Effect of Suspension Properties on the Electrochemical Method

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1 Introduction

The suspension mixing has been widespread operation, which occurs in many industrial branches. One must know the just off-bottom impeller speed to design mixing apparatuses form suspension mixing properly. However, the problem is to find the state of just off-bottom particle suspension since it can be done only by experiment. This state occurs when all suspension particle are dispersed in the liquid volume and do not lie on the vessel bottom. There are many experimental methods based on various principles that are instrumental to this purpose, nevertheless, all of which have their advantages and disadvantages. New electrochemical method has been lately investigated for this purpose on the Department of Process Engineering at CTU Prague.

The electrochemical method is supposed to be very objective method to determine the just off-bottom suspension state in comparison with classical visual Zwietering's concept [1] because the off-bottom state determination does not depend on the experimenter experience as in the case of visual methods where experimenter experience is very important. The electrochemical method is inexpensive and quite simple. It is possible to use it for measurements in nontransparent vessels and highly concentrated suspensions. The measurements can be done automatically without any interference of experimenter using computer programs and therefore the method is not influenced by subjective experience of experimenter. The only one disadvantage of this method is its usage just for suspensions, whose liquid phase creates suitable electrolyte.

This work deals with the limitations of the electrochemical method. The effects of electrolyte type, the probes area in comparison with particle size and suspension viscosity were investigated.

2 Theoretical background

2.1 Electrochemical method

The electrochemical method is based on measurement of the limiting diffusion current that is well known technique [2]. A two electrode cell consisting of a small working electrode and a large auxiliary electrode, a solution containing depolariser and supporting electrolyte is sufficient for measuring the limiting diffusion current. The applied voltage must have a value at which only the active species react on the working electrode. If the Péclet number is high enough, the molecular diffusion in the longitudinal direction can be neglected. The transport of species and, thereby, the electric current is then controlled by the velocity field in the vicinity of the working electrode only. The concentration boundary layer is much thinner than the momentum boundary layer due to Schmidt numbers of the order of 1000. The velocity distribution in such a thin concentration boundary layer can be approximated by a linear profile of slope equal to the velocity gradient at the wall, γ.

The current density i(x) and concentration boundary layer δ(x) on a working electrode are shown in *Fig.1*. The concentration of active species is negligibly small at the electrode surface and equals to c_0 in the bulk. Shaded areas in *Fig.1* represent decreasing of concentration values off the wall. The darker the shadow the smaller is the concentration is.

The measurements of velocity gradients require a very precise work and frequent verification of the system. Therefore, the electrochemical method is often used for measurements of current fluctuations or even fluctuations normalised by the current mean value. In these cases, a partially inactive (poisoned) electrode can give good results. We made profit of this fact and used the electrochemical probes for the measurements of current fluctuations.

