Evaporation of non-ideal binary solution drops

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Abstract. The study of the evaporation process of multicomponent liquid droplets was carried out in the work. In the simulation and experiments, an aqueous solution of ethanol of various concentrations, which is a binary non-ideal mixture with known physicochemical properties, was used as a mixture. The deviation of the solution properties from ideal was taken into account using the generalized dependence of the pressure of vapor components saturated above the solution on their concentration in the solution. Using an example of an aqueous ethanol solution, a deviation of the change in the diameter of the droplets from the “law d2” was shown, which is associated with a two-speed evaporation mode. During evaporation at a low concentration of ethanol, the temperature of the droplet was close to the temperature of adiabatic evaporation of water; at a high concentration of ethanol, it was close to the temperature of adiabatic evaporation of ethanol. Comparison of the results of the simulation with experiment showed satisfactory agreement.

1. Introduction
Evaporation of multicomponent droplets is an urgent scientific and applied problem. This problem has a direct connection with a number of industrial technologies. Among them are the production of pure components from liquid mixtures, the catalytic purification of air from harmful impurities, the production of alternative energy carriers, and the burning of fuel mixtures. Despite the prevalence of applications and increased interest in issues of heat and mass transfer during evaporation of a mixture of liquids, the problem remains poorly understood [1]. A large proportion of the work is devoted to high-temperature processes. There are also very few studies that consider the thermal state of a multicomponent evaporating drop throughout its lifetime. It should be noted that in most experimental studies, as a rule, only a change in the geometric parameters of the droplets is considered. To complete the analysis of the process of evaporation of droplets, it is also necessary to obtain the change in temperature.

In this paper, the study of evaporation of droplets of multicomponent liquids was conducted under conditions close to normal. In theoretical modeling and experiments, an aqueous solution of ethanol of various concentrations was used, which is a binary non-ideal mixture with known physicochemical properties [2]. The deviation of the properties of solution from the ideal was taken into account using empirical data for an aqueous solution of ethanol. The generalized dependence of the vapor pressure of the components above the solution on their concentration was used in the work. This dependency was obtained by processing tabular data. In the numerical simulation, the dependences of evaporation rates of the components of solution on time were obtained, and the influence of environmental humidity on the dynamics of evaporation of a multicomponent drop was considered.
2. Physical formulation of the problem

The basis of the physico-mathematical model is the concept of quasi-stationary evaporation of single free liquid droplets in an unlimited vapor-gas medium, the components of which obey the laws of an ideal gas. A relatively low mass transfer rate is assumed. As a result, the independence of the total concentration of the vapor-gas mixture from the distance to the drop is allowed. This differs significantly from the hypothesis of constant gas-vapor mixture density [3]. The model assumes that the process of evaporation of a drop of variable composition is due to diffusion of vapors in a non-condensable gas, free convection, and also Stefan flow induced by evaporation. It is believed that the process of diffusion of components in the gas phase is described by Fick law. The intensity of heat transfer on the surface of a sphere of constant diameter is taken in accordance with the empirical Rantz-Marshall relation for free convection [4]:

\[
\text{Nu}_h = 2 + 0.6 \text{Gr}^{1/4} \text{Pr}^{1/3},
\]

where \( \text{Gr} \) is the Grashof number and \( \text{Pr} \) is the Prandtl number for the surrounding gaseous medium. The modification of heat transfer with regard to induced flows around a drop is carried out within the framework of the Abramzon and Syrignano film evaporation model [5]:

\[
\text{Nu} = 2 + \frac{\text{Nu}_h - 2}{F(B_T)},
\]

where the correction factor \( F \) is determined according to

\[
F(B_T) = (1 + B_T)^{0.3} \ln(1 + B_T) / B_T.
\]

The Spalding number for temperature is here defined in the usual way

\[
B_T = c_p \cdot (T - T_\infty) / L,
\]

where \( c_p \) is the specific heat capacity of the solution, \( L \) is the latent heat of evaporation at the current temperature of the solution.

