https://doi.org/10.15407/ujpe67.8.592

L.A. BULAVIN, G.M. VERBINSKA, A.V. BRYTAN, YA.O. STEPOWYI

Taras Shevchenko National University of Kyiv, Faculty of Physics
(4b, Akademika Glushkova Ave., Kyiv 03022, Ukraine; e-mail: a_britan@ukr.net)

MODEL FOR EVAPORATION OF DROPLETS OF IDEAL ALCOHOL SOLUTIONS IN DIFFUSIVE AND TRANSIENT REGIMES

The development of models describing the process of evaporation of droplets of various solutions – in particular, alcohol ones – is a difficult task in the general case; namely, it is necessary to solve a system of coupled mass and heat transfer equations. An alternative approach consists in creating a simplified model making allowance for those physical mechanisms that are essential under specific evaporation conditions. On the basis of this approach and in the framework of the Maxwell–Fuchs evaporation theory, a model has been proposed to describe the evaporation process of ideal binary solutions in the diffusive and transient regimes. In order to verify the model, experimental studies were carried out dealing with the evaporation of droplets of binary alcohol solutions (propanol-octanol and butanol-octanol, with initial octanol mole fractions of 0.25, 0.5, and 0.75) in the dry nitrogen atmosphere at a temperature of 293 K in the diffusive and transient regimes. The proposed model was used to calculate the time dependences of the droplet surface area for the researched binary alcohol solutions. The obtained model curves are compared with experimental data. It is shown that, within the validity limits of its approximations, the model can be used to describe the evaporation process both in the diffusive and transient regimes.

Keywords: alcohols, solutions, evaporation regime.

1. Introduction

Currently, studies of the processes taking place at the evaporation of droplets of various liquids and liquid systems, as well as the evaporation processes occurring, when solids are dried, continue to remain a challenging task despite their more than a century's history. This fact is associated with both a wide range of objects for such studies [1–3] and a list, not shorter, of branches in technology and industry, where the results and models obtained in the course of similar studies can find their practical application.

One of the directions, whose the practical significance is extremely important, is the research of the evaporation of alcohols and alcohol solutions [4]. This is so, because alcohols and their solutions play now a substantial role in a lot of technological processes. The application areas of alcohols include their use as solvents for paints, varnishes, and natural and synthetic resins, as well as in manufactures producing leather, textiles, perfumes, and photographic films. Undoubtedly, especially promising is the use of alcohols as a basis for producing new kinds of fuel [5]. That is why the study of the evaporation kinetics of alcohol solutions in various environments under various temperatures and gas pressures, the elucidation of relevant physical mechanisms, and the development of corresponding models comprise today a challenging task.

2. Model of Evaporation Process of Binary Alcohol Solutions in Diffusive and Transient Regimes

The development of models describing the process of evaporation of solution droplets – in particular, droplets of alcohol solutions – is a difficult task in the general case. For its solution, it is necessary to solve a system of coupled mass and heat transfer equations. In general, solving such a system of equations analytically invokes rather complicated mathematical difficulties, which is associated with the necessity to take a large number of parameters into account. Another way to solve this problem consists in numerical calculations. Its disadvantage is its sensitivity to the accuracy with which the boundary and initial conditions are given. An alternative to describe the evaporation process can be the approach consisting in the application of a partially simplified model of the evaporation process and the further account for only those physical mechanisms that are essential for specific experimental conditions [6].

The simplest model for describing the evaporation was proposed by Maxwell. The model is based on the following approximations: the liquid droplet and the vapor-gas mixture around it are stationary, there is no temperature gradient, and the vapor mass transfer in the gas medium from the droplet surface takes place via the diffusion (the diffusive evaporation regime). The evaporation rate in this case is determined by the Maxwell formula [7]

$$I_m = -\frac{dm}{dt} = 4\pi D r (C_0 - C_\infty), \tag{1}$$

where D is the binary diffusion coefficient, C_0 is the vapor concentration near the droplet surface, C_∞ is the vapor concentration at an infinitely large distance from the droplet, and r is the droplet radius. It is convenient to rewrite this formula in the form

$$-\frac{dS}{dt} = \frac{8\pi D\,(C_0 - C_\infty)}{\rho}. \tag{2}$$

In the framework of Maxwell's evaporation model, it is assumed that the vapor of evaporated liquid is described by the equation of state for the ideal gas, and the parameter C_0 can be expressed via the partial pressure of saturated vapor having the droplet temperature. For calculating the saturated vapor pressure at the droplet temperature, the Antoine equation was used,

$$\ln(P) = A - \frac{B}{T - C}, \tag{3}$$

where the values of the parameters A, B, and C for the studied alcohols were taken from the reference literature [8].