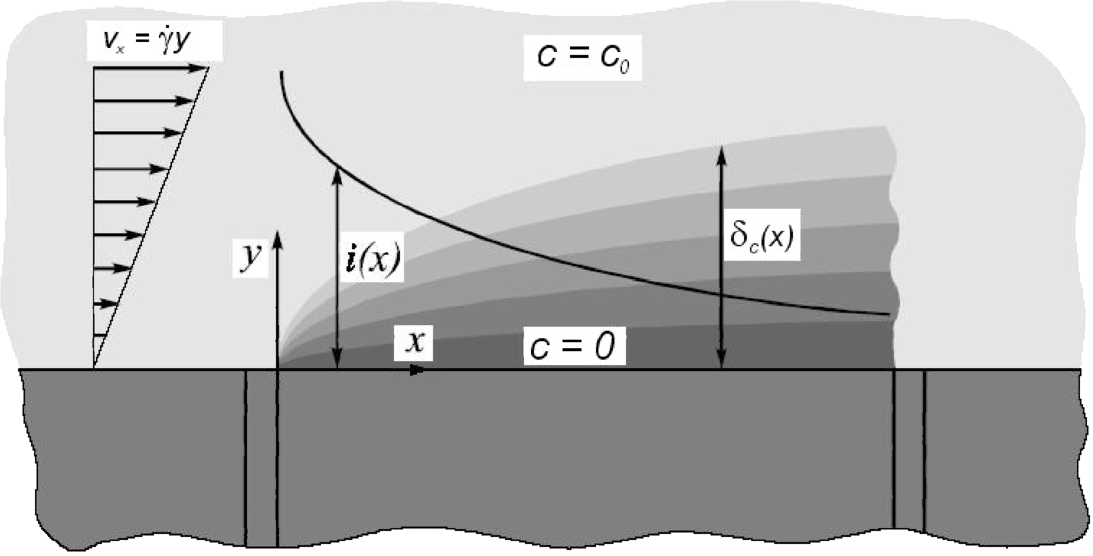


Fig. 1: *Electrodiffusion (ED) probe embedded in wall.*

2.2 Electrochemical method application for suspensions measurements [3]

Typical record from electrochemical measurement show three characteristic signals in *Fig. 2*. There are three typical signals that reflect the state of agitated batch. When there are no particles on the vessel bottom there can be seen the signal (C) which reflects the hydrodynamic fluctuations of flowing liquid. A fluctuating signal from probes located on the border of bottom regions covered and free of particles (B) is registered. That means these probes are not always covered by particles. Practically no signal is received when the probes were situated under layer of stationary particles (A).

As it can be seen in the *Fig. 2*, the characteristic signals differ in arithmetic mean value and standard deviation of probe electric current. it has been suggested to observe these parameters for practical measurements. Typical dependence of arithmetic mean value and standard deviation of probe electric current on impeller speed is shown in *Fig. 3*.