The model equations expressing the law of conservation of the amount of a substance for each component of the solution are written in accordance with the general approach developed in the works of Tonini and Cossali [6 - 8]. Accounting for the effect of free convection on the mass transfer process, in contrast to their work, is carried out at the stage of formulating and writing the original equations using the Sherwood numbers of components

\[
\text{Sh}_k = 2 + \frac{\text{Sh}_h^k - 2}{F(B_h^k)},
\]

where the Sherwood component number for a sphere of constant radius is

\[
\text{Sh}_h^k = 2 + 0.6 \text{Gr}^{1/4} \text{Sc}_k^{1/3}.
\]

The Schmidt number \( \text{Sc}_k \), like the Grashof number, is calculated from the parameters of the corresponding component. The Spalding number \( B_M \) for the mass is calculated according to the expression:

\[
B_M = \left( \sum \frac{m_k - m_k^\infty}{m_k^\infty} \right) / \left( 1 - \sum m_k^\infty \right),
\]

where \( m_k \) is the mass fraction of the k-th gaseous component near the surface of a drop of radius \( R \), and \( m_k^\infty \) is the mass fraction of the k-th gaseous component at an infinite distance from it. Taking into account the above, the molar rate of evaporation of the components is expressed as follows:

\[
\dot{z}_k = \frac{\text{Sh}_k}{2} \dot{z}_k^{df},
\]

where \( \dot{z}_k^{df} \) is the evaporation rate of the k-th component with only the diffusion transfer mechanism taken into account. The droplet evaporation rate is the sum of the component evaporation rates:

\[
\dot{z} = \sum \dot{z}_k.
\]

To determine \( \dot{z} \) we have the following nonlinear equation:
\[ \sum_{k} \frac{Sh_{k}}{2} \cdot \frac{Y_{k}^{R} - Y_{k}^{-}}{1 - e^{\gamma_{k}^{i}}} = 1 - \sum_{k} \frac{Sh_{k}}{2} \cdot Y_{k}^{-}, \]

where \( Y_{k}^{R} \) is the mole fraction of the k-th component in the gas phase near the surface of a drop of radius \( R \), \( Y_{k}^{-} \) is the mole fraction of the k-th component in the gas phase at an infinite distance from it. The value of the coefficient \( \gamma_{k} \) in the exponent is calculated by the formula

\[ \gamma_{k} = \frac{1}{4\pi D_{k} R} \]

Here, \( D_{k} \) is the diffusion coefficient of the k-th component in a gaseous medium; \( \nu \) is the molar concentration of the vapor – gas mixture. Using the evaporation rate of the entire solution \( \dot{z} \), the evaporation rate of each component is written as

\[ \dot{z}_{k} = \frac{Sh_{k}}{2} \cdot \frac{Y_{k}^{R} - Y_{k}^{-} e^{\gamma_{k}^{i}}}{1 - e^{\gamma_{k}^{i}}} \]

For a single-component droplet, the equation for the definition of \( \dot{z} \) becomes simpler and takes the form:

\[ \dot{z} = 4\pi \nu DR \cdot \ln \left( \frac{1 - \frac{Sh}{2} Y_{k}^{R}}{1 - \frac{Sh}{2} Y_{k}^{-}} \right) \]

The following simplification is obtained if we make the assumption that the molar fractions of the vapor component in the gas medium around the drop are small: \( \frac{Sh}{2} Y_{k}^{R} \ll 1 \) and \( \frac{Sh}{2} Y_{k}^{-} \ll 1 \). In this case, using the decomposition under the sign of the logarithm, we obtain the well-known formula for the evaporation rate according to the Maxwell diffusion model [4]:

\[ \dot{z} = 2\pi \nu DSh \cdot (Y_{k}^{R} - Y_{k}^{-}) \]

When simulating evaporation, diffusion in the liquid phase, as well as hydrodynamics flows inside the droplet, is neglected. The drop is assumed to be uniform in temperature and composition. The deviation of the properties of an aqueous solution of ethanol from ideality was taken into account using empirical data. For this, the tabular dependences of the ethanol vapor pressure over aqueous solutions of various concentrations were used [1]. The tabulated vapor pressure values were normalized to the saturation pressure at the corresponding temperature value. Then averaging was performed over all the obtained curves. The result of processing is presented in Figures 1a and 1b, respectively. The solid lines 1 in the figures are approximations of the dependences of the averaged

![Figure 1](image.png)

**Figure 1.** Generalized dependences of the vapor pressure of ethanol (a) and water (b) on the mole fraction of ethanol \( X_{eth} \) in solution with various temperatures.
values of pressure by polynomials of the fifth degree, dotted lines 2 show these dependences if the ethanol solution in water was ideal and obeyed the Raoul law. As a result of such data processing, the generalized empirical dependence of the vapor pressure of ethanol and water above the solution surface on the molar fraction of ethanol in the liquid phase for various temperatures was obtained.