In the vast majority of real systems, the process of droplet evaporation results in the droplet cooling. The droplet temperature decreases until the quasistationary evaporation regime is established [9]. The existence of a temperature gradient around the droplet makes it mandatory to account for the dependence of the diffusion coefficient on the temperature at large $(T_\infty - T_0)$-values, where T_∞ is the temperature of the background gas at a long distance from the droplet, and T_0 is the temperature of the droplet surface. In this case, the diffusion coefficient in Eq. (2) is calculated by the formula $D = \sqrt{D_0 D_\infty}$, where D is the effective diffusion coefficient, D_0 the diffusion coefficient calculated for the droplet temperature value, and D_∞ the diffusion coefficient calculated for the gas medium temperature value [9]. In our calculations, the following expression was used for the diffusion coefficient [8, 9]:

$$D = 0.002628 \frac{\sqrt{T^3 \,\frac{M_1 + M_2}{2 M_1 M_2}}}{P \sigma_{12}^2 \Omega_{12}(T_{12}^*)}, \tag{4}$$

where P is the pressure, and T the temperature of the gas medium, where the diffusion takes place, M_1 and M_2 are the molar masses of diffusing components, σ_{12} is the arithmetic mean of the molecular diameters of the diffusing components, and $\Omega_{12}(T_{12}^*)$ is the collision integral. The latter parameter is a function of the reduced temperature $T_{12}^* = \frac{kT}{\varepsilon_{12}}$, where ε_{12} is the geometric mean of the strength constants in the intermolecular potentials for the mixture components.

The existence of a temperature gradient around the evaporating droplet can stimulate the temperature-induced free convection [10]. Its analytical consideration is quite a difficult mathematical problem, so methods of the similarity theory are applied for its description. The physical properties of the medium, where the diffusion takes place, are characterized using the Schmidt criterion $\mathrm{Sc} = \frac{\nu}{D}$ (here, ν is the kinetic viscosity, and D is the diffusion coefficient) and the Grashof criterion $\mathrm{Gr} = \frac{8gr^3}{\nu^2}\frac{\Delta T}{T}$ (here, g is the free-fall acceleration, and ΔT is the temperature difference invoking the convection process). It is worth to mention the following expression [7] for the free-convection correction in the case of heat exchange from a metal ball:

$$\mathrm{Sh} = 2 + 0.6\,\mathrm{Sc}^{\frac{1}{3}}\,\mathrm{Gr}^{\frac{1}{4}}. \tag{5}$$

Nevertheless, it is used while analyzing experimental data on evaporation.

Churchill [11] proposed the following modified expression for the description of free convection:

$$\mathrm{Sh} = 2 + \frac{0.59\,(\mathrm{Sc\,Gr})^{1/4}}{\left[1 + \left(\frac{0.47}{\mathrm{Sc}}\right)^{9/16}\right]^{4/9}}. \tag{6}$$

Another important effect is the Stefan flow. Namely, near the evaporating droplet surface, there must exist a hydrodynamic flow of the background gas directed from the surface [7, 12]. This correction can be written in the form

$$\mathrm{St} = 1 + \frac{P_0 - P_\infty}{2P}, \tag{7}$$

where P is the total pressure in the medium, and P_0 and P_∞ are the vapor pressures of the substance of the evaporating droplet near the droplet surface and at an infinite distance from the droplet, respectively. This correction becomes essential in the case where the pressure of the saturated vapor of the droplet components becomes comparable with the total pressure in the gas medium [7]. In view of the above-mentioned corrections, the modified Maxwell formula looks like

$$-\frac{dS}{dt} = \frac{8\pi\sqrt{D_0 D_\infty}\,(C_0 - C_\infty)\,\mathrm{Sh}}{\rho}\left(1 + \frac{P_0 - P_\infty}{2P}\right). \tag{8}$$

However, at pressures lower than the atmospheric one, a deviation from the Maxwell formula may arise, which is a result of a macroscopic jump in the background gas concentration and the appearance of the so-called Δ-layer around the droplet. Fuks obtained an expression for the correction to the Maxwell formula associated with the concentration jump (the Fuks correction) [7]. If the droplet radius is much larger than the Δ-layer size, this correction reads

$$I_m = \frac{I_0}{\frac{D}{ru\alpha} + 1}, \tag{9}$$

where I_0 is the mass flow calculated according to the Maxwell formula, r is the droplet radius, $u = \sqrt{\frac{kT}{2\pi\mu}}$ is a quater of the average thermal velocity of vapor molecules, and μ is the molecular mass of the droplet substance.

The Knudsen number $\mathrm{Kn} = \frac{\lambda}{r}$ is a criterion used to distinguish between the evaporation regimes. However, as was shown in work [13], the value of this criterion at which the deviation from the diffusive regime appears can substantially depend on the coefficient of droplet substance evaporation.

Evaporation of droplets of liquid solutions is a process, where all solution components are evaporated simultaneously. As a result, the equilibrium vapor pressure above the droplet surface becomes a function of time. When modeling the process of solution evaporation, it is necessary to substantiate whether it is possible to consider the solution to be ideal or not, which requires an additional research.

The ideal solution is a solution that satisfies, in particular, Raoult's law I [14]. The latter is formulated as follows: the partial pressure of the saturated vapor of a solution component, P_i, is equal to the product of the mole fraction of this component in the solution, n_i, and the saturated vapor pressure over the pure component, P_i^0:

$$P_i = P_i^0 n_i. \tag{10}$$

The reduction in the saturated vapor pressure of the solvent above the solution does not depend on the nature of a dissolved substance, but is determined only by its concentration. If two or more components of the solution are similar to each other and their formation does not occur owing to the volume, thermal, or other effects, then such a solution can be considered ideal at arbitrary concentrations, and its mixing is governed exclusively by entropy factors. Ideal at any concentration are solutions whose components have very close physical and chemical properties, and the formation of which is not accompanied by a volume change and the heat release or absorption. Formula (10) describes the pressure variation of saturated vapor above the surface only for solutions with the same parameters of the intermolecular interaction. In all other cases, it can be used, only if the concentrations of impurities are low.

