Jour.Chem.Soc.Pak. Vol. 13, No. 4, 1991

Role of Polyvinylpyrrolidone on Mass-Transfer Processes of AgBr and AgI

NAJMUNISA ABBASI[*] AND ACHIM WINZER
Institute of Inorganic Chemistry, Technical University, Carl Schorlemmer Leuna-Merseburg,
0-4200 Merseburg, Germany

(Received 28th December, 1990 revised 6th October, 1991)

Summary: The effect of photographically active substance, like polyvinylpyrrolidone (PVP), on the rate of mass-transfer processes has been investigated in course of Ostwald-ripening of AgBr and AgI. The influence of PVP is determined at the interface processes of ionic crystals in the presence of various concentrations of PVP in the system, AgBr-^{82}Br- and AgI-^{131}I-. Since a very low supersaturation lies during Ostwald-ripening therefore under these conditions very low concentration of substance is very effective which adsorbs on the surface of AgBr and AgI crystals and reduces the rate of mass-transfer processes, which can be quantitatively measured by means of radiochemical measuring technique.

Introduction

The knowledge of kinetics at the interface processes, during crystallisation and the Ostwald-ripening of silver halide crystals, is very important for practical purpose, in the presence of photographically active substances. Therefore the photographical properties of AgBr suspension is affected strongly by the applied polymer substances. Here only those molecules are active which adsorbs on the surface of AgBr crystals.

The quality of a sample of AgBr crystals, for photographical application, depends mostly on the condition of precipitation during preparation of AgBr - dipersions.

The steps of crystallisation, like nucleation, crystal growth, Ostwald-ripening and agglomeration, are affected from the type and the concentration of given foreign substance.The action of this substance depends on the adosrbed amount of additive on the AgBr as well as AgI crystals and the supersaturation in system, the lower the supersaturation in the system, greater will be the adsorption of photographically active substances on the surface of the crystal and hence greater will be the action of additive on mass-transfer of ionic crystals.

A defined and relatively a very low supersaturation lies during the Ostwald-ripening, which is termed as physical ripening.

During the Ostwald-ripening the smaller crystal goes into the solution due to their high thermodynamic potentials, while the larger crystal grows further [1]. Under such conditions, a very small amount of additive acts as a stronger retardation of mass- transfer processes, during the physical-ripening, when it is adsorbed on the surface of silver halide crystals. Here the concentration of substance is to be considered in connection with the supersaturation of the system [2].

The mass transfer during the Ostwald-ripening of microcrystals of silver halide, can be quantitatively measured with the help of radiochemical measurement technique [3].

The purpose of these investigations was to examine the kinetics of mass-transfer processes in presence of various concentrations of this photographically active substance i.e. Polyvinylpyrrolidone (PVP), during the Ostwald-ripening of AgBr and AgI.

Polyvinylpyrrolidone is often used as a additive in the photographic system. It is one of the constituent of Lith, PVP inhibits hydroquinone development [4].

The applied PVP having an average molecular weight of 25000.

Results and Discusssion

The effect of Polyvinylpyrrolidone (PVP), at the rate of mass- transfer processes is investigated

---

[*] To whom all correspondance should be addressed.

during the Ostwald-ripening of the following systems:-

$AgBr + {}^{82}Br^-$,
$AgI + {}^{131}I^-$

Near by, at the same time a statement is obtained upon the influenced rate of mass-transfer processes in each case of concentration region of polyvinylpyrrolidone. Therefore the decrease of $^{82}Br^-$ activity of solution has been investigated, in dependence of the time, for various concentrations of the PVP in the solution. For this purpose a definite sample AgBr crystals is applied to keep constant the particle size distribution and the pretreatment of the crystals, because these factors are also essential to determine the rate at the interface processes.

Figure 1 represents the relative $^{82}Br^-$ activity of AgBr crystals (α), in dependence of time, for various concentrations of PVP. For the comparison, the rate of mass- transfer is shown in the absence of PVP (Fig. 1, curve 1). It also expresses that a decrease in the rate of mass-transfer processes is produced by increasing the concentration of PVP, during Ostwald-ripening of AgBr. It has also been noticed that the rate of exhange as well as the total amount of AgBr decreases by increasing the concentration of PVP.

