Limiting current technique in the research of mass/heat transfer in nanofluid

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Abstract. In the paper the authors focused on the application of the electrochemical limiting diffusion current technique to the study of mass transfer in nanofluid flow. As mass and heat transfer are analogical phenomena, analysing mass transfer helps understand heat transfer processes in nanofluids. The paper begins with a short review of the available literature on the subject followed by the authors' results of mass transfer coefficient measurements and the conclusions concerning mass/heat transfer enhancement in nanofluids.

1. Introduction
Nanofluids are heat transfer fluids consisting of base fluid and dispersed nanoparticles suspended in it. Due to specific thermophysical properties nanofluids are more and more often applied to industrial processes involving heat transfer as using them enhances heat transfer significantly compared with heat transfer where base fluids are used.
Investigations into heat transfer in nanofluids are numerous. A good number of them are mentioned in reviews [1, 2]. Trisaksri and Wongwises [1] indicate the fact that suspended nanoparticles enhance heat transfer processes of the base fluid in forced convective heat transfer. However, with regard to natural convective heat transfer, they show discrepancies between the results of experimental and analytical investigations. Godson et al. [2] who also deal with recent theoretical and experimental studies on natural and forced convective heat transfer in nanofluids conclude, based on the literature published so far, that the available experimental results are insufficient to predict the trend for heat transfer enhancement so further investigations are necessary.
As mass and heat transfer are analogical phenomena [3], it can be assumed that similarities may occur between enhanced heat transfer processes in nanofluids and convective mass transfer. Both phenomena have been studied recently, however, the number of studies on heat transfer significantly exceeds that one concerning mass transfer. Beiki et al. [4] summarize the results on nanofluid mass transfer research obtained so far. They show mass transfer enhancement obtained using different kinds of experiments. The quoted data were acquired from gaseous media absorption, dye diffusion, self diffusion, liquid - liquid extraction and the electrochemical limiting diffusion current technique. Based on [4], it can be concluded that experimental results of mass transfer in nanofluids vary. There occur both enhancement and reduction in nanofluid relative to base fluid so further investigations into the problem are needed.
In this paper the authors focused on the application of the electrochemical limiting diffusion current technique to mass transfer in nanofluid. A short review of available literature data is given followed by preliminary experimental results of electrochemical measurements. The possibility of applying mass/heat transfer analogy to nanofluids is discussed.

2. Investigations of mass transfer in nanofluid using the electrochemical limiting diffusion current technique

2.1. Literature review

There is little available literature data on the mass transfer investigations in nanofluids using the limiting current technique. Given in papers [4, 5, 6, 7] are the results of electrochemical measurements of the mass transfer coefficient during laminar and turbulent nanofluid flow through channels of different design whereas article [8] shows the results of electrochemical experiments on mass transfer to a rotating disc electrode using nano-electrolyte ie the electrolyte with suspended nanoparticles. The characteristics of the nanoparticles applied and the ranges of the Reynolds numbers are summarized in Table 1. In all of these experiments the electrolyte consisted of the aqueous solution of equimolar quantities of $K_3\text{Fe(Cn)}_6$, $K_4\text{Fe(Cn)}_5$ and aqueous $\text{NaOH}$. This was the base fluid for the nanofluid – nano-electrolyte. The effect of both the volume concentration of nanoparticles and the Reynolds number on the mass transfer coefficients were studied. In the case of circular channels mass transfer enhancement relative to base fluid was observed at lower nanoparticle concentrations while for higher nanoparticle concentrations, the reduction of mass transfer occurred. The optimum volume of nanoparticle concentration appeared. Its value depended on nanoparticle size. However, in the case of annular channels, adding nanoparticles to the electrolyte (base fluid) resulted in the reduction of the mass transfer coefficient compared with that of the base fluid.