The relative mole fraction n_i of the ith droplet component ($i = 1, 2$) is defined as $n_i = \frac{\nu_i}{\nu_1 + \nu_2}$, where ν_i is the number of molecules of the ith substance in the droplet. Since the equality $n_1 + n_2 = 1$ holds, it suffices to consider only one of the relative fractions. In what follows, it will be n_1, although we will use the both quantities, if needed. The approximation of the uniform mass density over the droplet is applied.

In the ideal solution approximation, the droplet radius r is related to the relative mole fractions of droplet components n_i via the equality

$$r = \left[\frac{3\nu}{4\pi}\,\rho_\nu\right]^{1/3} = \left[\frac{3\nu}{4\pi}\,\frac{1}{(n_1\,\upsilon_1 + n_2\,\upsilon_2)}\right]^{1/3}, \tag{11}$$

where υ_i is the specific volume (per mole) of the ith solution component, namely, the increase of the solution volume, if one molecule of the ith component is added. If the solution is ideal, its formation is not accompanied by volumetric or thermal effects, and the pressures of the saturated vapors of solution components above its surface obey the Raoult's law I. Therefore, the evaporation of each component of the ideal solution can be considered as independent, so

$$\frac{dm}{dt}=\frac{dm_1}{dt}+\frac{dm_2}{dt}. \tag{12}$$

Hence, the total mass change of the evaporating droplet is an additive quantity and consists of mass changes of all components. The expression describing the corresponding variation can be written for each component on the basis of the data concerning the evaporation of droplets of individual pure substances. Additional is the assumption about the establishment of the equilibrium concentration of the solution components in the droplet.

As a rule, when developing models for the evaporation of binary-solution droplets, the hydrodynamic equations of heat and mass transfer are used, which corresponds to the assumption that the evaporation takes place in the diffusive regime. In this regime, the mass variation of the ith component can be represented as follows:

$$I_m=-\frac{dm}{dt}=4\pi D_{i-\mathrm{gas}}r(C_i-C_\infty)\mathrm{Sh}_i, \tag{13}$$

where the subscript $i=1.2$ enumerates the components of the binary solution.

Expressions (12) and (13) can be used for numerical calculations of the time dependences of the mass and the surface area of the droplet of the examined solution in the case where the Stefan flow can be neglected. The calculation algorithm is as follows:

- using expression (13), the mass change during the selected time step Δt is calculated for each solution component;
- the relative mass and molar fractions of the solution components in the droplet are calculated; on the basis of the obtained values and in the framework of the ideal solution approximation, the vapor pressures of the solution components above the droplet surface and the density of the liquid droplet are calculated; on the basis of the values obtained for the droplet mass and density, the droplet radius and surface area are determined;
- these values are used to calculate the droplet mass change at the next time step. The value of the droplet temperature, which is used for the calculation of thermophysical parameters in the framework of this model, is obtained from experimental data.

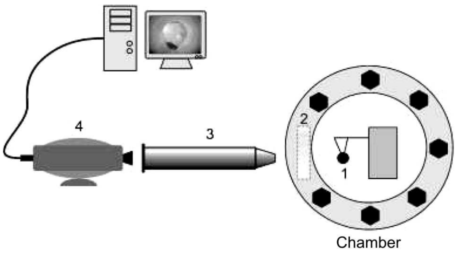

Fig. 1. Schematic diagram of the experimental setup for measuring the evaporation rate of liquid droplets

If the evaporation is considered in the transient mode, then, according to the Fuks theory of evaporation, it is necessary to consider the existence of Δ-layer near the droplet surface. Therefore, for the calculation of mass changes of the solution components, expression (13) has to be corrected for the concentration jump in the Fuks form. In view of a substantial difference between the vapor concentration values for the components of researched solutions, the assumption was made that the evaporations of the solution components run independently of each other in the transient regime as well. Accordingly, the expression for calculating the mass change of the solution components can be written in the form

$$-\frac{dm_i}{dt}=I_m=\frac{4\pi D_{ig}r\left(C_0-C_\infty\right)\mathrm{Sh}_i}{\frac{D_{ig}}{u_i(r\alpha)_i}+1}. \tag{14}$$

The value of the quantity $(r\alpha)_i$ can be obtained from evaporation data for the droplets of a pure substance. The application of the product of the evaporation coefficient and the droplet radius is associated with the fact that, according to work [10], just this expression is constant during the evaporation, whereas the evaporation coefficient depends on the droplet radius.

3. Methodology of Experimental Studies of Evaporation Kinetics of Liquid Droplets

In order to study the rate of droplet evaporation, we used an installation, the scheme of which is shown in Fig. 1.