The purpose of these radiochemical investigations was also to determine the amount of the applied substance, where begins a characteristic alteration in the rate of mass-transfer. From the relative ^{82}Br-activity of AgBr- crystals (α), the dissolved quantity of Br - (m_{Br}) was calculated from which it results that the total amount of Br^- remains constant in the solution, while the specific activity $^{82}Br^-$ ions in the solution decreases with time. Simultaneously it was attempted to bring the represented curves of Fig. 1 in a linear dependence. For this purpose the amount of $^{82}Br^-$ which is calculated from α/t curves (Fig. 1), is plotted against $t^{1/3}$ for various concentration of PVP. (Fig. 2). Straight lines are obtained in the time interval of 5-120 minutes, whose slope decreases with increasing concentration of a given substance. The deviation in the linearity in the first 5 minutes is due to the processes, which, by the addition of $^{82}Br^-$ activity begins the rapid heterogeneous isotopic-exchange on the crystal surface of AgBr, fast dissolution of a very small AgBr crystal and influencing the adsorptions equilibrium of PVP. If the slope of straight line in m_{Br} - $t^{1/3}$ curves is plotted against the concentration of PVP then the following representation is obtained (Fig. 3). First of all, the exponential decrease is going to be noticed in the rate of exchange. By increasing the concentration of PVP, the rate of Ostwald-ripening reaches to a saturation value, which lies near 2mg PVP/0.5 g AgBr.

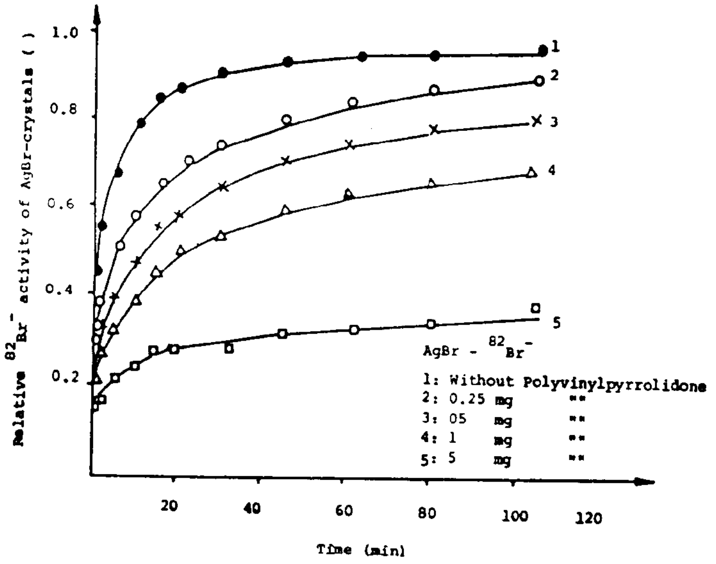

Fig.1: Relative $^{82}Br^-$-activity of AgBr (α) against time in presence of various concentration of Polyvinylpyrrolidone.

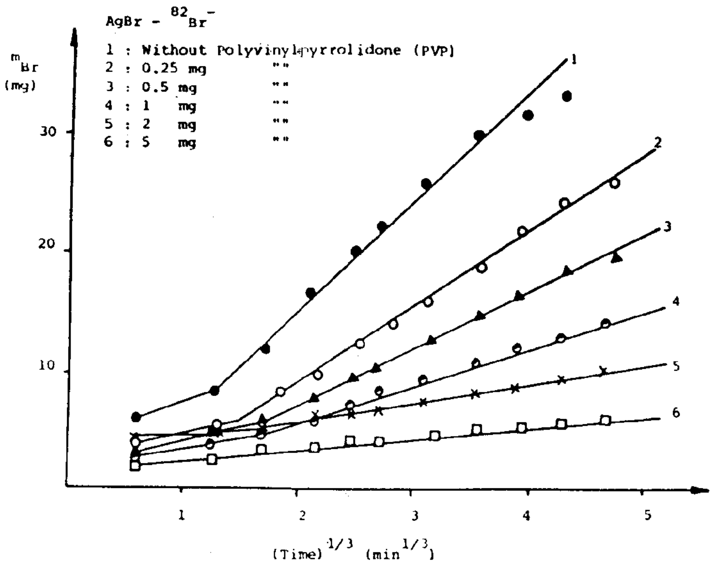

Fig.2: Calculated amount of $Br2^-$ from α/t curves against $t_{1/3}$ in presence of PVP.

