Effect of surfactants on the removal of copper from waste water by cementation

M.A. Drweesh

Chemical Eng. Dept., Faculty of Eng., Tanta University, Tanta, Egypt

The rate of copper II/iron cementation on a rotating cylinder in presence of surfactants SAS was measured at different temperatures using atomic absorption. It was found that, the rate of cementation decreases with increasing the concentration of SAS, and increases by increasing temperature and cylinder rotation speed. Thermodynamic parameters ΔH*, ΔG* and ΔS* were calculated for the reaction. The effect of the presence of alcohol and mixed SAS was also studied.

تم قياس معدل احلال أيونات النحاس السامة بأيونات الحديد الذائبة بأستخدام أسطوانة دوارة من الحديد عند سرعات مختلفة و عند درجات حرارة مختلفة بأستخدام جهاز مطياف الكتلة. و تم الدراسة في وجود و غياب ثلاث أنواع من المواد النشطة سطحيا و هي صوديوم ديدسيل بنزين سلفونات كمادة أنيونية و ستيل تراي ميثيل أمونيوم بروميد كمادة كاتيونية و ترثيون x-١٠٠ كمادة غيرأيونية. ووجد أن معدل الاحلال يقل في وجود تلك المواد و يزداد بزيادة درجة الحرارة و عدد دورات أسطوانة الحديد و تم حساب الدوال الثرمودينمكية *ΔH* , *ΔG* , *ΔS* و تم اجراء هذه الدراسة في وجود الكحول و المواد النشطة سطحيا.

Keywords: Surfactants, Waste water, Cementation, Copper removal

1. Introduction

Cementation is one of the most effective and economic techniques for recovering toxic and valuable metals from industrial waste solution [1]. Cementation is also used in purifying leach liquor prior to electrowinning of metal [2] from its solution by less noble metal which is usually cheap and non toxic. For example, in the process of zinc winning, zinc powder is added to Zn electrolyte in order to eliminate cations such as copper and cadmium which would otherwise reduce the current efficiency of the subsequent step of zinc electrodeposition [3]. More recently the effect of surfactants on the removal of Cu^{++} from waste water has been studied [4-12].

The object of the present work is to study the effect of SAS and alcohol on the cementation of copper using a rotating zinc cylinder at different concentrations of alcohol with emphasis on the following aspects:

1. Study of the kinetics of copper cementation on rotating iron cylinder in presence of surfactants as (SDS) Sodium dedocyl sulphate, (CTAB) Cetyl trimethyl ammonium bromide, and Triton-X-100 at different temperature.

2. Determination of the thermodynamic parameters of activation of the process.
3. The effect of binary mixtures of surfactants on the rate of cementation.
4. Effect of addition of small quantity of alcohols on the behavior of surfactants.

2. Experimental methods:

2.1. The apparatus

An iron cylinder driven by variable speed motor was rotated in 200cm³ $CuSO_4$ solution. The frequency of rotation recorded as revolution per second was counted by an optical tachometer. The reaction vessel was set in a constant temperature (±0.05°C) ultrthermostat.

2.2. Kinetic measurements

Reagent-grade chemicals and redistilled water were used in preparing $CuSO_4$ solutions. Five different solutions of $CuSO_4$ of concentrations 6.25, 31.75, 63.56, 95.25 and 127 ppm were used. The active length of the rotating cylinder was 7cm.

The cementation reaction proceeds as follow [12]:

$$Cu^{++} + Fe \rightarrow Cu + Fe^{++}. \tag{1}$$
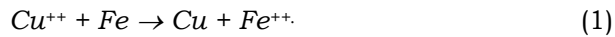
This reaction is diffusion controlled [1] whose rate in the batch reactor can be represented by the eq. (2):

$$-V\frac{dC}{dt} = kAC. \tag{2}$$

Eq. (2) can be integrated to:

$$V \ln\frac{C_0}{C} = kAt . \tag{3}$$

Where V is the volume of solution containing copper ions and C_0 is the initial concentration. Eq. (2) was obtained assuming that, copper ion concentration is negligibly low at iron /solution interface) solution interface, C is the copper concentration (Mol l^{-1}) in solution at time t (sec), k is the rate constant of cementation or mass transfer coefficient which depends upon fluid flow and temperature concentrations (cm.sec^{-1}), A is the exposed area (cm^2) of iron/cm^2 solution and V is the volume of solution (cm^3).