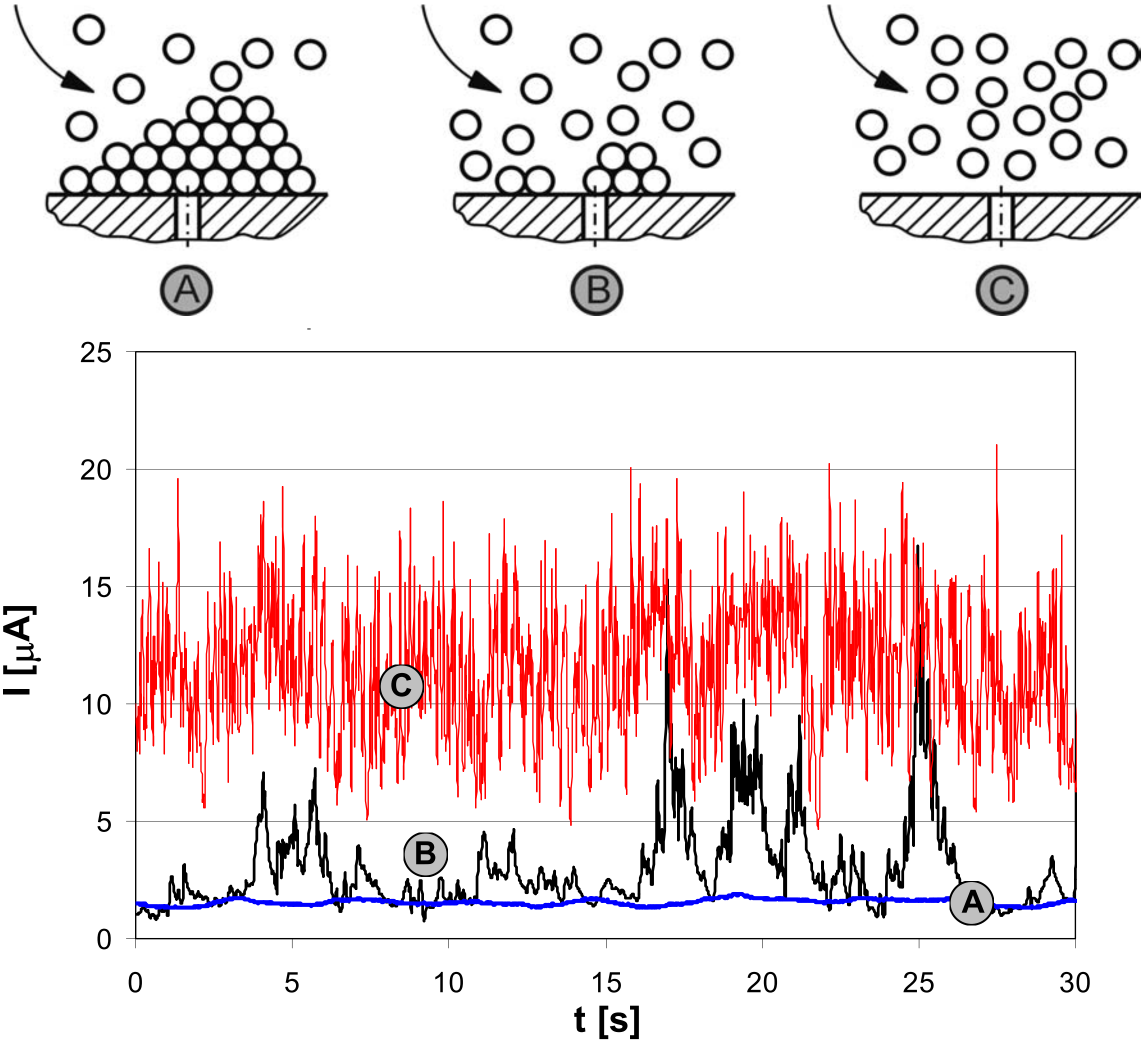


Fig. 2: *Typical record of electrochemical measurement.*

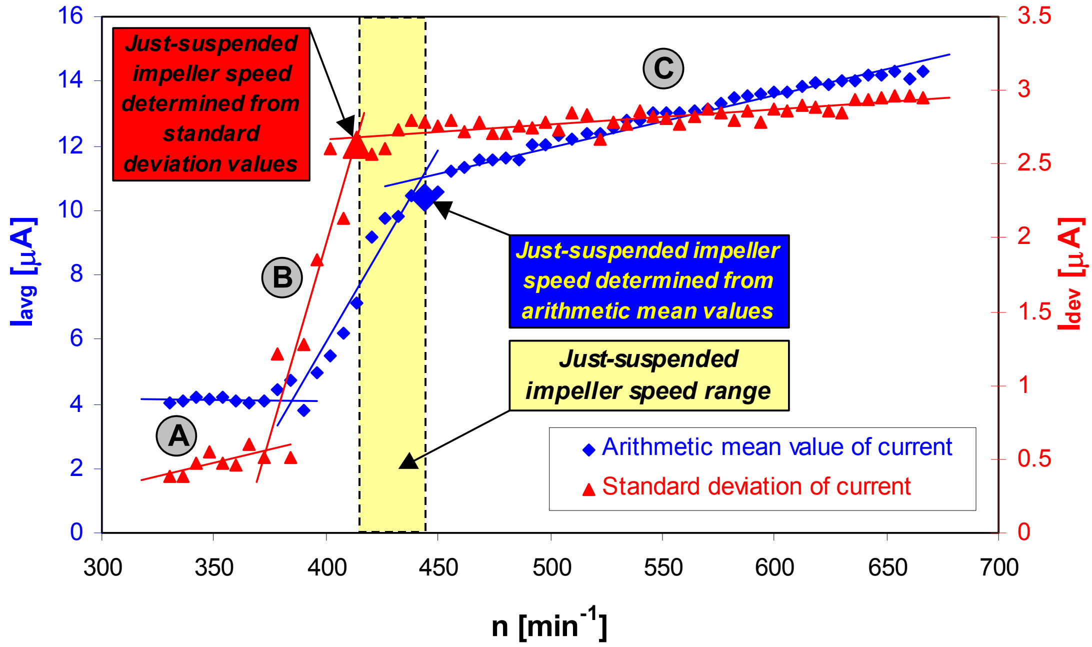


Fig. 3: *Typical dependence of arithmetic mean value and standard deviation of probe electric current on impeller speed.*

It can be seen that just off-bottom particle suspension state at ED probe location is represented by the increase in arithmetic mean value and standard deviation of the current. The just-suspended impeller speed can be determined by the rapid increase both of these parameters. To completely remove the influence of the experimenter on observing critical impeller speed, all the data records were manipulated by computer programs including determining just-suspended impeller speed for off-bottom suspension of dependencies of arithmetic mean values and standard deviations of probe electric current on impeller speed.

Just-suspended impeller speeds determined from electrochemical measurements by this way were verified by results from visual observation of particle layer sediment on the vessel bottom by classical Zwietering`s concept provided at the same time as the electrochemical measurements.

It can be seen that the electrochemical method is usable for observation of particle layer sediment on the vessel bottom and for identification of just off-bottom particle suspension state in *Fig. 3*.

3 Experimental

All experiments were carried out in transparent cylindrical vessels with flat and dished bottom. These vessels were of inside diameter T = 300 mm equipped with four radial baffles of width b = 0.1·T. The height of the liquid level was equal to the vessel diameter H = T. The ratio of vessel to impeller diameter was T/D = 3. The impeller off-bottom clearance was equal to one half of the impeller diameter C = 0.5·D. The experiments were carried out with pitched six-blade down pumping turbine with pitch angle 45°. The geometrical arrangement of the agitated vessel equipped with ED probes is shown in *Fig. 4 & 5*.