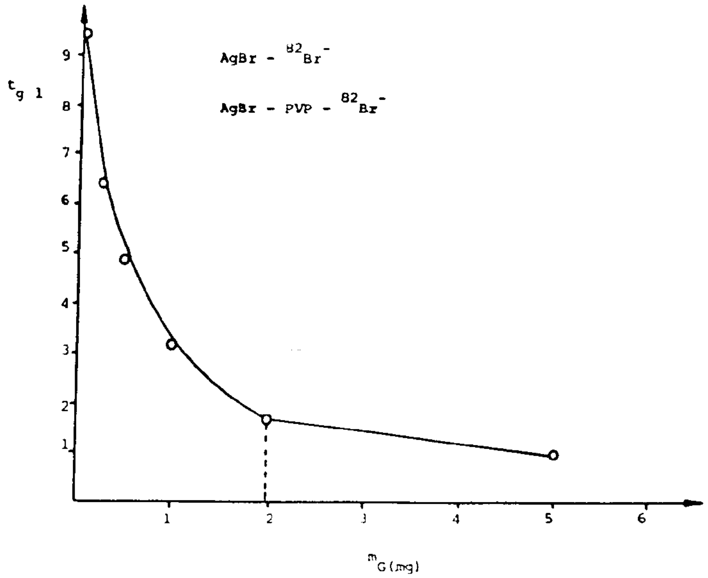

Fig.3: The slope of straight lines of m_{Br^-} t curves ($t_g\beta_1$) versus amount of PVP.

The measured average surface of AgBr of - $0.147m^2/g$, submits surface concentration of about 27 mg/m^2 on the crystal surface of AgBr.

It has been shown by plotting the degree of exchange against log, exchange time t, a linear relation is obtained for the mass transfer curves. As it is shown in Fig. 4 that this dependence is accomplished during the time interval of 10 to > 120 minutes.

By plotting the slope of these straight lines against the concentration of PVP, the following representation is obtained. (Fig. 5). A characteristic break point is also obtained from these interpretation, which lies near 2mg PVP/0.5g AgBr.

Fig. 6 shows the degree of exchange against the amount of PVP in the solution, for constant time. Here by a decrease in relative $^{82}Br^-$ activity has been noticed by increasing the concentration of PVP.

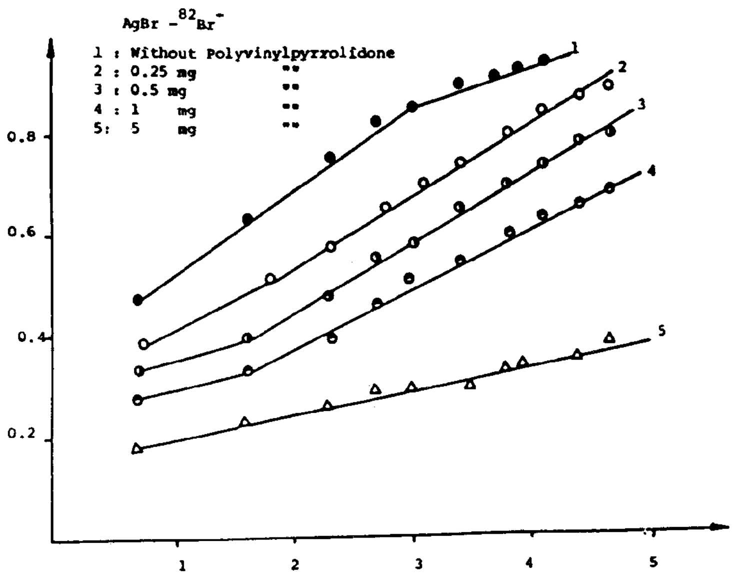

Fig.4: Degree of exchange versus log exchange time .