Fig. 1 gives the relation between log C_0/C against time for cementation of copper from copper sulphate, the rate constant k were calculated graphically from this relation and is given in table 1.

Fig. 1 shows that the cementation reaction is a first order reaction which was verified by other authors [11-15]. It is clear from table 1, that the rate of cementation increases by increasing concentration CuSO$_4$ and increases also by increasing temperatures.

Fig. 2 shows the relation between log C_0/C against time for different temperatures at constant CuSO$_4$ concentration (95.25 ppm) containing Triton-X-100 as example. The plots pass through origin, which prove that the cementation reaction is still a first order in presence of SAS. The rate constant of reaction for different surfactant composition were calculated from the slopes of $ln C_0/C$ vs time lines. Table 2 summarizes the obtained results at different temperatures.

It is found that the cementation process is inhibited by addition of surfactants. The percentage of inhibition for cementation reaction is calculated from the following relation:

$$\% \text{ inhibition} = \frac{k - \overline{k}}{k}100 , \tag{4}$$

where k is reaction rate constant in blank solution [95.22 ppm CuSO$_4$] and k is the rate constant of the reaction in presence of SAS. Table 3 gives the relation between the percentages of inhibition of the rate of cementation and SAS cementation. It was found that the % inhibition ranges from 32.2% to 94 % depending on the types of SAS and its concentration. The order of cementation inhibition is Triton-X-100< CTAB<SDS.
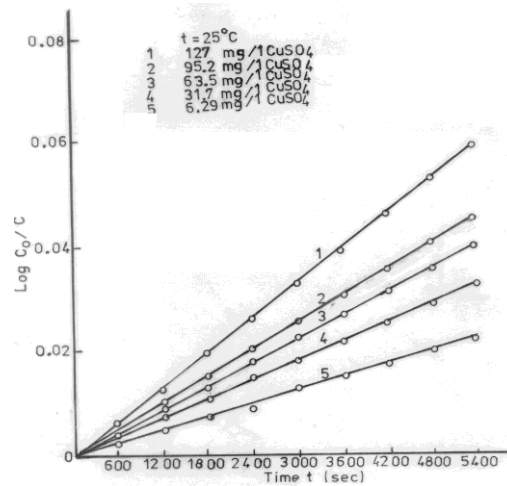

Fig. 1. Log C_0/C V$_s$ time of different CuSO$_4$ concentration.

Table 1
Values of k x10^2 at different *CuSO$_4$* concentration and different temperatures

k at different CuSO$_4$ conc. ppm $t\overset{\circ}{o}$ C	k x10^2 cm sec^{-1}				
	6.25 ppm	31.3 Ppm	63.50 ppm	95.25 ppm	127 Ppm
25	3.2	4.1	4.28	5.33	5.83
30	3.80	4.91	5.001	6.81	7.20
35	4.02	5.46	5.90	7.30	8.02
40	4.30	5.90	6.01	8.4	9.3

Table 2
First order rate constant (k:10^{-4} cm Sec^{-1}) for cementation of copper on iron metal in presence of SAS at different temperature.
(a) Triton-X-100

k at different Triton-x-100 conc. mol.l^{-1} t$\overset{\circ}{\text{o}}$ C	k x 10^4 cm sec^{-1}				
	1x10^{-5} mol. l^{-1}	5x10^{-5} mol. l^{-1}	10x10^{-5} mol. l^{-1}	50x10^{-5} mol. l^{-1}	100x10^{-5} mol. l^{-1}
25	3.61	2.81	2.22	2.16	1.41
30	4.35	3.52	2.80	2.71	1.75
35	4.65	5.15	3.42	3.65	2.08
40	4.91	5.76	4.80	4.31	2.35

(b) CTAB

k at different CTAB conc. mol.l^{-1}t$\overset{\circ}{\text{o}}$ C	k x 10^4 cm sec^{-1}				
	1x10^{-5} mol.l^{-1}	5x10^{-5} mol.l^{-1}	10x10^{-5} mol.l^{-1}	50x10^{-5} mol.l^{-1}	100x10^{-5} mol.l^{-1}
25	1.85	1.35	0.331	0.641	0.60
30	2.02	1.49	1.202	0.624	0.600
35	2.20	1.60	1.380	0.736	0.782
40	2.88	2.21	1.823	0.928	0.801