Chamber *2*, where the evaporation from suspended droplet *1* was studied, looked like a horizontally ori-

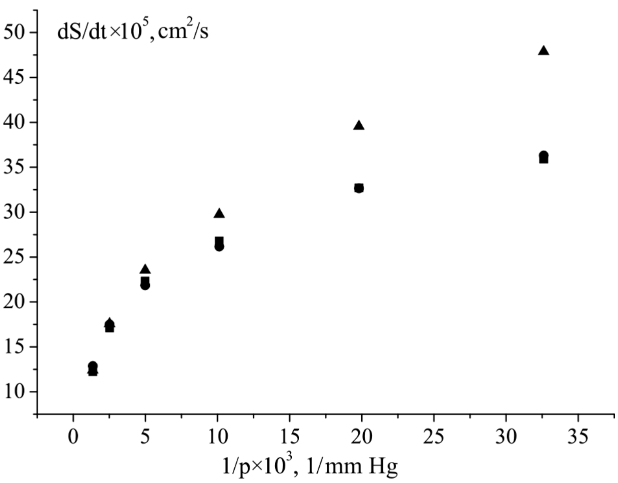

Fig. 2. Dependences of the butanol droplet evaporation rate on the inverse gas environment pressure at a gas environment temperature of 293 K: experimental (■), calculated according to the Maxwell formula (13) (▲), and calculated according to the Maxwell formula and considering the correction for the concentration jump (14) (○)

ented cylinder 20 l in volume. It had double walls, with a thermostatic liquid being passed between them. The thermostat allowed the temperature in the chamber to be maintained within an interval of 5–40 °C with an accuracy of ±0.1°C. The temperature in the chamber was monitored using a temperature sensor. As a sensor, the *p-n* junction of a chip transistor was applied. It allowed the inertia of the temperature control system to be substantially reduced. The electronic system made it possible to measure the temperature with an accuracy of ±0.03 °C. Another similar sensor was used to monitor the droplet temperature. To provide a better contact with the liquid, this sensor was also used as a droplet hanger. The application of a chip transistor simultaneously as a hanger and a temperature sensor made it possible to substantially diminish the thermal conductivity through the hanger, and approach as close as possible the evaporation conditions for a free droplet. The geometric dimensions of the chip transistor 2T307A-1 used as a sensor were $0.7\times0.7\times0.8$ mm^3. The droplet radius varied within the interval from 1.2 to 0.9 mm during the measurement. Hence, the relative volume of the transistor with respect to the droplet volume varied from 6% to 15%.

In order to measure the evaporation of droplets in a wide pressure interval (from normal to 3–5 mm Hg), the chamber was connected to a vacuum pump, which allowed us to obtain low pressures in the chamber. The pressure in the chamber was measured by means of a mercury U-tube manometer and controlled with the help of an electronic device. The high hermeticity of the chamber made it possible to carry out measurements at a constant pressure during long time intervals.

Glass windows were hermetically mounted into the chamber end wall, which allowed us to illuminate the chamber and monitor the evaporation process visually.

Video camera *4* with a specially selected objective *3* was located outside the vacuum chamber. It was used to photograph the suspended droplet at given time intervals. For high-quality measurements, we had to install such a lighting regime that produced a distinct dark edge of the droplet against a light background. A wire of known thickness was arranged near the droplet to control the snapshot scale. Droplet images were recorded automatically at selected time intervals, and the time of image registration was determined by the time of file creation.

The described experimental setup made it possible to study the evaporation of liquid droplets at pressures lower than the atmospheric one both in the diffusive and transient evaporation regimes.

The experimental procedure was described in more details in work [15].

4. Discussion of Experimental Results

In order to determine the pressure values in the gas mixture under which the diffusive and transient evaporation regimes are realized, the experimental pressure dependences of the evaporation rate dS/dt of pure alcohols (propanol, butanol, and octanol) were analyzed by comparing them with the corresponding dS/dt-values calculated using the Maxwell model and considering the correction for free convection.

Figure 2 demonstrates the dependences of the butanol evaporation rate on the reciprocal pressure of the gas medium for a gas medium temperature of 293 K: experimental (*1*), calculated according to the Maxwell formula and considering the correction for free convection (*2*), and calculated according to the Maxwell formula with regard for Fuks's correction for the concentration jump. Their analysis brought us to the conclusion that the application of the Maxwell formula in form (13) without Fuks's correction makes it possible to obtain the value of the evaporation rate in a pressure interval of 740–200 mm Hg that coincides with the experimentally obtained dS/dt-value within the experimental error limits. In particular, for a gas pressure value of 740 mm Hg the experimental value of dS/dt is $(6.37 \pm 0.07) \times 10^{-5}$ cm^2/s, whereas the calculated value equals 6.2×10^{-5} cm^2/s. The diffusion coefficient calculated using formula (4) equals 0.083 cm^2/s, and the butanol density equals 0.810 g/cm^3.

Additional estimates testify that the Stefan correction for the existence of a hydrodynamic flow amounts to 1–2% for butanol within the whole pressure interval. Hence, the evaporation of butanol in a pressure interval of 740–200 mm Hg takes place in the diffusive regime, and, for its description, it is possible to neglect the influence of the Stefan flow. A similar situation occurs for other studied alcohols. Therefore, for the further research of the evaporation kinetics of binary alcohol solutions in the diffusive regime, a gas pressure value of 740 mm Hg was chosen.