| Authors               | Nanoparticles (size in nm) | Nanoparticle volume concentration | Channel geometry | Range of Reynolds number |
|-----------------------|----------------------------|----------------------------------|------------------|--------------------------|
| Beiki et al. [5]      | $\gamma$-Al$_2$O$_3$ (40)  | 0.005% ÷ 0.025%                 | circular         | 320÷1250                 |
| Beiki et al. [4]      | $\gamma$-Al$_2$O$_3$ (40)  | 0.005% ÷ 0.025%                 | circular         | 5000÷25000               |
|                       | TiO$_2$ (1÷3)              | 0.01% ÷ 0.05%                   |                  |                          |
| Keshishian et al. [6] | silica (7÷13)              | 0.0002% ÷ 0.0018%              | circular         | 320÷1250                 |
|                       |                           |                                  |                  | 4500÷18000               |
| Grosicki [7]          | $\gamma$-Al$_2$O$_3$ (40)  | 0.01%                           | annular          | 2100÷9200                |

2.2. Limiting current technique

Well known limiting current method is often used in the research of mass transfer processes. Examples of recent studies can be found in: [9, 10, 11, 12, 13, 14]. The method involves observing controlled ion diffusion at one of the electrodes. Once an external voltage is applied to the electrodes which are immersed in the electrolyte, anionic reduction occurs at the cathode and oxidation at the anode. As a result, electric current arises in the external circuit. The current is proportional to the number of ions
reacting at the electrode per unit time. According to Faraday’s law, the magnitude $I$ of the current generated is given by

$$I = nFAn$$

where: $A$ – surface area of the cathode $[m^2]$, $F$ – Faraday constant, 96 493 $[A\cdot s/kmol]$, $I$ – current in the circuit $[A]$, $N$ – molar flux density $[kmol/(m^2 s)]$, $n$ – valence charge of reacting ions.

According to Fick’s law [3] and the Nernst model of ion concentration, and taking into account only diffusion processes of mass transfer, can be obtained

$$I = nFh_D \left(C_b - C_w\right)$$

where: $h_D$ – mass transfer coefficient $[m/s]$, $C_b$, $C_w$ – bulk ion concentration and ion concentration at the cathode surface, respectively $[kmol/m^3]$. In the limiting current technique an increasing current is caused to flow across the electrodes by increasing the voltage. The measured current reaches constant value at a certain voltage – the controlled diffusion occurs, and the ion concentration at the cathode surface $C_w$ is zero. Based on the measurement of the limiting current $I_L$, the mass transfer coefficient can be calculated from the equation

$$h_D = I_L / \left(nFAC_b\right).$$

A classical system for mass transfer measurements using the limiting current technique is the reduction of ferricyanide ions at the cathode and oxidation of ferrocyanide ions at the anode. A solution $NaOH$ or $KOH$ is used as the basic electrolyte. The oxidation-reduction process under convective-diffusion controlled conditions is written as

$$Fe(CN)_6^{3-} \xrightarrow{\text{red}} Fe(CN)_6^{4-} + e.$$  

2.3. Experimental procedure, results and discussion

The experiment was carried out on the universal rig described in detail in [9, 12]. The measuring test section was presented in the previous work [7]. The annular channel of hydraulic diameter $d_H = 10.5\, mm$ was tested. Channel geometry has provided fully developed velocity profile. Performed investigations are the continuation and enlargement of the previous work presented in [7]. Presented above the electrochemical system for mass transfer measurements was applied. Nanofluids – nano-electrolyte with $Al_2O_3$ nanoparticle volume concentration $\phi = 0.005\%; 0.01\%; 0.015\%$ and $0.02\%$ were used. The two-step method was applied to preparation the nano-electrolyte of suitable nanoparticle concentration. In the first step the base electrolyte was prepared under suitable terms [15]. In the second step $Al_2O_3$ nanoparticles were suspended into the electrolyte. In order to disperse $Al_2O_3$ particles the flask filled with the tested fluid was placed into the ultrasonic system for two hours. Nanoelectrolyte properties: density $\rho$ and dynamic viscosity $\mu$, necessary for measurement, were obtained on the basis of base electrolyte properties [9] and recalculated according to the formulas[6]