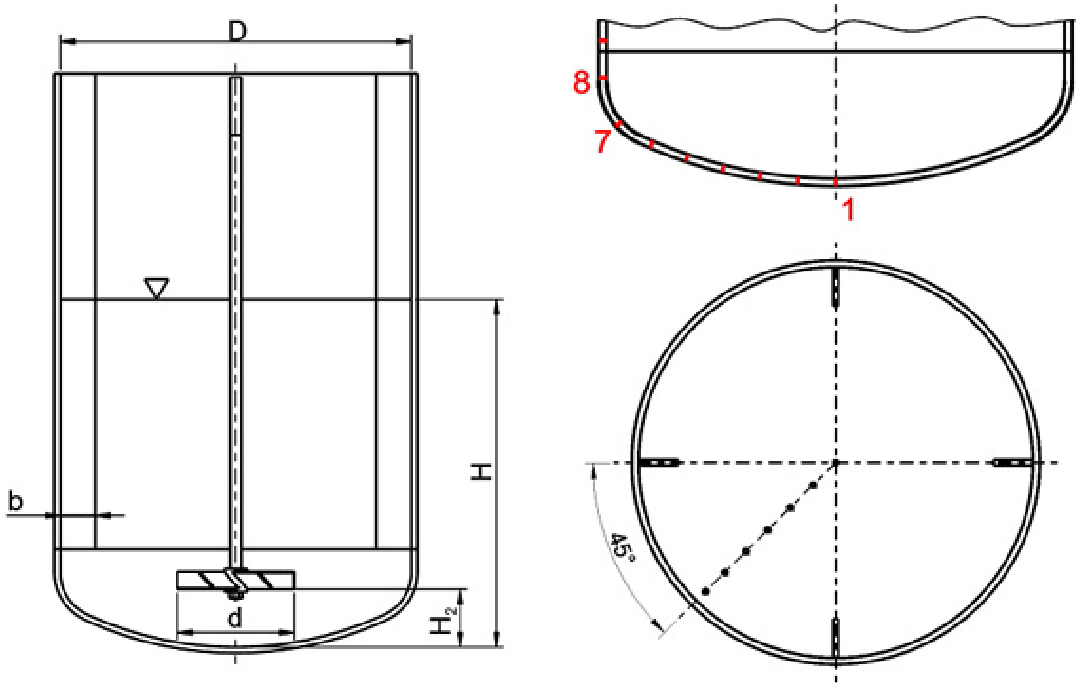


Fig. 4: *Geometrical layout of the experiment – dished bottom vessel.*

The dished bottom was equipped with nine ED probes, thanks to which the suspension state in any part of bottom could be observed. The probes were fabricated of platinum wire with a diameter of 0.5 mm. The stainless steel baffle was used as a counter electrode (see *Fig. 4*).

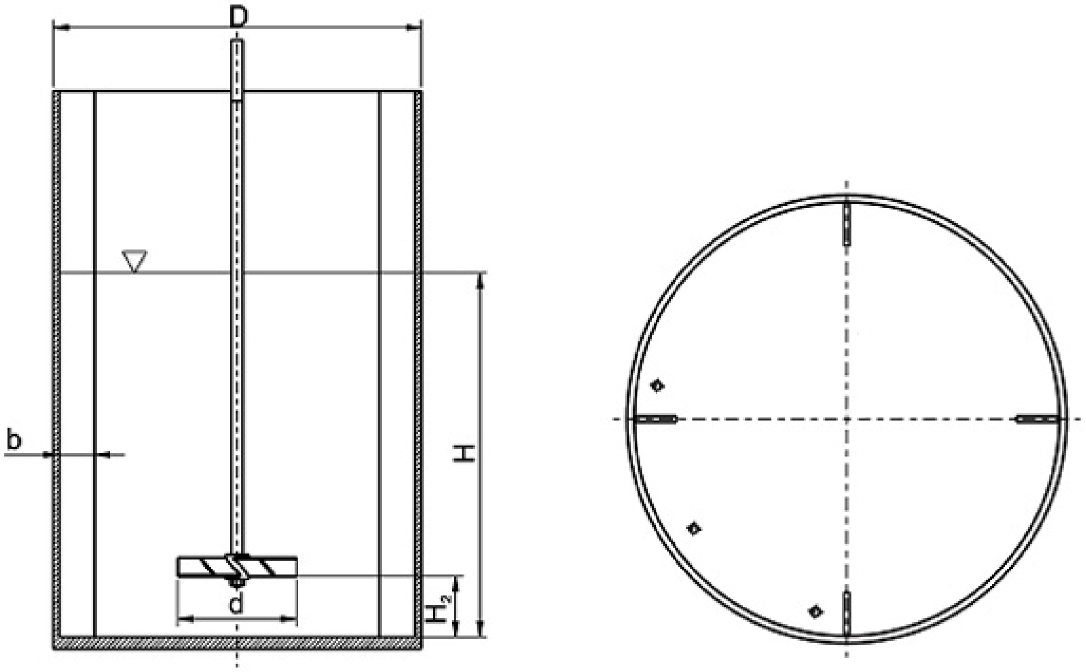
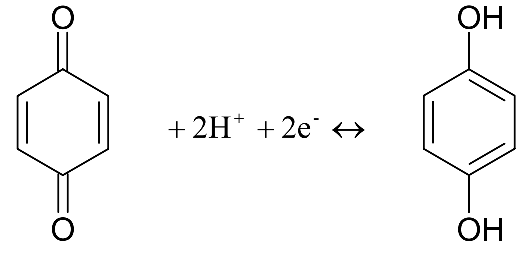