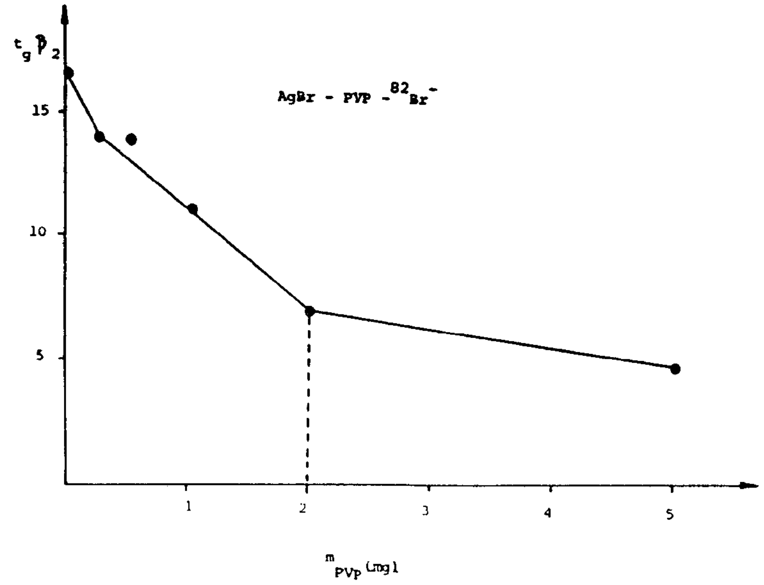

Fig.5: Slope of straight lines of α/int ($t_g\beta_2$) against the amount of PVP.

The appearance of these characteristics break points are associated with the adsorption of PVP on the surface of AgBr crystal. The surface of AgBr crystal is only partially covered with the extremely small amount of PVP, that means the rate of Ostwald-ripening is only insignificantly retarded. If a monomolecular covering of PVP is build up on the surface of AgBr- crystal, then in connection, it shows a characteristic change in the rate of mass-transfer which has been also observed experimentally. Investigation to the Ostwald-ripening of AgBr confirm this assumption in presence of gelatin. Near by, the analytically determined value for the adsorbed amount of gelatin was also found out by Zimkin and Klyuchewich [6]. The affect of temperature has been also examined at the rate of Ostwald- ripening of AgBr, in presence of constant quantity of PVP. By increasing the temperature, the

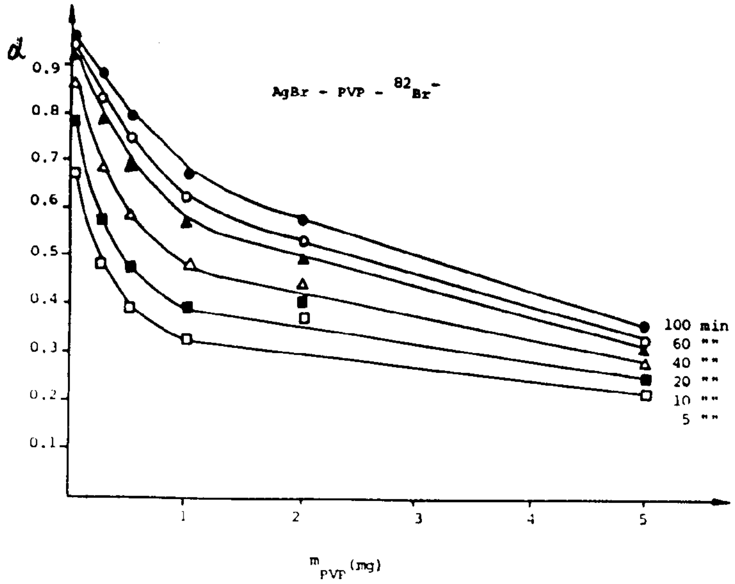

Fig.6: Degree of exchange against the amount of PVP.