The discrepancy between the experimentally measured and calculated dS/dt-values obtained for a gas medium pressure of 100 mm Hg and below testifies to the transition from the diffusive regime of evaporation to the transient one according to Fuks's theory and the emergence of a Δ-layer [4]. Since the deviation from the diffusive evaporation regime at a gas environment pressure of 100 mm Hg is substantial for all considered alcohols, this value was chosen to study the evaporation kinetics of binary alcohol solutions in the transient evaporation regime.

The time dependences of the droplet surface area $S(t)$ for pure alcohols are linear, which allows the evaporation rates of those substances to be determined from the slope angle. The dependences $S(t)$ for the solutions are nonlinear, because the evaporation rates of the mixture components differ substantially. Figures 3 and 4 demonstrate the experimental time dependences of the surface area and the surface temperature, respectively, for the droplets of pure butanol (*1*), pure octanol (*5*), and octanol-butanol solutions (*2–4*) with initial octanol concentrations of 0.25 (*2*), 0.5 (*3*), and 0.75 mole fraction (*4*) during their evaporation in the nitrogen atmosphere at a pressure of 740 mm Hg and a gas medium temperature of 293 K. The experimental values of droplet temperature were used while carrying on the model calculations.

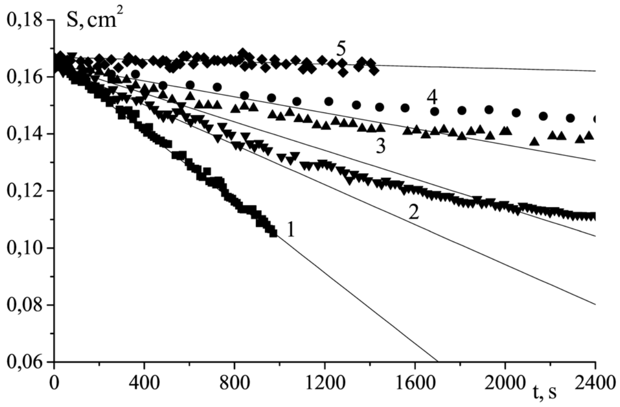

Fig. 3. Time dependences of the surface area of butanol (*1*) and octanol (*5*) droplets and droplets of butanol-octanol solutions with initial octanol concentrations of 0.25 (*2*), 0.5 (*3*), and 0.75 mole fraction (*4*) at a pressure of 740 mm Hg and a temperature of 293 K of the gas environment

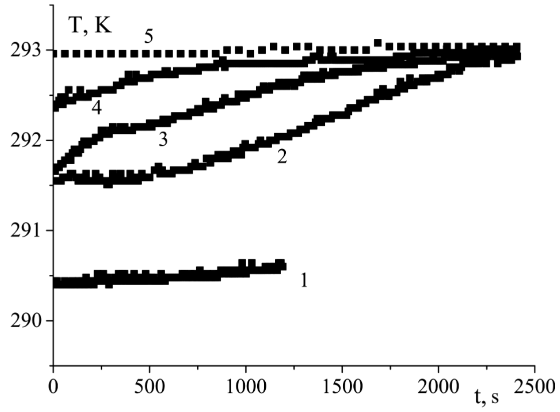

Fig. 4. Time dependences of the temperature of droplets of butanol (*1*), octanol(*5*), and butanol-octanol solutions with initial octanol concentrations of 0.25 (*2*), 0.5 (*3*), and 0.75 mole fraction (*4*) at a pressure of 740 mm Hg and a temperature of 293 K of the gas environment

The analysis of the experimental values obtained for the evaporation rates of butanol and octanol droplets testifies that, within the whole interval of pressures, the evaporation rate of octanol is two orders of magnitude lower than those of propanol and butanol. In particular, the evaporation rate of the octanol droplet in the nitrogen atmosphere at a gas environment pressure of 740 mm Hg and a temperature of 293 K amounts to $(0.065 \pm 0.004) \times \times 10^{-5}$ cm^2/s; the corresponding value equals $(6.37 \pm$

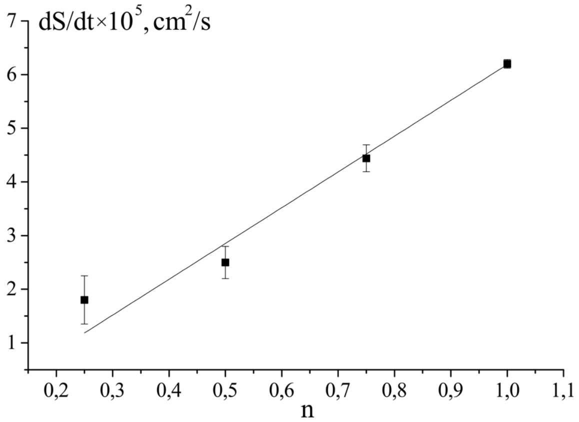

Fig. 5. Dependence of the butanol-octanol solution evaporation rate on the butanol molar concentration at the beginning of evaporation process

$\pm 0.07) \times 10^{-5}$ cm^2/s for the butanol droplet and $(12.89\pm0.54)\times10^{-5}$ cm^2/s for the propanol one. Therefore, it is reasonable to assume that the total evaporation rate and, accordingly, the droplet temperature at the beginning of the evaporation process are determined by the evaporation of the more volatile component, i.e., the alcohol with a higher evaporation rate and a lower quasistationary droplet temperature.