Fig. 5: *Geometrical layout of the experiment – dished bottom vessel.*

The flat bottomed vessel was equipped with 3 ED probes. They were placed 20 mm far from the baffle and 128 mm from the centre of the vessel as shown in *Fig. 5*. The platinum wire was of different diameters of 0,2; 0,5 and 0,8 mm.

An electrochemical interface connected with a PC secured on-line measurement of the current of six electrodes at a time. However it wasn't necessary to observe so many places on the vessel bottom to identify just off-bottom suspension state and therefore, just three electrodes located in critical places from this point of view were used in measurements. These were probes number 1, 7 and 8 (see *Fig. 4*).

Tab. 1: *Electrochemical reactions, material of working probes and supporting electrolytes for electrochemical measurements.*

	Electrochemical reaction	**E^0 [V]**	**Probe material**	**Supporting electrolyte**
1	$2H^+ + 2e^- \leftrightarrow H_2$	0,00	Pt	H_2SO_4
2	$Fe(CN)_6^{-3} + e^- \leftrightarrow Fe(CN)_6^{-4}$	+ 0,36	Pt, Ni	KOH, K_2SO_4
3	$1/2O_2 + H_2O + 2e^- \leftrightarrow 2OH^-$	+ 0,40	Pt, Ag, Ni	NaOH, NaCl
4	$I_3^- + 2e^- \leftrightarrow 3I^-$	+ 0,54	Pt	KI
5	 $+2H^+ + 2e^- \leftrightarrow$	+ 0,70	Pt, Ag	KH_2PO_4+Na_2HPO_4
6	$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$	+ 0,77	Pt, Cu	H_2SO_4
7	$\frac{1}{2}O_2 + 2H^+ + 2e^- \leftrightarrow 2H_2O$	+ 1,23	Pt	H_2SO_4

Two different electrolytes according *Tab. 1* were used because the appropriate reaction on the electrode must be guaranteed. The electrolytes potassium ferri/ferrocyanide aqueous solution with K_2SO_4 as a supporting electrolyte and aqueous solution with sodium chloride as a supporting electrolyte were used.

In the measurements different concentration of electrolytes components were used. The concentration of ferri/ferrocyanide was in the range from 0.25 $mol \cdot m^{-3}$ to 25 $mol \cdot m^{-3}$. The concentration of K_2SO_4 was ranged from 0.5 % b.w. to 1.5 % b.w. The NaCl concentration in the second type of electrolyte was in the range from 1 % b.w. to 20 % b.w.

The experiments were carried out in suspension of glass ballotine. Various mean volumetric particle diameter of ballotine were used in range from 0,025 mm to 4 mm. The mean volumetric concentration of solid phase was in range from 2,5% to 30 %.

When the viscosity effect was investigated the glucose and glycerine water solutions were used with sodium chloride as a supporting electrolyte. The dilution of solutions was carried according the viscosity value. The viscosity was in range from 200 mPa·s to 20 mPa·s.

4 Results and discussion

4.1 Electrolyte

Two electrolytes were used according to the reactions in *Tab.1*. The experiments proved that both of them are suitable for these types of measurements in wide range of their concentrations. The sodium chloride is substance that is cheap and one can buy it without problems and there are no harmful effects of it. The usage of both electrolytes is equivalent as it can be seen in *Fig. 6 & 7*.