The above assumptions about a droplet allow us to consider it as an object with lumped parameters, the thermal state of which can be characterized by the average temperature. To determine the temperature of a drop, the energy conservation law is used. At the same time, in the model, accounting for radiant heat transfer is carried out as for a “gray” body:

\[ Mc \frac{dT}{dt} = (L + c \cdot (T_\infty - T)) \frac{dM}{dt} + 2\pi \lambda R \cdot Nu \cdot (T_\infty - T) + 4\pi \varepsilon \sigma R^2 \cdot (T^4 - T_\infty^4). \]

Here \( M \) is the current value of the drop mass, \( c \) is the current value of the specific heat capacity of a solution of variable composition, \( \varepsilon \) is the “grayness” factor of the solution, \( \lambda \) is the thermal conductivity coefficient of the gaseous medium, \( T \) is the droplet temperature, \( T_\infty \) is the ambient temperature.

3. Results and discussion

A theoretical and experimental study of the evaporation of droplets of non-ideal two-component solutions was carried out. Water and ethanol, which are able to be mixed in an arbitrary ratio, were used as components of the solution. This allows us to set any necessary initial concentration of ethanol in solution for the study. The temperature and humidity conditions of the environment corresponded to a temperature range of 20–26°C and relative humidity of 3–10%. The calculations determined the evaporation time, size, as well as the current composition and temperature of the evaporating droplets. The results of calculations of the dynamics of evaporation of droplets with an initial diameter \( d_0 = 2.1 \) mm at an ambient air temperature of 20°C and relative humidity of 10% are shown in Figure 2. Here and below, in the graphs, time \( t \) is normalized to the time of evaporation of a drop of the same size entirely composed of water, calculated using the Maxwell diffusion model [4]. The initial concentration of ethanol in the solution varied in the analysis. The linear dependence of the square of the droplet diameter on time, well known as the “d^2 law”, was observed only for a single-component drop. In the figure, it corresponds to line 1, which shows the course of evaporation of a drop of pure water without ethanol admixture. As follows from the figure, the deviation from linearity becomes noticeable when the initial mass fraction of ethanol in the solution exceeds 5%. With an increase in the initial content of ethanol in the solution, the two-rate character of droplet evaporation becomes more

![Figure 2](image-url)

**Figure 2.** Change in the relative square of the droplet diameter for an evaporating droplet with \( d_0 = 2.1 \) mm in air at a temperature of 20°C and relative humidity of 10%:

1 – water, 2–5% ethanol (mas.), 3–20%, 4–40%, 5–60%, 6–80%.
noticeable. A characteristic bend on the graphs (lines 5 and 6), which corresponds to a rather drastic change in the evaporation rate towards its decrease, is observed in the final part of the existence of droplets with ethanol content of more than 60% (mass). An increase in the ethanol content in the solution resulted in a decrease in the evaporation time of the drop.

The effect of ethanol concentration in a drop on its temperature during evaporation under the same conditions as above is shown in Figure 3. Line 1 here corresponds to a single-component drop of water. As it can be seen from the figure, at the first stage of evaporation, a drop of water quickly cools down to the temperature of adiabatic evaporation. In this state, the drop can be relatively long. Adding ethanol to the solution lowers the temperature of the drop relative to line 1. In the limit, its value tends to an adiabatic evaporation temperature for pure ethanol. Thus, all the dependences of the temperature of droplets on time, which correspond to different initial concentrations of ethanol in the solution, are in the range between the values of temperatures of adiabatic evaporation of pure ethanol $T_{wtr}^{ad}$ and water $T_{wtr}^{ad}$. For example, line 6 in the figure demonstrates that a drop with 80% ethanol content first

![Figure 3](image)

**Figure 3.** Dependence of droplet temperature $d_0 = 2.1$ mm on time during evaporation into air with a temperature of 20°C and relative humidity of 10% at different initial concentrations of ethanol in solution: 1 – water, 2–5% (mas.), 3–20%, 4–40%, 5–60%, 6–80%.

