Physico-chemikal properties of a system $\text{H}_2\text{O}-\text{H}_2\text{SO}_4-\text{Al}_2(\text{SO}_4)_3 \times 18\text{H}_2\text{O}$

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Abstract. In this paper, the concentration and temperature dependences of the density and the viscosity of a system $\text{H}_2\text{O}-\text{H}_2\text{SO}_4-\text{Al}_2(\text{SO}_4)_3 \times 18\text{H}_2\text{O}$ in the temperature range of 20-50°C were studied. The sulfuric acid concentration was varied from 2 to 40 wt %, the aluminum sulfate content in the system was varied from 5 to 30 wt %. The viscosity was determined by high precision capillary viscometry, the density was determined by pycnometry. The formulated regression equations can be used for the calculation of the density and the viscosity at different salt and acid concentrations and at different temperatures with the accuracy sufficient for practical purposes, and the results can be presented as reference data.

1. Introduction

The properties of electrolyte solutions are studied by different methods based on the changes in compressibility, density, viscosity, electroconductivity, permittivity, diffusion coefficients, X-ray scattering, registration of nuclear magnetic and electron paramagnetic resonance, etc. In [1], the latest achievements in modeling the thermodynamic and transport properties of solutions are analyzed. The current research is primarily focused on the determination of the microstructure characteristics of solutions (hydration shell of ions, bond energy between particles), the evaluation of the changes in the properties of systems under varying outer conditions. The comparison of these multiple data and the discussion, on a whole, can give a more appropriate understanding of the nature of interaction in solutions. The absence of these data impedes the development of the right understanding of the ion close environment formation mechanism.

There are available data on the density and the viscosity of aqueous solutions of aluminum sulfate [2] in a wide concentration range at the temperature of 273–373 K. The electroconductivity of a sulfuric acid solution of aluminum and hydrochloric acid solution of magnesium is determined [3,4]. There are data on the physico-chemical properties of some binary electrolyte solutions [5,6]; however, there are no available density and viscosity data for a ternary system $\text{H}_2\text{O}-\text{H}_2\text{SO}_4-\text{Al}_2(\text{SO}_4)_3 \times 18\text{H}_2\text{O}$ in a wide temperature and concentration range.

The aim of this work is to study the density and the viscosity of ternary solutions $\text{H}_2\text{O}-\text{H}_2\text{SO}_4-\text{Al}_2(\text{SO}_4)_3 \times 18\text{H}_2\text{O}$ at the temperatures of 293–323 K and the concentrations varying from diluted to saturated.
2. Experimental

The density was determined by pycnometry [7]. A clean and dry pycnometer was weighed using an analytical balance with the accuracy of up to 0.0002 g. Then, it was filled with distilled water slightly higher than the mark, plugged with a stopper, and placed in a thermostat. After 20 min of exposure in a thermostat at the temperature of 20 ± 0.1°C, the water level in a pycnometer was rapidly made up to the mark blotting the excess water with a rolled up strip of clean non-fibrous filter paper. A pycnometer was again plugged with a stopper and exposed in a thermostat for another 10 min, after which the correspondence of the fluid level to the mark was checked, a pycnometer was wiped dry from outside with clean soft cloth or filter paper, and allowed to stand for 10 min behind the glass of an analytical balance box; then, it was weighed again. Further, a pycnometer was freed from water, rinsed successively with alcohol and ether, then the ether residue was eliminated by air-blowing, a pycnometer was filled with the tested fluid, and the same operations as with distilled water were performed.

The fluid density was calculated using the following formula

$$\rho_t = \frac{m_3 - m_1}{m_2 - m_1} \left( \rho_D - D \right) + D$$

where $\rho_t$ is the solution density, g/cm³;
$m_1$ is the weight of an empty pycnometer, g;
$m_2$ is the weight of a pycnometer with water, g;
$m_3$ is the weight of a pycnometer with a solution, g;
$\rho$ is the density of water, g/cm³;
$D$ is the density of air, g/cm³;
$t$ is the solution temperature, ºC.

The viscosity was varied using a VPZh-1 viscometer designed for varying the kinematic viscosity. Viscometers of this type are the most accurate because their design provides the hanging level of the fluid flow. Thus, the time of fluid flow does not depend on the hydrostatic pressure and the amount of fluid poured into a viscometer. The viscosity measurement is based on the determination of the time of outflow of the fluid volume from a measuring tank through a capillary [7].

The kinematic viscosity is determined using the following formula

$$v = \frac{g}{9807} \tau K$$

where $v$ is the kinematic viscosity, mm²/s; $g$ is the acceleration of gravity, m/s²; $K$ is the viscometer constant, mm²/s; $\tau$ is the arithmetic mean time of outflow of a solution in a viscometer, s.