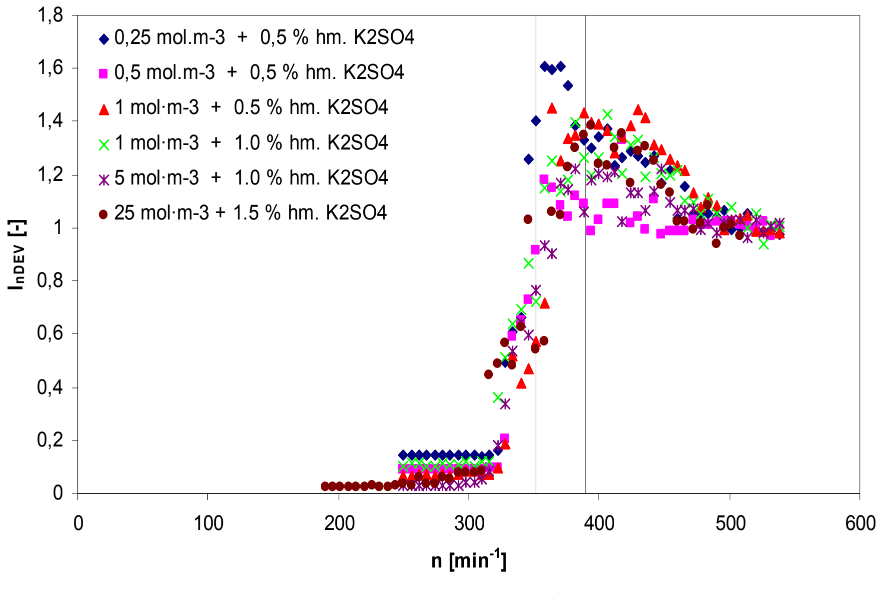


Fig. 6: *Dependencies of normalized values standard deviations of probe electric current on impeller speed in potassium ferri/ferrocyanide aqueous solution with* K_2SO_4*.*

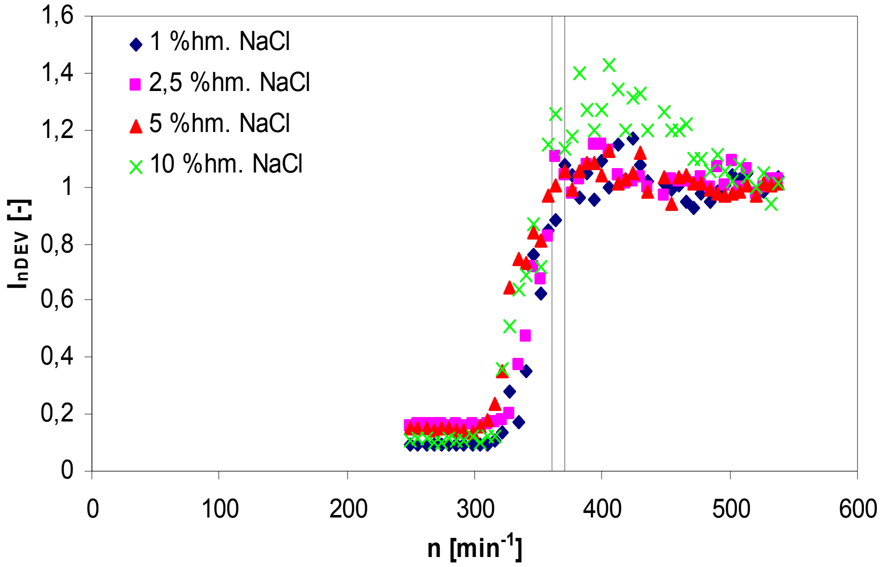


Fig. 7: *Dependencies of normalized standard deviations of probe electric current on impeller speed in aqueous solution with NaCl.*

4.2 The ED probe area and particle size

It was found out the effect of the range of ED probe area and particle size. There are recommendations in *Tab. 2* what particle size and probe area to use when one needs good readable dependencies of arithmetic mean values and standard deviations of probe electric current on impeller speed. The colours in the *Tab.2* show the lower described tendencies.

Tab. 2: *The ratio of the probe area to particle size.*

d_p/d_s	ED probe diameter		
particle size	0,2	0,5	0,8
0,025	0,13	0,05	0,03
0,250	1,25	0,50	0,31
0,425	2,13	0,85	0,53
0,714	3,57	1,43	0,89
1,495	7,48	2,99	1,87
4,000	20,00	8,00	5,00

There were more states observed during these measurements. When the particle size is much less than probe area, there is no problem to determine the just off-bottom suspension state. The particles are washed out the vessel bottom by increasing impeller speed and the just off-bottom state is evident in the dependencies as shown in *Fig. 8*.