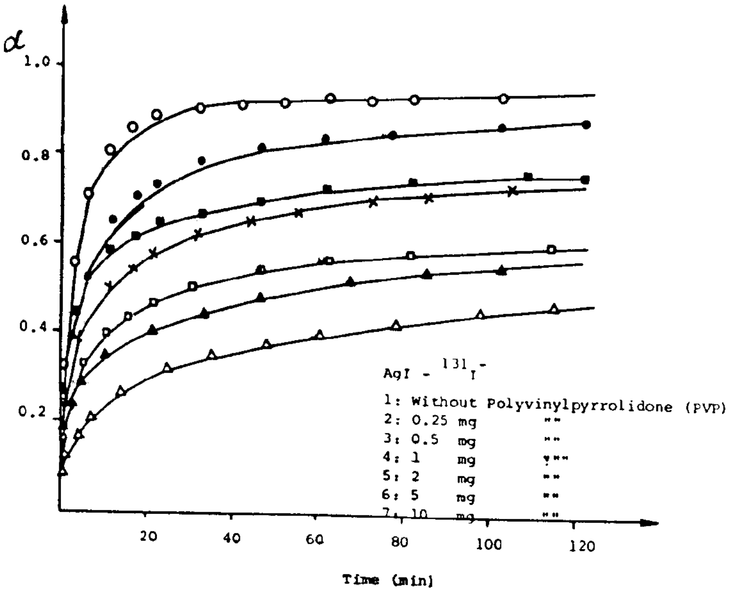

Fig.7: Relative $^{131}I^-$-activity of AgI(α) against time in presence of PVP.

rate of isotopic exchange is going to increase slightly. The corresponding activation energies is not determined for the mass-transfer in presence of foreign substances. The action of polymers additive shows also a very interesting results in the system of AgI-PVP- $^{131}I^-$ in the course of Ostwald-ripening. The influence of PVP at the rate of Ostwald- ripening of AgI is represented in Fig.7 and Fig.8. Similar to AgBr, PVP also retard relatively strong the Ostwald-ripening of AgI.

A characteristic amount of PVP has been also determined (from Fig. 8) in the system AgI-PVP $^{131}I^-$, which lies near 0.5 mg PVP/0.5g AgI. By plotting the slope of the line, from the α/lnt-diagram. (α/lnt-degree of exchange as a function of log ex-

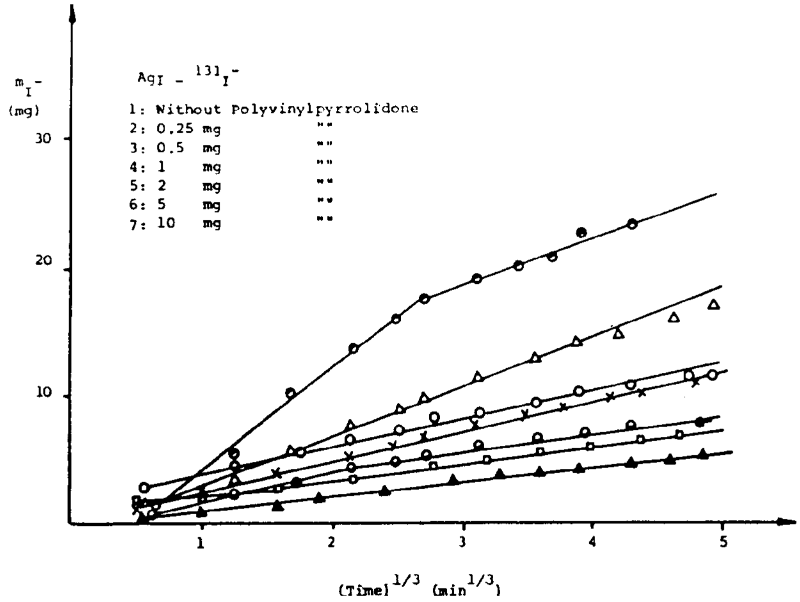

Fig.8: Calculated amount of I⁻, from α/t curves against $t^{1/3}$ in presence of PVP.

change time t) against the mass of PVP, a characteristic break point is obtained at 0.5 mg PVP/0.5g AgI. The determined surface of AgI, i.e. $0.147 m^2/g$, submits a surface concentration of PVP of about $6.80 mg/m^2$. Figure 9 expresses the degree of exchange (α) at a constant time of exchange against the amount of PVP in solution.