$$\rho = (1 - \phi)\rho_{BF} + \phi\rho_P$$

and

$$\mu = (1 + 2.5\phi)\mu_{BF},$$

where: $\rho_{BF}$, $\rho_P$ – base fluid and nanoparticle density, respectively $[kg/m^3]$, $\mu_{BF}$ – base fluid dynamic viscosity $[Pa\cdot s]$. Current parameters of the experiment were measured using multimeters. The volumetric flow rate necessary to obtained the mean fluid velocity $w$ was measured with the use of float flow meter.
Investigations were conducted in the range of Reynolds number 8000÷11600. The ferricyanide ion concentration $C_b$ was measured using iodometric titration. The experiment was carried out with the stabilization of temperature and nitrogen bubbling for release of oxygen from the electrolyte. The uncertainty of mass transfer coefficient measurements was estimated about 3.7% [10]. As the first results of the research, voltammograms of ferricyanide ion reduction at the cathode were obtained. Fig.1 shows the examples of received voltammograms. They are characterized by the flat section – the value of limiting current.

![Figure 1](image1.png)

**Figure 1.** Specimen voltammograms: a) for base fluid – the electrolyte, b) for nano-electrolyte of 0.015% volume nanoparticle concentration

Fig.2 presents the values mass transfer coefficients $h_D$ in the case of different volume nanoparticle concentrations. $h_D$ was calculated from eq.(3). The received $I_p$ values was used in calculations.

![Figure 2](image2.png)

**Figure 2.** Values of mass transfer coefficient of nano-electrolyte in function of volume nanoparticle concentration $\phi$ and Reynolds number, $Re = \frac{wd_H \rho}{\mu}$, in compare to base fluid

As can be seen in Fig.2 the enhancement of mass transfer with Reynolds number occurs what is an obvious phenomenon. In the other hand, there is a decrease of mass transfer coefficients with the
increase of $\phi$. It can be explained by the appearance of particle clusters which could be greater with the increase of $\phi$. The particle clusters may decrease the Brownian motion and thus the reduction of mass transfer occurs. The ratio of mass transfer coefficient of nano-electrolyte $h_D$ to the mass transfer coefficient of base fluid $h_{DBF}$ is showed in Fig.3.

Figure 3. Mass transfer coefficient reduction vs. nanoparticle volume concentration in the case of the flow through the annular channel – presented tests

In turn Fig.4 presents the literature results on mass transfer measurements with the use of limiting current technique in the case of turbulent flow of $Al_2O_3$ nano-electrolyte through the circular channel with 16.3 mm inner diameter. As can be seen in Fig.4 at low $\phi$ the enhancement of mass transfer occurs with the increase of $\phi$. Further increase in $\phi$ causes the reduction in mass transfer coefficient of nano-electrolyte relative to base fluid.

3. Concluding remarks on mass/heat transfer analogy method in the research of heat transfer in nanofluid

On the basis of the performed experimental investigations on mass transfer in nano-electrolyte during the flow through the annular channel some conclusions can be formulated:

- The addition of $Al_2O_3$ nanoparticles to the base electrolyte (a suitable solution of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ in $NaOH$ and $H_2O$) does not change the controlled diffusion processes and the clear limiting current values are obtained.
- Mass transfer coefficients increase with Reynolds numbers and decrease with nanoparticle concentration.
- The literature study shows that the optimum of volume nanoparticle concentration exists, the maximum enhancement of mass transfer occurs at optimum $\phi$.
- Because of the obtained results are not consistent with literature data, there is need for further research in order to look for optimum $\phi$. Channel geometry may have a significant impact on the mass transfer results.

The application of mass/heat transfer analogy method in the research of heat transfer in nanofluid requires further experimental and theoretical study. Available literature data show the enhancement of heat transfer in nanofluids unlike the mass transfer results, where both an augmentation and a reduction of mass transfer relative to base fluids occurs. The influence of nanoparticle thermal
conductivity on heat transfer processes in nanofluid is important. The analogical phenomenon in mass transfer processes is not defined. Further study for obtaining the complete analogy between mass and heat transfer in nanofluid are necessary.

4. References

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