The kinematic viscosity was calculated with the accuracy to four significant figures.

Further, the dynamic viscosity was calculated using the following formula

$$\eta = \nu \rho$$

The physico-chemical properties of a ternary system H₂O-H₂SO₄-Al₂(SO₄)₃ × 18H₂O were studied by varying the H₂SO₄ concentration from 2 to 40 wt % and the Al₂(SO₄)₃ concentration from 5 to 30 wt %. The experimentally determined density values are given in Table 1.

**TABLE 1. Dependence of density ($\rho \times 10^3$, kg/m³) of ternary solutions on the concentrations of components at 20°C**

| Concentration of Al₂(SO₄)₃×18H₂O, | Concentration of H₂SO₄, wt % |
|----------------------------------|-------------------------------|
| 2                               | 5                             |
| 5                               | 10                            |
| 10                              | 15                            |
| 15                              | 20                            |
| 20                              | 25                            |
| 25                              | 30                            |
| 30                              | 40                            |
### Table 2: Dependence of viscosity ($\eta \times 10^3$, Pas) of ternary solutions on the concentrations of components at 20°C

| Concentration of $\text{Al}_2\text{(SO}_4\text{)}_3 \times 18\text{H}_2\text{O}$, wt % | Concentration of $\text{H}_2\text{SO}_4$, wt % |
|---------------------------------|-------------------------------|
| 5                              | 2   | 5   | 10  | 15  | 20  | 25  | 30  | 40  |
| 1.1982                         | 1.2793 | 1.3902 | 1.5424 | 1.7135 | 1.9203 | 2.1866 | 2.8378 |
| 1.4848                         | 1.5439 | 1.6723 | 1.8344 | 2.0747 | 2.3151 | 2.6274 | 3.4689 |
| 1.8278                         | 1.9280 | 2.0434 | 2.2949 | 2.5746 | 2.8949 | 3.3092 | -   |
| 2.0526                         | 2.2524 | 2.4938 | 2.7588 | 3.3517 | 3.6937 | 4.1881 | -   |
| 3.0865                         | 3.3842 | 2.5676 | 3.8751 | 4.1269 | 4.7765 | -     | -   |
| 4.4848                         | 4.6813 | 4.8618 | 5.2959 | -     | -     | -     | -   |

**Empirical coefficients**

| Empirical coefficients | A       | B       | D       |
|------------------------|---------|---------|---------|
| 2                      | 0.0060  | 0.0058  | 0.0861  |
| 1                      | 0.0056  | 0.0059  | -       |
| 0.0037                 | 0.0049  | 0.0044  | 0.1260  |
| 0.0065                 | 0.0112  | 0.0065  | 0.0236  |
| 0.0062                 | 0.0062  | 0.0062  | 1.9600  |

The solution viscosities can be determined using the following equation

$$\eta = ac^2 + bc + d$$

where $c$ is the salt concentration, wt %;

$a$, $b$, $d$ are the empirical coefficients depending on the nature of a system and the acid concentration.
For example, for a ternary solution with the acid concentration of 15 wt % and the salt concentration of 5 wt %, the viscosity can be calculated using the following equation: $\eta = 0.0059 \times 5^2 + (-0.062) \times 5 + 1.773 = 1.6105$ Pa.s.

For a solution containing 10 wt % $\text{Al}_2(\text{SO}_4)_3 \times 18\text{H}_2\text{O}$ in a 20 wt % sulfuric acid solution, $\eta = 0.0037 \times 10^2 + 0.012 \times 10 + 1.564 = 2.054$ Pa.s.

The resulting regression equations can be used for the calculation of the dynamic viscosity values of solutions with the accuracy sufficient for practical purposes, the relative error being within 4%.

The influence of temperature on the considered system was studied for a solution containing 5% $\text{H}_2\text{SO}_4$. The density and the viscosity of a system $\text{H}_2\text{O}-\text{H}_2\text{SO}_4-\text{Al}_2(\text{SO}_4)_3 \times 18\text{H}_2\text{O}$ was studied in the temperature range of 20-50°C. The experimental data are given in Table 3.