![Figure 4](image)

**Figure 4.** Mole fraction of ethanol in the vapor-gas medium near the surface of the drop (1) with the evaporation of 78% (mass.) of ethanol solution; (2) if the solution evaporated in accordance with the Raoult law.
cools quickly to a temperature close to $T_{\text{adh}}^{\text{eth}}$, and then smoothly, as the composition of the solution changes, approaches the temperature $T_{\text{adh}}^{\text{adT}}$. The change in the vapor–gas composition at the droplet surface during evaporation determined in calculations is shown in Figure 4. The dependence of the mole fraction of ethanol in the gas phase $X_{\text{g}}^{\text{eth}}$ on its mole fraction in the solution liquid $X_{\text{l}}^{\text{eth}}$ is given here. The calculation was carried out for droplets with an initial diameter of 1.6 mm at an ambient temperature of 20°C and relative humidity of 10%. The initial ethanol content in the solution was 78%. The arrow in the figure shows the direction of change in the content of ethanol in a solution of an evaporating droplet from the initial value to the final value.

In the experiments, the evaporation of suspended droplets into a vapor-gas medium with different moisture content was studied. For suspension, polypropylene monofilament with a diameter of 200 μm and low thermal conductivity was used. During evaporation, evaporation time, droplet diameter, and their surface temperature were measured. The droplet sizes were determined by video fixing the image of droplets taken with a digital microscope. The surface temperature of droplets was determined by the contactless method of infrared thermography. Thermograms were filmed with a NEC TH 7102WV camera with an interval of 5 seconds. The paper compares the results of calculations for the proposed model of evaporation of multicomponent droplets with experimental data. Figures 5a and 5b show the experimental results and the calculated temperature dependences of droplets with initial ethanol concentration of 20% (mass.) and 75%, respectively. Droplets with an initial diameter of 1.6 mm were studied at an ambient air temperature of 24°C and relative humidity of 3%.

The comparison showed satisfactory agreement on the evaporation time of the droplets. In addition, the graphs show three characteristic phases of evaporation, which were reported in [9,10] in the study of the evaporation of single-component droplets. In general, when comparing the dependences of the temperature of droplets on time, we can only speak of a certain qualitative correspondence. The reasons for the observed discrepancies may lie in the absence of taking into account the inhomogeneous distribution of ethanol concentration in the droplet volume, the non-stationarity of the evaporation process, and the assumption that the surface temperature at measurements is close to the average one in the droplet volume.
Conclusions
The evaporation of droplets of binary solutions in air at moderate temperatures and low relative humidity was considered in the work. Studies on the example of an aqueous solution of ethanol showed a deviation from the “d^2 law”. It is associated with a two-speed regime of evaporation of the solution. When the concentration of ethanol in the solution is significant, it makes the greatest contribution to the change in the amount of a droplet substance during evaporation, since its evaporation rate is higher. The observed deviation from linearity is the result of the fact that the more volatile component (ethanol) is primarily predominantly vaporized. When its concentration in the solution falls, the evaporation of water begins to give the prevailing contribution to the change in the mass of the droplet.

With a low ethanol concentration, the droplet temperature during evaporation is close to the adiabatic evaporation of water for ambient conditions, with a high ethanol concentration, it is close to the adiabatic evaporation temperature of ethanol. All temperature dependences for intermediate ethanol concentrations are within this range.

Comparison of the results of mathematical modeling of evaporation of a drop of an aqueous solution of ethanol with experiment showed satisfactory agreement. To accurately describe the nature of changes in the temperature of droplets, it is necessary to modify the quasi-stationary model of evaporation and take into account the non-stationarity of the process, heterogeneity of distribution of components over the drop volume, and also the features of the hydrodynamic flows inside the droplet itself.

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