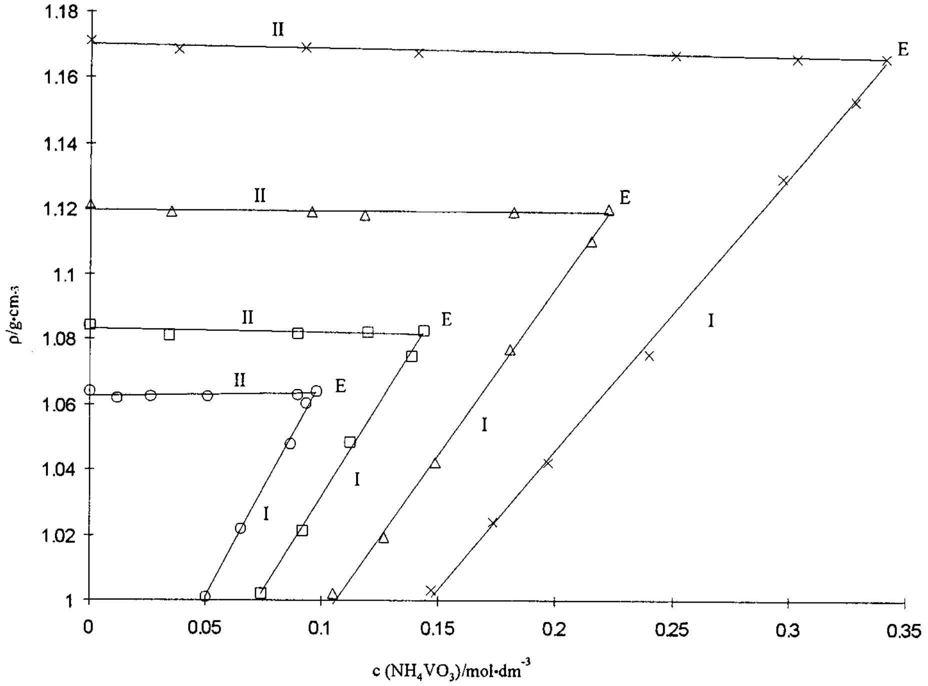

**Figure 2.** Density–concentration relationships of $NH_4VO_3$ in the $KVO_3 + NH_4VO_3 + H_2O$ system: (○) $T = 293$ K ; (□) $T = 303$ K ; (△) $T = 313$ K; (×) $T = 323$ K.

The concentration of ammonium ions was estimated on the basis of the ion balance outcome. To minimize the uncertainties in the calculated results, random sample analyses of determining the ammonium ions' concentration by the distillation method with the addition of Devarda's alloy were applied. The presence of this alloy protected $NH_4^+$ ions from being oxidized to $N_2$ in the presence of $VO_3^-$ under the given laboratory conditions (Struszyński, 1954). The average relative error of the determination was less than 1%.

The identification of the solid phase in the equilibrium state with the solutions was carried out by an X-ray diffractometer HZG-4/A-2 (former GDR) using Cu Kα radiation. The basis of X-ray analysis was the distribution curves of the dispersed radiation intensity $I = f(\theta)$, conducted with continuous registration at the speed of angle arm shift of 1 deg/min.

Additionally, derivatographic analyses of the precipitates being in equilibrium with the examined solutions—$KVO_3$, $NH_4VO_3$, and $KVO_3 + NH_4VO_3$—were made in order to compare both obtained curves DTA and DTG with those for the initial compounds used for the preparation of the solutions. The analyses were conducted on a derivatograph MOM (Budapest, Hungary).

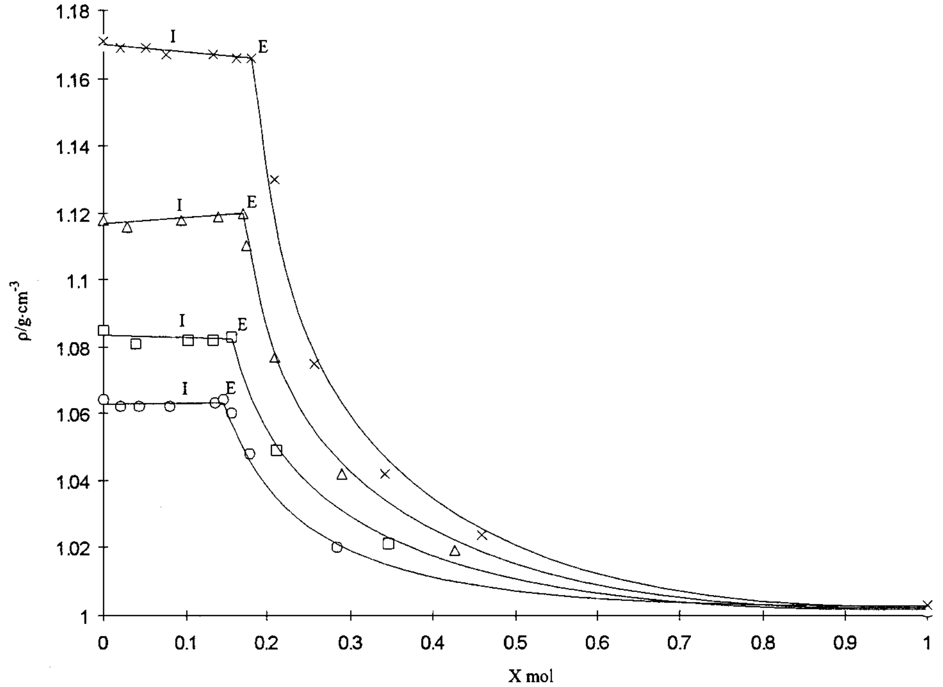

**Figure 3.** Density–mole fraction relationships of $NH_4VO_3$ in the $KVO_3 + NH_4VO_3 + H_2O$ system: (○) $T = 293$ K ; (□) $T = 303$ K ; (△) $T = 313$ K; (×) $T = 323$ K.