(c) SDS

k at different SDS conc. mol.l^{-1} t$\overset{\circ}{\text{o}}$ C	k x 10^4 sec^{-1}				
	1x10^{-5} mol.l^{-1}	5x10^{-5} mol.l^{-1}	10x10^{-5} mol.l^{-1}	50x10^{-5} mol.l^{-1}	100x10^{-5} mol.l^{-1}
25	1.62	1.12	0.801	0.402	0.352
30	2.02	1.40	1.005	0.708	0.603
35	2.02	1.53	1.12	0.804	0.70
40	2.60	2.02	1.80	0.801	0.85

Table 3
The relation between % inhibition and concentration for all SAS at 25$\overset{\circ}{\text{o}}$ C.
(a) Triton-X-100

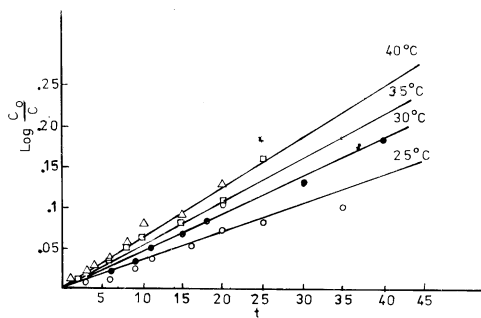| C x 10^5 mol l^{-1}		1x10^{-5} mol.l^{-1}	5x10^{-5} mol.l^{-1}	10x10^{-5} mol.l^{-1}	50x10^{-5} mol.l^{-1}	100x10^{-5} mol.l^{-1}
	Triton-X-100	32.2	47.28	58.35	59.47	79.50
% inhibition	SOS	65.266	74.67	84.40	88.50	88.80
	SDS	69.61	97.89	79.0	85.00	92.50

Fig. 2. Log C_0/C V_s time of different temperatures in presence of triton-x-100.

The decrease in the rate of cementation in the presence of surfactant may be attributed to:

i. SAS may form a thin adsorbed film on the iron metal which leads to decrease the rate of cementation reaction, adsorption of SAS on the surface depends mainly on the structure of the SAS. Triton-X-100 which is non ionic SAS has no charge is adsorbed on the surface of the metal less than SDS which is anionic surfactant. Anionic surfactants electrostatically adsorbs on the iron surface while CTAB repels from the surface which is negatively charged [16].

ii. The decrease in the diffusion coefficient (D); of Cu^{++} in solutions containing SAS due to the increase in the interfacial viscosity η in accordance to Stokes-Einstein eqs. (16) and (17):

$$\eta \frac{D}{T} = \text{ constant.} \qquad (5)$$

Where T is the absolute temperature. The increase in the interfacial viscosity is caused by the adsorption SAS molecules on the iron surface.

3. Effect of stirring on the reaction

The rate of cementation was calculated at different cylinder rotation speed 50, 100, 200, 400, 500 and 600 revolution /minute. The values of k are given in table 4 at $CuSO_4$ concentration 63.5 ppm containing 1×10^{-4} mol l^{-1} surfactant.

From the above table, it is obvious that the rate of cementation reaction in presence of SAS increases by increasing rpm. The effect of rotational speed on the rate of reaction can also be used to determine whether a reaction is a diffusion or chemically controlled. If the rate of reaction increases with increasing stirring speed, it is diffusion controlled. On the other hand if the rate of the reaction is independent on the stirring speed, it is chemically controlled. The data given in the above table proves that, the present cementation reaction is diffusion controlled, this agrees with the previous studies [16,17].

4. Effect of addition alcohol on the behavior of SAS

It was found that the addition of small amount of alcohol (ranged from 0.3 to 0.9 ml) to SAS decreases the rate of cementation by an amount ranging from 11.47% to 47.8% depending on the type of alcohols and its concentration as well as on the type of SAS. It is obvious that:
1. The percentage inhibition increases as the concentration of alcohols increases. This may be attributed to the formation of a hydrogen bond with the surface of metal [19].
2. The order of increasing inhibition is as follows n-butanol> propanol> ethanol> methanol.

This may be explained as the length of hydrocarbon increases, the molecule become more retarding to cementation reaction. Table 5 shows the relation between the % inhibition

and concentration of alcohol, the finding that n-butanol is the strongest inhibitor is explained by the fact that n-butanol act as co-surfactants better than other alcohols [16] owing to its longer chain.