Hereby it is noticed that the rate of exchange first decreases relatively fast upto 2 mg PVP/0.5 g AgI and then attained a saturation value.

It is concluded from these experimental investigations that Polyvinylpyrrolidone, in comparison to AgI, blocked very strongly the mass-transfer in course of Ostwald-ripening of AgBr.

The acceleration of Physical-ripening of AgBr- dispersion which has been proved by Zaitsewa [7], has not been confirmed by these radiochemical measurements in the system of AgBr-PVP^{82}-Br-and AgI-PVP-^{131}I⁻. On the contrary, it has been proved that the rate of mass-transfer retards relatively strong by PVP in course of physical-ripening of AgBr and AgI. The retardation of Ostwald- ripening increases with increasing concentration of PVP. All the measurements are carried out at pH.7, whereas a pH dependence of PVP influence is not investigated.

In connection with the investigation of Sugiura [8], according to which the PVP is adsorbed relatively strong on the crystals of silver halide, shows that the radiochemical results as a well defined and reproducible results to give a judgement on PVP- action.

The given results of Tanaka and Fujii [9], that the cationic surface active agents can be better adsorbed on AgBr rather than the anionic surfactants, corresponds with these radiochemical investigations to the Ostwald-ripening of AgBr crystals.

A corresponding influence has been found out in special cases, when this given surface active agent reacting with a component of AgBr in solution, and with that, it influences the equilibrium concentration. It has been proved that even a very low concentration of cationic surface active agents, retards or totally blocks, nearly in all the cases, the rate of mass-transfer during Ostwald-ripening. These results show clearly a connection with the observation of Tanaka and Fujii [9]. Deposition of surface active agent and polymer additive on the surface of AgBr crystals, leads to a retardation of the rate of mass-transfer during Ostwald-ripening and crystal growth. As the crystal growth in comparison to Ostwald-ripening, proceeds at higher supersaturation in the system, therefore it requires a

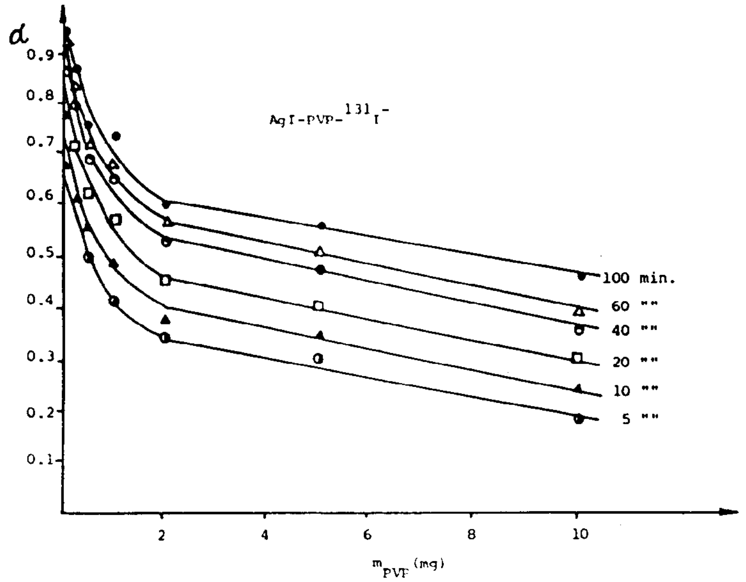

Fig.9: Degree of exchange against the amount of PVP.

corresponding high concentration of the given substance so as to prove the influence. Generally it can be so stated that the higher is the action of given substance, the lower will be the supersaturation in the system. It is concluded that the action of this polymer substance at the interface of crystals of silver halide (AgX) depends decisively upon the strength of adsorptive deposition on the surface of AgX.