## Results and Discussion

The results concerning the salts solubility from the chemical analysis of the solutions are shown in Table 1. The concentration of each solution component is given both in mol/dm$^3$ and mole fractions. Table 1 presents also the solid-phase composition being in equilibrium with the studied solutions. The experimental values provided the basis for plotting a polytherm section of the examined solubility system, as shown in Figure 1.

The course of branch I of isotherms corresponding to the saturated solutions toward $KVO_3$ salt indicates, in the selected range of temperatures, that the $KVO_3$ concentration in solutions in the presence of $NH_4VO_3$ slightly decreases toward the eutonic points.

The difference between the $KVO_3$ concentrations for the $KVO_3 + H_2O$ system and that in the eutonic point E increases with temperature. It amounts adequately to 0.035 mol/dm$^3$ for 293 K, 0.064 mol/dm$^3$ for 303 K, and 0.084 mol/dm$^3$ for 313 K, to reach 0.225 mol/dm$^3$ for 323 K.

The observed increase of the $KVO_3$ solubility in water shows obvious linearity. The increase of the $KVO_3$ concentration together with temperature is accordingly 0.220, 0.345, and 0.599 mol/dm$^3$ per 10° interval.

The course of branch II for each particular isotherm, corresponding to the saturated solutions toward $NH_4VO_3$ salt, indicates that together with the temperature rise the solubility of $NH_4VO_3$ in the presence of $KVO_3$ shows a significant increase toward the eutonic points. The difference in the $NH_4VO_3$ concentrations for the eutonic point E and in the $NH_4VO_3 + H_2O$ system amounts to 0.047 mol/dm$^3$ for 293 K, 0.070 mol/dm$^3$ for 303 K, 0.117 mol/dm$^3$ for 313 K, 0.194 mol/dm$^3$ for 323 K. As compared to the growth of the $NH_4VO_3$ solubility in pure water according to temperature, it is small and amounts 0.024, 0.031, and 0.042 mol/dm$^3$ per 10°.

The similar situation of $NH_4VO_3$ salting-in effect in the presence of a common ion was observed for the formerly examined $NH_4HCO_3 + NH_4VO_3 + H_2O$ system (Trypuć and Kiełkowska, 1996) and the $NaVO_3 + NH_4VO_3 + H_2O$ system (Trypuć and Kiełkowska, 1997). In those cases the effect of salting-in was much higher due to better solubility of $NH_4HCO_3$ or $NaVO_3$ as compared to $KVO_3$.

The increase of the $NH_4VO_3$ solubility in the presence of $KVO_3$ for the technological assessment purposes will not influence the vanadium losses. According to eq 1, during the carbonization process of water + ammonia solutions of $KVO_3$, the concentration of $KVO_3$ will decrease and there will be no further influence of $KVO_3$ on the $NH_4VO_3$ solubility.

The minimum salting-out effect for $KVO_3$ in the presence of $NH_4VO_3$, with the rise of temperature, will not have a considerably high influence on the course of reaction 1 between $KVO_3$ and $NH_4HCO_3$, in which $NH_4VO_3$ (as a precipitate of a relatively low solubility) and $KHCO_3$ (remaining in the solution) are generated.

Using data presented in Table 1, in Figure 2 the relation between the solution density and the concentration of $NH_4VO_3$ salt is shown for the given range of temperatures.

The above-presented dependence as a function of $NH_4VO_3$ concentration results from the fact that the $KVO_3$ concentration at the points located on branch I of the isotherms depends very little on the concentration of $NH_4VO_3$, whereas the concentration of $NH_4VO_3$ for the points located on the branches corresponding to the saturation with $NH_4VO_3$ salt (branch II) increases rapidly with the rise of the $KVO_3$ concentration in the solution.

The linear mode of these changes in the solution's density depending on the $NH_4VO_3$ concentration indicates that in the system there are no changes related to the creation of a new solid phase.

In the connected literature data (Sułajmankułow, 1971; Trypuć, 1989), the equilibrium diagrams property-composition type are used to identify the generated binary salts or addition compounds.

In the case of constructing a new solid phase on the curves presenting the density change with the concentration of components, given in mole fractions, some visible inflections or the dashed line at points corresponding to the creation of a new addition will appear.

Using the values of mole fractions of $KVO_3$ and $NH_4VO_3$ and solution's density presented in Table 1, their reciprocal dependency is shown in Figure 3. The courses of the plots obtained indicate that the solution density rises monotonically with the rise of the $KVO_3$ concentration in the solution toward the eutonic point E. Then it slightly changes and reaches the value corresponding to the saturated $KVO_3$ solution. The course of curves in Figure 3 does not indicate that a new solid phase is created in the system examined.

This fact is proved by the results of the conducted X-ray and derivatographic analyses of the solid phases. The use of these methods in the precipitates analysis showed clearly the composition of the solid phase coexisting with the equilibrium solutions in the system examined. The analyses confirmed that $KVO_3$ or $NH_4VO_3$ existed only for the specific points of branches I and II, as well as $KVO_3$ and $NH_4VO_3$ at eutonic points E of the drawn isotherms of the $KVO_3 + NH_4VO_3 + H_2O$ system.

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