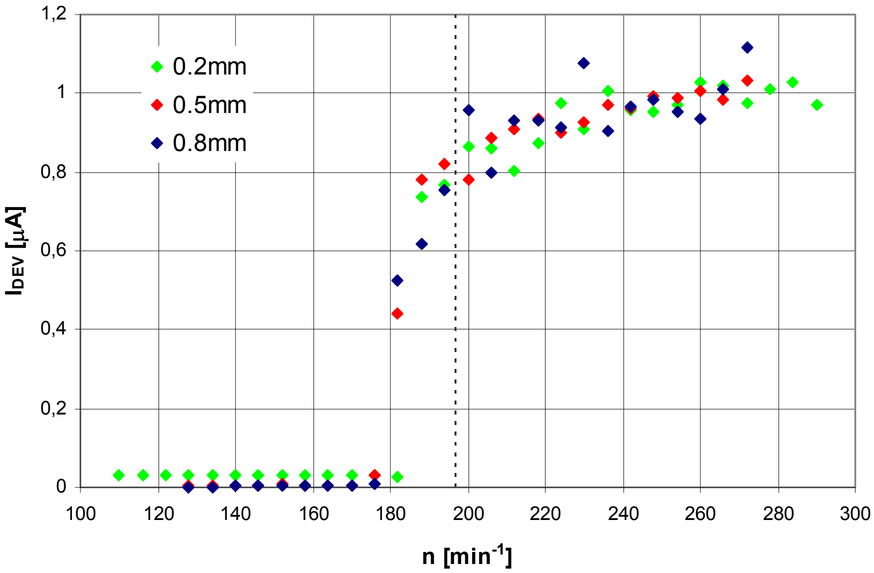


Fig. 8: *Dependencies of normalized standard deviations of probe electric current on impeller speed in potassium ferri/ferrocyanide aqueous solution with* K_2SO_4*; particles:* $d_p = 0{,}025mm$*,* $c_V = 30\ \%$.

When the particle size is approximately the same as the area probe the problem occurs. Low particle concentration causes worse determination of just off-bottom state (see *Fig. 9*). It is due to conductivity of the sediment. The big influence of particles is observed when there is high particles concentration in suspension it is displayed in the dependences.

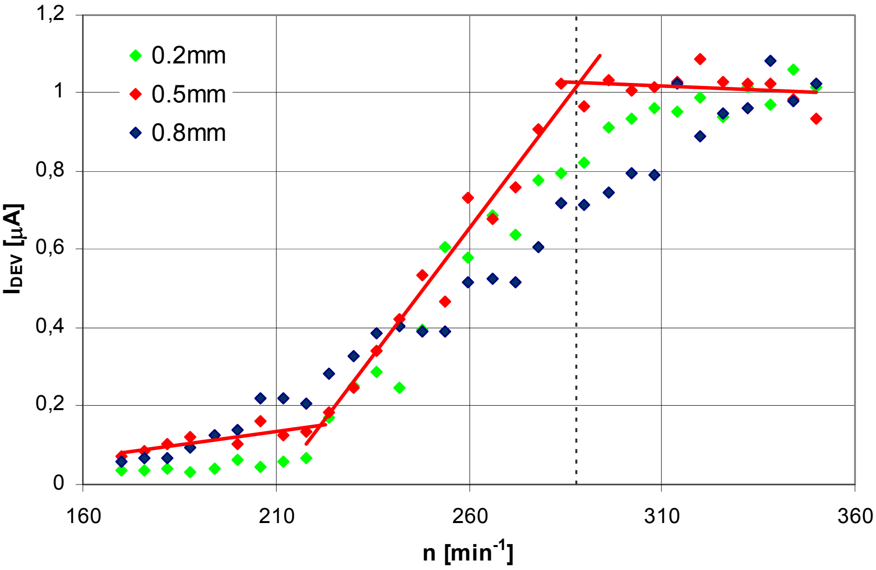


Fig. 9: *Dependencies of normalized standard deviations of probe electric current on impeller speed in potassium ferri/ferrocyanide aqueous solution with* K_2SO_4*; particles:* $d_p = 0{,}25mm$*,* $c_V = 2{,}5\ \%$.

When the particle size is much larger than the probe area, there is different mechanism of the suspension. And two states can occur. The peak or the dispersed values of the arithmetic mean and standard deviations is observed in the dependences as in *Fig. 10*.