4.1. Cementation in presence of mixed SAS

The effect of binary mixture of SAS compounds has been studied in several cases. In many industrial applications, SAS are invariably mixture as they are produced from feed stock containing mixed hydrocarbon chain length. The surfactants used in practical application are usually mixture of SAS. This due to:
i. The very high cost of pure substance production.
ii. The fact that, the SAS mixture in many practical applications has much better properties than those of their individual components.

4.2. The rate of cementation in the presence of anionic- cationic SAS

The addition of CTAB as (anionic SAS) to SDS (anionic SAS) greatly increases adsorption as shown in table 6. The superiority in performance for mixture of similar or dissimilar SAS is largely attributed to synergistic behavior among the molecule mixtures [20]. In this case the expected micelle will be formed from two head group and double chain of surfactants. The mixed SAS exhibit a large synergin surface tension reduction and they form mixed adsorption films and make more inhibition [21] to the rate of cementation.

4.3. The rate of cementation in presence of non ionic + anionic SAS

In presence of Triton-X-100 (non ion SAS) and SDS (anionic SAS) or (CTAB) (SAS) the percentage inhibition is larger than Triton-X-100 alone as shown in table 6 due to dipole charge interaction [21,22].

4.4. Thermodynamic treatment of the results

The activation energy of the reaction E was obtained from Arrhenius equation:

Table 4
Effect of rpm on reaction rate constant

Rpm	50	100	200	300	400	500	600
$k.10^3$ cm.sec^{-1}	7.10	7.51	8.01	8.98	12.14	15.63	20.43

Table 5
The effect of SAS on the rate of cementation in presence of alcohol at 25° C
(a) Triton-X-100+ alcohol

Alcohol	$C_{alc.}$ ml	C_{SAS} x10^5 mol.l^{-1}	k blank x 10^4	k in presence of alc. X 10^4	% reduction in k
Methanol	0.3	10	5.32	5.12	4.10
	0.6			5.08	4.37
	0.9			5.01	6.19
Ethanol	0.3	10	5.32	4.95	7.12
	0.6			4.90	8.10
	0.9			4.82	9.56
n-propanol	0.3	10	5.32	4.73	11.25
	0.6			4.70	11.89
	0.9			4.60	13.70
n-butanol	0.3	10	5.32	4.50	15.56
	0.6			4.43	16.13
	0.9			4.413	17.22

(b) SDS + alcohol t 25° C

Alcohol	$C_{alc.}$ Ml	C_{SAS} x10^5 mol.l^{-1}	k blank x 10^4	k in presence of alc. X 10^4	% reduction in k
Methanol	0.3	10	5.32	4.61	13.35
	0.6			4.32	18.78
	0.9			4.01	24.62
Ethanol	0.3	10	5.32	3.83	28.00
	0.6			3.515	33.93
	0.9			3.50	34.21
n-propanol	0.3	10	5.32	3.50	34.26
	0.6			3.41	35.46
	0.9			3.31	38.00
n-butanol	0.3	10	5.32	3.81	28.0
	0.6			3.42	36.0
	0.9			3.32	37.7

(c) CTAB alcohol at 25° C

Alcohol	$C_{alc.}$ Ml	C_{SAS} x10^5 mol.l^{-1}	k blank x 10^4	k in presence of alc. X 10^4	% reduction in k
Methanol	0.3	10	5.32	4.711	11.47
	0.6			4.211	20.86
	0.9			4.08	23.31
Ethanol	0.3	10	5.32	3.80	28.57
	0.6			3.46	39.50
	0.9			3.443	35.28
n-propanol	0.3	10	5.32	36.41	27.82
	0.6			36.30	31.17
	0.9			36.21	31.20
n-butanol	0.3	10	5.32	3.36	32.14
	0.6			3.30	37.97
	0.9			3.10	41.17

Table 6
The effect of mixed sas on the rate of cementation at 25° C
(a) SDS +CTAB