Accordingly, in the framework of the proposed model, i.e., when the evaporation of solution components occurs independently, the evaporation can be divided into two stages. The first stage occurs, when the droplet mass changes mainly due to the evaporation of the more volatile component. On the second stage, the total evaporation rate and the temperature of the droplet are determined by the parameters of the component that evaporates more slowly, i.e., octanol.

This conclusion is confirmed by the analysis of the dependences shown in Figs. 3 and 4. As one can see from Fig. 3, at large times of the evaporation of droplets of butanol-octanol solutions, the corresponding dependences $S(t)$ gradually become parallel to the dependence $S(t)$ for the octanol droplet. Their slope angles become identical, which means that only one component of the solution – namely, octanol – remains in the droplet. The plots in Fig. 4 testify that the temperatures of the droplets of those solutions approach the quasistationary temperature of the octanol droplet.

At the initial stage of evaporation, the amount of the second solution component in the droplet remains almost constant, and the rate of the surface area variation is governed by the evaporation of the more volatile component. Therefore, the conclusion can be made that if the solution is ideal, the asymptote drawn to the plot of the time dependence of the droplet surface area at the initial evaporation stage has a slope proportional to the initial mole fraction of the more volatile component in the solution. This method aimed at the verification of the assumption concerning the solution ideality was used to analyze the evaporation process of propanol-octanol solution droplets in the diffusive regime [16]. It is shown that propanol-octanol solutions can be considered ideal for all initial concentrations studied in work [16].

In order to test if the ideal solution approximation is applicable to butanol-octanol solutions, the asymptotic slope values of the time dependences of the droplet surface area were determined for droplets with various initial (at the beginning of the evaporation process) solution concentrations. The obtained data were used to plot the dependence of the asymptotic droplet evaporation rates of butanol-octanol solutions on the initial butanol mole fraction (see Fig. 5). From Fig. 5, one can see that the evaporation rate of the butanol-octanol solution at the initial stage can really be approximated by a linear function, which indicates that this solution is ideal.

The algorithm for calculating the evaporation kinetics for binary-solution droplets, which was proposed in Section 2, was applied to calculate the time dependences of the droplet surface area for the examined propanol-octanol and butanol-octanol binary solutions with initial octanol molar fractions of 0.25, 0.5, and 0.75 at their evaporation in the nitrogen atmosphere in the diffusive (740 mm Hg) and transient (100 mm Hg) evaporation regimes. In calculations, the experimental values of the droplet temperature were used. The resulting dependences are shown in Figs. 6 and 7.

The analysis of the experimental and numerically calculated time dependences $S(t)$ presented in Figs. 6 and 7 demonstrate their good agreement throughout the whole evaporation process, which testifies that the model of the independent evaporation of solution components describes well this process in the diffusive regime and can be used to analyze experimental data. Good agreement means that the concentrations of solution components have enough time to reach their equilibrium values over the entire volume of the

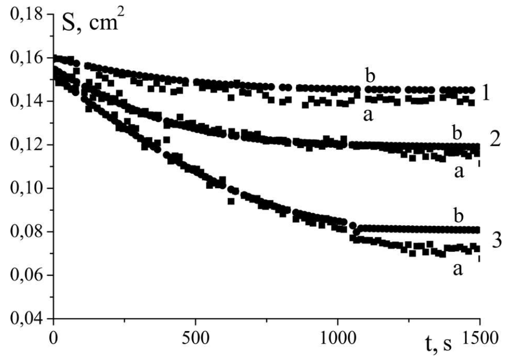

Fig. 6. Time dependences of the surface area of droplets of propanol-octanol solutions with initial octanol concentrations of 0.25 (*1*), 0.5 (*2*), and 0.75 mole fraction (*3*) at their evaporation in the nitrogen atmosphere at a pressure of 740 mm Hg and a temperature of 293 K: experimental (*a*) and calculated using the proposed model (*b*)

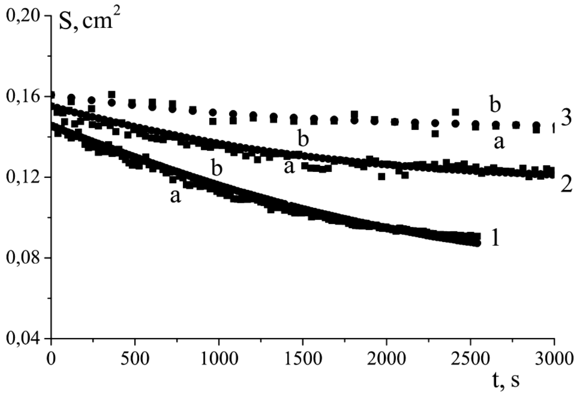

Fig. 7. Time dependences of the surface area of droplets of butanol-octanol solutions with initial octanol concentrations of 0.25 (*1*), 0.5 (*2*), and 0.75 mole fraction (*3*) at their evaporation in the nitrogen atmosphere at a pressure of 740 mm Hg and a temperature of 293 K: experimental (*a*) and calculated using the proposed model (*b*)

droplets of studied solutions during their evaporation in the diffusive regime.