Experimentally, it has been observed that the mass transfer processes during Ostwald-ripening, is slightly affected in the presence of PVP in the given system, AgBr-PVP-^{110}Ag^{+}. The statement by Reber [10] that, the organic compound, which adsorbs on the surface of the crystal, in the system AgBr-^{110}Ag^{+}, influences not so considerable the rate of Ag^{+} mass transfer, which is also confirmed by these given radiochemical measurements. In this system i.e. AgBr-PVP-^{110}Ag^{+}, the rate of mass-transfer does not depends on the concentgration of PVP. It concludes that in such experimental condition, the rate determining step is the self-diffusion in the crystals rather than the mass-transfer processes in course of Ostwald-ripening [11,12].

Following conclusion has been drawn from these radiochemical investigations that the polyvinylpyrrolidone is strongly adsorbed on the surface of AgBr as well as AgI crystals, through the pyrolidone ring, which retarded relatively strong, even in a very slight concentration, the rate of mass-transfer in the course of Ostwald-ripening of AgBr and AgI. Simultaneously, the optimal concentration of this photographically active substance i.e. PVP can also be determined through the quantitative calculation of measured mass-transfer curves by. means of radiochemical analyse method. It is further concluded that with the help of this method, a useful statement can be obtained upon the mechanism of mass- transfer at the interface of ionic crystals.

Experimental

0.5 g of AgBr or AgI, 100 ml of double distilled water and a certain amount of polyvinylpyrrolidone (PVP) is to be put in the flask which is then allowed to stir for a few minutes. After stirring a definite quantity of ^{82}Br-nuclide with a calculated amount of KBr (13.3 mg Br$^-$) is added and a decreased in radioactivity is examined as a function of time at a temperature of 40°C, while in the system of AgI-^{131} I$^-$, the determined quantity of ^{131}I$^-$ nuclide is applied with a given amount of inactive K1 (8.45 mg I$^-$).

AgBr and AgI is prepared by double jet method at 50°C. The radioactivity is determined by means of a radiation measuring assembly type VA-V-100/VA-G-120 in connection with a Scintillation probe type VA-S-980 (RFT Messelektronik Dresden).

The radioactivity of the solution is measured for the determination of the mass transfer processes in the dependence of the time.

As to prove the influence of given polymer substances on the rate of mass-transfer during Ostwald-ripening, the following factors such as stirring rate, particle size distribution, surface properties, supersaturation of systems and pretreatment of Ag halide crystals, must be kept constant [5]. This can be accomplished when all the investigation has been done from the same Ag halide sample, while other technical parameter remains constant.

References

1. W. Ostwald, *Z.Physik.Chem.*, **34** 495 (1900)
2. A. Winzer, H-H. Emons and B. Jugel, Freiberger Forschungshefte. A 600 p. 31 (1979).
3. K-H. Lieser, Ph. Gutlich and I. Rosenbaum, *Radiochim.Acta* **5** (1966); **4** 216 (1965).
4. G.F. Van Veelen and R. Berendsen, *J.Photogr. Sci.*, **15** (1967) 226 (from C.A. 68 (1968) No. 25405 C).
5. A. Winzer, H-H. Emons and B. Jugel; Freiberger Forschungschefte, A 600 p. 27 (1979).
6. E.A. Zimkin and V.F. Klyuchevich, *Zh. Nau.Chem. Prikl. Photogr.Kinematogr.* **24** 203 (1979).
7. L.M. Zaitsewa; Tr. Leningrad Inst. Kinoinzh, (1967).
   Nr. 42, 105 (from C.A. 70 (1969) No. 72954 g).
8. M. Sugiura, *Bull.Chem.Soc.Jap.*, **43** (1970) (from C.A. **73** (1970) No. 102345 r).
9. T. Keiichi and E. Fujii, *Tokyo Kogyo Shikenscho Hokoku* **69** 463 (1965).
10. K. Reber, *Photogr.Korresp.* 1969 105 (11) 175 12 191.
11. A. Langer, *J.Chem.Phys.*, **10**, 321 (1942).
12. A. Langer, *J.Chem.Phys.*, **11** 11 (1943).