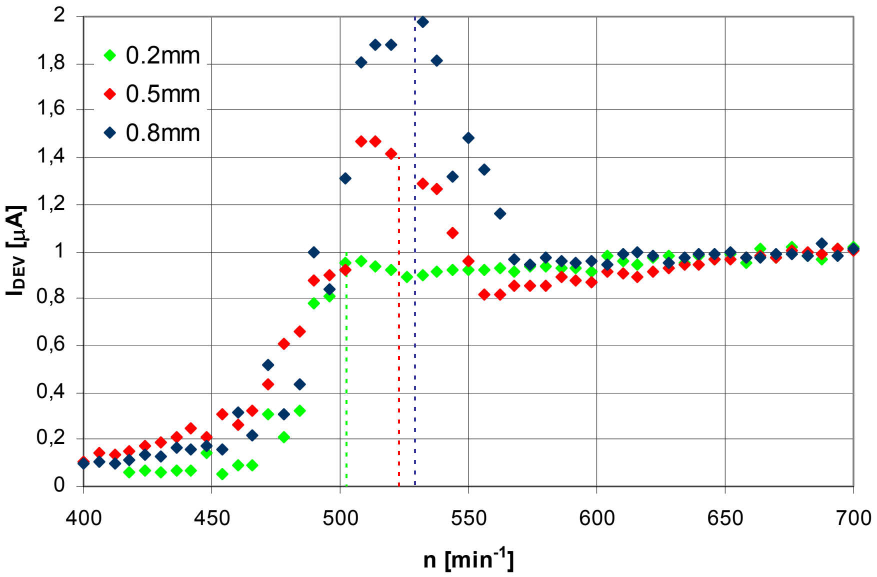


Fig. 10: *Dependencies of normalized standard deviations of probe electric current on impeller speed in potassium ferri/ferrocyanide aqueous solution with* K_2SO_4*; particles:* $d_p = 0{,}714$ *mm,* $c_V = 10$ *%.*

4.3 The viscosity – glucose and glycerine water solutions

The goal of these experiments was to investigate usage of the electrochemical method for high viscous suspension measurement. The measurements showed the method is applicable for suspension measurement. But the "new" region is observed when the impeller speed is low and particles lie on the vessel bottom. It is probably caused by the different mechanism than the molecular diffusion according to low impeller speed and the high viscosity of the solution (see *Fig. 11*).

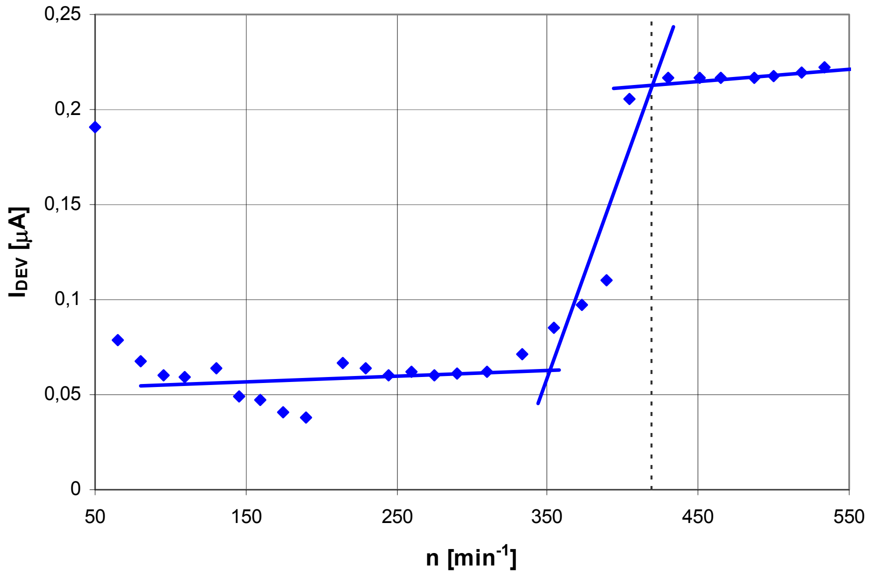


Fig. 11: *Dependencies of normalized standard deviations of probe electric current on impeller speed in aqueous solution with NaCl; glucose solution:* $\mu = 105$ *mPa·s; particles:* $d_p = 0{,}25$ *mm,* $c_V = 10$ *%.*

5 Conclusions

The experiments proved that the electrochemical method is suitable for objective determination of just off-bottom suspension state. Some conditions must be held such as suitable electrolyte, nonconductive suspension particles. There are some recommendations for the probe area and particles size using as shown in *Tab. 2*. Last but not least the electrochemical method can be used for the viscous particle suspension measurement as was shown in glucose and glycerine water solutions measurements.

6 Nomenclature

b	[m]	baffle width
c	[$mol \cdot m^{-3}$]	concentration of species
c_0	[$mol \cdot m^{-3}$]	concentration of species in bulk
c_v	[1]	mean volumetric concentration of solid phase
C	[m]	impeller off-bottom clearance
d_p	[m]	mean volumetric particle diameter
D	[m]	impeller diameter
E^0	[V]	electrode potential
H	[m]	height of the liquid level
i	[$A \cdot m^{-2}$]	density of electric current
I	[A]	electric current
n	[s^{-1}]	impeller speed
t	[s]	time
T	[m]	vessel diameter
v	[$m \cdot s^{-1}$]	flow velocity
x	[m]	distance measured from the forward edge of electrode
y	[m]	perpendicular distance from the electrode

Index:

avg	average value
dev	standard deviation
n	normalized values

Greek symbols:

$\dot{\gamma}$	[s^{-1}]	wall shear rate
δ	[m]	boundary layer width

7 References

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