When considering the evaporation in the transient regime, expression (12) was used to calculate the time dependence of the surface area of droplets of the propanol-octanol and butanol-octanol binary solutions. The resulting dependences are shown in Figs. 8 and 9.

A comparison of the experimentally obtained and model time dependences of the droplet surface area $S(t)$ presented in Fig. 8 demonstrates their good agreement in the case of the propanol-octanol solution

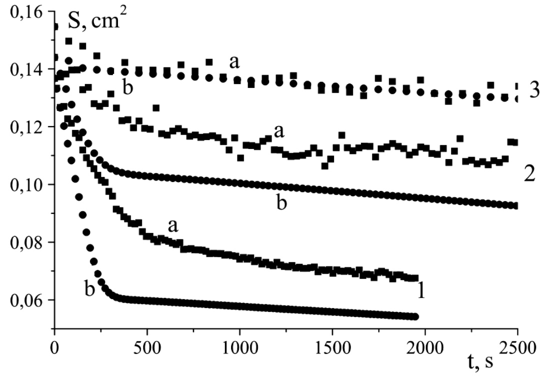

Fig. 8. Time dependences of the surface area of droplets of propanol-octanol solutions with initial octanol concentrations of 0.25 (*1*), 0.5 (*2*), and 0.75 mole fraction (*3*) at their evaporation in the nitrogen atmosphere at a pressure of 100 mm Hg and a temperature of 293 K: experimental (*a*) and calculated using the proposed model (*b*)

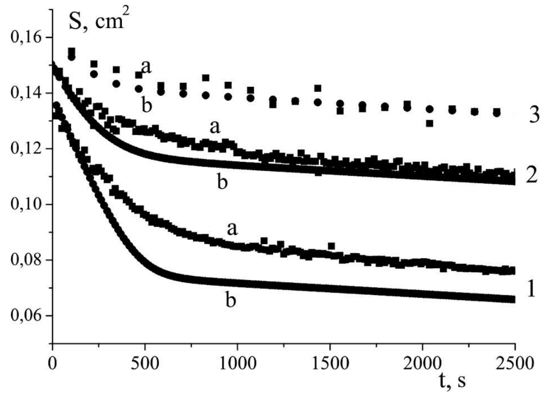

Fig. 9. Time dependences of the surface area of droplets of butanol-octanol solutions with initial octanol concentrations of 0.25 (*1*), 0.5 (*2*), and 0.75 mole fraction (*3*) at their evaporation in the nitrogen atmosphere at a pressure of 100 mm Hg and a temperature of 293 K: experimental (*a*) and calculated using the proposed model (*b*)

with an initial propanol concentration of 0.25 mole fraction in the droplet. For an initial propanol concentration of 0.5 mole fraction, there is a discrepancy between the experimental and calculated dependences $S(t)$. For an initial propanol concentration of 0.75 mole fraction, this discrepancy is larger.

An analogous comparison procedure in the case of butanol-octanol solutions shown in Fig. 9 allows us to conclude that the agreement between the experimental and calculated dependences $S(t)$ takes place for initial butanol concentrations of 0.25 and 0.5 mole fraction. For an initial concentration of 0.75 mole fraction, a discrepancy between the experimental and calculated dependences is observed.

When deriving expression (14), which was used to model the transient evaporation regime, an assumption was made that it is possible to take the value of the product of the droplet radius and the evaporation coefficient, $(r\alpha)_i$, obtained from the evaporation data for a droplet of pure substance. The observed agreement between the experimental and model dependences $S(t)$ makes it possible to draw the conclusion that, while modeling the evaporation of droplets of ideal solutions in the transient regime, the evaporation coefficients for the components of those solutions can be used.

The more detailed analysis of the revealed discrepancy shows that the dependences $S(t)$ calculated in the framework of the proposed model predict a faster reduction of the droplet surface area in comparison with experimentally obtained data. When considering the model proposed in this work, besides the assumption about the independence of the component evaporation processes, we also adopted the model of the instant establishment of the equilibrium concentrations of the solution components over the droplet. Therefore, since the discussed discrepancy is observed just in the cases where the concentration of the more volatile solution component prevails in the droplet, the mass transfer in the droplet has to be taken into consideration.

5. Conclusions

In the framework of the Maxwell–Fuks evaporation theory, a model describing the evaporation of droplets of ideal binary alcohol solutions is developed. It is based on the assumptions that the evaporation processes of solution components are independent of each other, and the concentrations of solution components are uniformly distributed over the droplet volume. By comparing the experimental and calculated time dependences of the droplet surface area obtained for the diffusive and transient evaporation modes, it is shown that the proposed model makes it possible to effectively simulate the evaporation of binary alcohol solutions provided that its initial approximations are satisfied. It was shown that when modeling the evaporation of droplets of ideal binary solutions in the transient regime, it is possible to use the evaporation coefficients obtained from the data on the evaporation of droplets of pure components of those solutions.