### Table 3: Density and viscosity of $\text{H}_2\text{O}-\text{H}_2\text{SO}_4-\text{Al}_2(\text{SO}_4)_3 \times 18\text{H}_2\text{O}$ in the temperature range of 293-323 K ($C_{\text{H}_2\text{SO}_4} = 5\%$)

| Concentration of $\text{Al}_2(\text{SO}_4)_3 \times 18\text{H}_2\text{O}, \text{wt }\%$ | 293 | 303 | 313 | 323 |
|---|---|---|---|---|
| $\rho, 10^3 \text{kg/m}^3$ | $\eta, 10^3 \text{Pa}s$ | $\rho, 10^3 \text{kg/m}^3$ | $\eta, 10^3 \text{Pa}s$ | $\rho, 10^3 \text{kg/m}^3$ | $\eta, 10^3 \text{Pa}s$ | $\rho, 10^3 \text{kg/m}^3$ | $\eta, 10^3 \text{Pa}s$ |
| 5 | 1.0500 | 1.2793 | 1.0457 | 0.9894 | 1.0417 | 0.7866 | 1.0373 | 0.6498 |
| 10 | 1.0830 | 1.5439 | 1.0746 | 1.1796 | 1.0698 | 0.9312 | 1.0654 | 0.7581 |
| 15 | 1.1093 | 1.9280 | 1.1064 | 1.5027 | 1.1020 | 1.1448 | 1.0962 | 0.9202 |
| 20 | 1.1396 | 2.2524 | 1.1390 | 1.9164 | 1.1350 | 1.4701 | 1.1295 | 1.1490 |
| 25 | 1.1732 | 3.3842 | 1.1729 | 2.6276 | 1.1684 | 1.9145 | 1.1635 | 1.4810 |
| 30 | 1.2083 | 4.6813 | 1.2050 | 3.6875 | 1.2046 | 2.7066 | 1.1996 | 2.0621 |

The results show that the density and the viscosity of solutions depend significantly on the salt concentration and, under the temperature increase, the density and the viscosity values of solutions of the same concentration decrease.

The equations for the temperature dependence of the density and the viscosity of solutions were formulated. These equations are given in Table 4.

### Table 4: Equations of the temperature dependence of density and viscosity

| Concentration of $\text{Al}_2(\text{SO}_4)_3 \times 18\text{H}_2\text{O}, \text{wt }\%$ | Type of equation | Correlation coefficient |
|---|---|---|
| 5 | $\rho = -0.0004t + 1.0584$ | 0.999 |
| | $\eta = 0.0004t^2 - 0.0477t + 2.0793$ | 0.999 |
| 10 | $\rho = -0.0006t + 1.0934$ | 0.974 |
| | $\eta = 0.0005t^2 - 0.0595t + 2.541$ | 0.999 |
| 15 | $\rho = -0.0004t + 1.1188$ | 0.979 |
| | $\eta = 0.0005t^2 - 0.0689t + 3.1093$ | 0.999 |
| 20 | $\rho = -0.0003t + 1.1478$ | 0.905 |
| | $\eta = 4E-05t^2 - 0.0402t + 3.0527$ | 0.996 |
| 25 | $\rho = -0.0003t + 1.1813$ | 0.904 |
| | $\eta = 0.0008t^2 - 0.1208t + 5.4883$ | 0.999 |
| 30 | $\rho = -0.0003t + 1.2137$ | 0.909 |
| | $\eta = 0.0009t^2 - 0.1495t + 7.3384$ | 0.999 |
In these dependences, the temperature is expressed in degrees Celsius, the density is expressed in kg/m³, and the viscosity is expressed in Pa.s.

Using these equations, the density and the viscosity of solutions can be calculated for a wide temperature range in the studied concentration interval.

3. Results and discussion

The experimental density and viscosity values for a ternary system H₂O-H₂SO₄-Al₂(SO₄)₃ × 18H₂O were determined in a wide range of solution concentrations (the H₂SO₄ concentration was varied from 2 to 40%, the Al₂(SO₄)₃ concentration was varied from 5 to 30 wt %) and in the temperature range of 293–323 K. The research results can be used as reference data.

It was established that, under the increase in the concentrations of both aluminum sulfate and sulfuric acid, the density and the viscosity of solutions increase. The density dependence is linear while the viscosity dependence on the concentration is non-linear. However, it is noteworthy that the Al₂(SO₄)₃ content affects the change in the density and the viscosity of solutions more significantly.

The comparison of the resulting data with the values in [2] shows that the density and the viscosity of binary aluminum sulfate solutions is higher than the density and the viscosity of ternary solutions containing free sulfuric acid.

This is, probably, caused by the fact that, in dilute solutions, outer sphere complexes [Al(H₂O)₅]SO₄⁺ are formed. In addition, dimers [Al₂(H₂O)₈(OH)₂]₄⁺ and more complex particles can be formed. The formation of such large structural molecules increases the density and the viscosity. In ternary systems including H₂SO₄, the possibility of the dimer formation decreases, which leads to the decrease in the values of the mentioned physico-chemical properties.

Hence, the temperature dependences of the density and the viscosity were studied, and it was shown that, under the temperature increase, the numerical values of the studied properties decrease.

The equations were proposed that can be used for the calculation of the density and the viscosity under different salt and acid concentrations and for different temperatures with the accuracy sufficient for practical purposes.

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