$C_{SDS} \times 10^5$ mol.l^{-1}	$C_{CTAB} \times 10^5$ mol.l^{-1}	k blank x 10^4	k in presence of mixed x 10^4	% reduction
	1		1.60	58.86
	5	5.32	1.54	71.06
1	10		1.50	71.80
	100		1.43	73.132
	1		1.42	73.3
	5	5.32	1.40	73.68
5	10		1.31	75.38
	100		1.2	7.44
	1		1.40	73.3
	5	5.32	1.32	75.56
10	10		1.22	77.06
	100		1.118	77.92

(b)

$C_{SDS} \times 10^5$ mol.l^{-1}	$C_{Triton-X-100X} \times 10^5$ mol.l^{-1}	k blank x 10^4	k in presence of mixed x 10^4	% reduction
	1		1.61	58.80
	5	5.32	1.58	70.30
1	10		1.53	71.24
	100		1.46	72.56
	1		1.46	72.56
	5	5.32	1.43	73.12
5	10		1.33	75.0
	100		1.25	76.80
	1		1.4	73.30
	5	5.32	1.38	74.00
10	10		1.28	76.00
	100		1.18	77.92

$$lnk = -E/RT + lnA. \tag{6}$$

Where R is the gas constant [8.314K J^{-1} mol^{-1}]: E is the activation energy and A is the frequency factor fig. 3, 4 give the relation between log k gainst $1/T$ for SAS used. The values of E are given in table 7. These values were used to calculate enthalpy of activation ΔH^*, entropy of activation ΔS^* and free energy of activation ΔG^* using the following equations:

$$\Delta H^* = E\text{-}RT, \tag{7}$$

$$\Delta S^*/R = lnA - lnB\ Te/h, \tag{8}$$

$$\Delta G^* = \Delta H^* - T\Delta S^*. \tag{9}$$

Where B is the Boltzman constant, e is 2.7183, h is Plank's constant. The increase in the heat of adsorption led to an increase in the energy of adsorption forces, however raising of the temperature acts in the reverse direction,

increasing the kinetic energy of the molecules, facilitating physical adsorption. In absence of SAS the activation energy was found to be 25kj mol^{-1} which is smaller than when SAS is used as inhibitor. Thus the high values of activation energies show that:
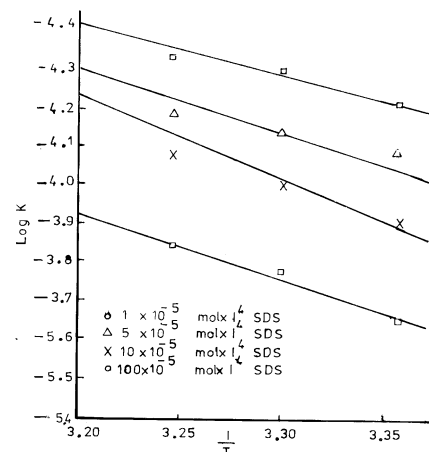

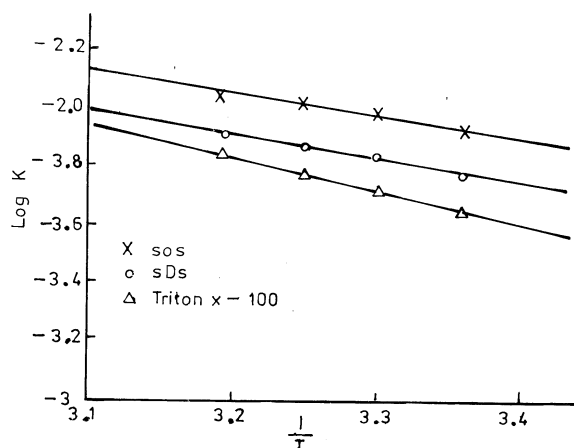Fig. 3. Relation between Log K and $1/T$ for SDS at different concentrations.

Fig. 4. Relation between Log K and $1/T$ for SDS at different concentrations.