1. *Droplet Wetting and Evaporation. From Pure to Complex Liquids.* Edited by D. Brutin (Elsevier, 2015) [ISBN: 9780128007228].
2. *Heat and Mass Transfer in Drying of Porous Media.* Edited by Peng Xu, A.P. Sasmito, A.S. Mujumdar (CRC Press Taylor Francis Group, 2020) [ISBN: 9780367779399].
3. K.M. Kovalov, O.M. Alekseev, M.M. Lazarenko, Y.F. Zabashta, Y.E. Grabovskii, S.Y. Tkachov. Influence of water on the structure and dielectric properties of the microcrystalline and nano-cellulose. *Nanoscale Res. Lett.* **12**, 468 (2017).
4. O.K. Kopiyka, Yu.O. Olifirenko, V.V. Kalinchak, D.S. Darakov, T.O. Fudulei, L. Raslavicius. Evaporation of binary ethanol-butanol mixture droplets. *Int. Combust. Eng.* **2**, 25 (2018).
5. Ping Yi, Ming Jia, Wuqiang Long *et al.* Evaporation of pure and blended droplets of diesel and alcohols $C_2 - C_9$ under diesel engine conditions *Numer. Heat Transf. A* **71**, 311 (2017).
6. S.S. Sazhin. Modeling of fuel droplet heating and evaporation: Recent results and unsolved problems. *Fuel* **196**, 69 (2017).
7. N.A. Fuchs. *Evaporation and Droplet Growth in Gaseous Media* (Pergamon Press, 1959) [ISBN: 9781483225630].
8. B.E. Poling, J.M. Prausnitz, J.P. O'Connell. *The Properties of Gases and Liquids* (McGraw-Hill, 2001) [ISBN: 9780070116825].
9. G. Miliauskas, V. Garmus. The peculiarities of hot liquid droplets heating and evaporation. *Int. J. of Heat Mass Transf.* **52**, 3726 (2009).
10. R.B. Bird, W.E. Stewart, E.N. Lightfoot. *Transport Phenomena* (Wiley International, 2002) [ISBN: 0471410772].
11. S.W. Churchill. *Free Convection around Immersed Bodies Heat Exchanger Design Handbook* (Hemisphere Publishing, 1983).
12. W.A Sirignano. *Fluids Dynamics and Transport of Droplet and Sprays* (Cambridge University Press, 2010) [ISBN: 9780521884891].
13. N. Fukuta, L.A. Walter. Kinetics of hydrometeor growth from vapor-spherical model. *J. Atmos. Sci.* **27**, 1160 (1970).
14. W. Acree. *Thermodynamic Properties of Nonelectrolyte Solutions* (Elsevier Science, 1984) [ISBN: 9780124121591].
15. H.M. Verbins'ka, A.V. Brytan, V.L. Karbovs'kyi, T.V. Kleshchonok. Evaporation of water and nitrobenzene droplets under the action of ultraviolet irradiation. *Fiz. Aerodysp. Syst.* **47**, 49 (2020) (in Ukrainian).
16. H.M. Verbins'ka, A.V. Brytan, V.L. Karbovs'kyi, T.V. Kleshchonok Evaporation of alcohols and binary alcohol solutions in the diffusive regime. *Fiz. Aerodysp. Syst.* **56**, 71 (2019) (in Ukrainian).

Received 14.01.22.
Translated from Ukrainian by O.I. Voitenko

Л.А. Булавін, Г.М. Вербінська,
А.В. Британ, Я.О. Степовий

МОДЕЛЬ ВИПАРОВУВАННЯ КРАПЕЛЬ ІДЕАЛЬНИХ БІНАРНИХ СПИРТОВИХ РОЗЧИНІВ У ДИФУЗІЙНОМУ ТА ПЕРЕХІДНОМУ РЕЖИМАХ

Створення моделей процесу випаровування крапель розчинів, зокрема розчинів спиртів, у загальному випадку є складною задачею, для дослідження якої потрібно розв'язати систему рівнянь масо- та теплопереносу. Альтернативним підходом може бути підхід, який полягає у створенні спрощеної моделі та подальшому врахуванні тих фізичних механізмів, які є суттєвими для конкретних умов, в яких відбувається випаровування. В статті за використанням даного підходу на основі теорії випаровування Максвелла–Фукса запропоновано модель опису процесу випаровування ідеальних бінарних розчинів у дифузійному та перехідному режимах випаровування. З метою перевірки даної моделі було проведено експериментальні дослідження випаровування краплин бінарних спиртових розчинів пропанол–октанол та бутанол–октанол в атмосфері сухого азоту за температури газу 293 K в дифузійному та перехідному режимах для значень початкових концентрацій октанолу 0,25, 0,5 та 0,75 мольних часток. Запропонована модель була використана для розрахунку залежностей площі поверхні краплини від часу для даних бінарних спиртових розчинів. Проведено порівняння одержаних модельних кривих з експериментальними даними. Показано, що, в межах справедливості наближень моделі, вона може бути використана для опису процесу випаровування як в дифузійному, так і в перехідному режимах випаровування.

Ключові слова: спирт, розчин, режим випаровування.