Table 7
Thermodynamic parameters of activation at different SAS concentration and 25° C
(a) Triton-X-100

$C \times 10^5$ mol.l^{-1}	ΔG^* KJ mol^{-1}	ΔH^* KJ mol^{-1}	$-\Delta S^*$ JK^{-1} mol^{-1}	ΔE^* KJ mol^{-1}
1	90.6726±3.3	35.843±3.4	185.2±10.20	38.322
5	79.342±4.20	25.702±4.80	190.01±9.30	28.181
10	94.348±5.12	37.403±4.31	191.10±12.10	39.91
100	87.959±6.12	31.041±3.21	182.30±10	33.521

(b) CTAB

$C \times 10^5$ mol.l^{-1}	ΔG^* KJ mol^{-1}	ΔH^* KJ mol^{-1}	$-\Delta S^*$ JK^{-1} mol^{-1}	ΔE^* KJ mol^{-1}
1	96.137±3.87	24.02±0.66	242.0±2.19	26.50
5	105.587±10.21	35.841±2.161	235.02±9.6	38.32
10	105.060±8.12	36.520±1.21	230.2±1.67	39.00
100	97.693±6.12	24.981±4.08	244±11.5	27.40

(c) SDS

$C \times 10^5$ mol.l^{-1}	ΔG^* KJ mol^{-1}	ΔH^* KJ mol^{-1}	$-\Delta S^*$ JK^{-1} mol^{-1}	ΔE^* KJ mol^{-1}
1	92.9520±1.66	22.9206±0.66	235.1±2.12	25.40
5	99.652±3.68	31.112±1.68	230.1±3.12	33.60
10	103.57±2.89	36.521±2.52	225±2.16	39.00
100	96.441±5.30	24.921±4.02	240±3.15	27.40

1. The rate of cementation of copper is increased by addition of SAS at temperature above 20° C.
2. The adsorption process is physical adsorption [17].

Table 7 shows that the change in the entropy ΔS possesses high negative values indicating a highly ordered organic species in the solution under investigation.

5. Conclusion

The rates of copper/Fe cementation reaction in presence of organic as formic, acetic, lactic and glycine decreased than blank solution. The order of decreasing reaction rate is as follow: formic, acetic, lactic and glycine.

The rate of cementation reaction is increasing by temperature and the value of ΔG^* raged between 25-39 KJ mol^{-1} which

indicates that, the reaction is diffusion controlled process.

References

[1] A.K. Biswas, W.G. Daven part, Extractive Metallurgy of Copper, Pergamon Press, New York (1979).

[2] V. Ettel, in Comprehensive Treatise in Electrochemistry, ed. O'M. Bockris Plenum, Vol. 2, New York (1981).

[3] P. Bro and K.C. Lang, Environ. Sci. Technol. Vol. 8, p. 925 (1974).

[4] G. Genon and P. Parti, Gaglia, Chim. Ind. (Milan), Vol. 65, p. 79 (1983).

[5] G.P. power and I.M. Richie, Metal Displacement Reactions, In Modern Aspects of Electrochemistry, Vol. 11 Plenum press, London, P. 190.

[6] F.W. Van Straten and W.F. Ehret, J. Electrochem. Socity Vol. 61, p. 1798 (1939).

[7] P.H. Stricki and F. Lawson, Proc Australas, Inst. Mm Metall, Vol. 249, 1 (1973).

[8] Idem, Ibid, Vol. 239, p. 25 (1970).

[9] E.C. Lec, F. Lowson, K.K.N. Han, Hydrometallurgy, 3, 7 (1978).

[10] G. Power, I.M. Richie, Ausr. J. Chem., Vol. 29, p. 699 (1976).

[11] Hanaa Hamam, Ph.D Thesis, Faculty of Science Alex. University (1998).

[12] M. El. Batouty, Revue des Comptes Rendue France. C.R.Acod. Sci. Daris, Vol. 323, p. 455(1996).

[13] G.A. Vidulich and R.L. Kay, Rev. Sci. Instium., Vol. 37, p. 1662 (1987).

[14] M.A. Gobashy and M.A. Fawzy, Metall Vol. 2, p. 41 (1987).

[15] N. Tanaka, Electrochimica Acta 21, 201 (1976).

[16] A.A Taha, A.M. Ahmed and Dalia. A. Ebrahim, Egypt. J. Chem, Vol. 43, p. 435 (2000).

[17] A.M. Ahmed and Zoarb Mettalked, Vol. 74, p. 436 (1988).

[18] M.A. Quraishi, M.A.S.Ahmed and V.E.Venkatachari, Bull. Electrchem, Vol. 13, p. 257 (1997).

[19] C.R. Hamdan and K. Anour, J. Dispersion Scienceand Technology Vol. 15, p. 73 (1994).

[20] Goralezylk, Colloid polymer Sci. Vol. 272, p. 204 (1994).

[21] Chambion et al., an. J. chem. Vol. 223, p. 73 (1995).