

## Research Article

# Extraction Studies of Hypochlorite Ion from Aqueous To Organic Medium under Phase Transfer Catalysis

K. Bijudas

Department of Chemistry, N. S. S. College, Manjeri, Malappuram, Kerala 676122

**Abstract**

Hypochlorite is a selective and an environmental friendly reagent for the oxidation of various organic substrates. But it is ineffective due to its insoluble behaviour in organic solvents whereas most of the organic substrates are soluble only in organic solvents. This is the case in various organic reactions in which inorganic reagents are used. The introduction of phase transfer catalysis helped in a greater extent to solve this problem. The extraction of hypochlorite ions from the aqueous to organic medium was carried out by adding phase transfer catalyst like tetrabutylammonium chloride, tetrabutylphosphonium bromide, tetrabutylammonium hydrogen sulphate, cetyltrimethylammonium bromide and tricapyrylmethylammonium chloride. Hypochlorite ions were extracted to organic solvents like toluene, ethyl acetate and dichloromethane by gentle shaking for about one hour after adding phase transfer catalyst. The extracted hypochlorite in organic phase is found to be fairly stable for about ten hours. The effect of catalyst, its concentration and the effect of solvent on extraction were studied.

**Keywords:** Hypochlorite, extraction, organic medium, phase transfer catalysis, phase transfer catalyst

**\*Correspondence**

Author: K. Bijudas  
Email: bijudask@gmail.com

**Introduction**

Reactions between substrates located partly in aqueous phase and partly in organic phase are mutually immiscible and hence very slow and ineffective. This is due to the inability of the reactant and substrate to mutually cross over the phase boundary to come together for effective interaction by collisions. Such difficulty was initially resolved to some extent by employing dipolar aprotic solvents like DMSO, DMF etc. which ensures mutual solubility and miscibility of both ionic reagent and organic substrate [1-4]. But the use of dipolar aprotic solvents has many disadvantages like toxicity, lack of availability, purity, high cost etc.

Introduction of phase transfer catalysis (PTC) in the latter half of last century was highly successful to overcome the difficulties in a biphasic reaction [5-9]. PTC has emerged as an excellent technique for organic synthesis to carry out two phase reactions involving lyophilic organic substrates and hydrophilic reagents. This method involves the usage of phase transfer catalyst (PT catalyst) which enjoys solubility in both the solvents. When used in catalytic quantities, it can bring one of the reactants from its normal phase into the normal phase of the other reactant in a more reactive form. This ensures smooth reaction with advantages like high yield, selectivity, cost reduction, optimum temperature etc. [10-14]. Commonly used PT catalysts are crown ethers and quaternary ammonium or phosphonium salts.

PTC technique is significant in organic oxidation reactions in which various inorganic oxidants like permanganate, chromate, hypochlorite etc. are used. These reactions are carried out in presence of small quantity of PT catalyst by which inorganic oxidant ion is transferred to organic phase as an ion pair which is highly reactive. There are reports on such oxidation reactions using permanganate [15-18], chromate [19-22], and hypochlorite [23-25].

Hypochlorite ions are superior to other inorganic oxidants in the way that they are easily available, low cost, environmental friendly and highly selective in product formation. The extraction studies of inorganic oxidants from aqueous phase to organic phase are scanty and this prompted to carry out this investigation. The extraction of hypochlorite ion from aqueous phase to various organic solvents like ethyl acetate, toluene and dichloromethane was carried out by using PT catalyst like tetrabutylammonium bromide (TBAB), tetrabutylammonium hydrogen sulphate (TBAHS), tetrabutylphosphonium bromide (TBPB), cetyltrimethylammonium bromide (CTMAB) and tricapyrylmethylammonium chloride (TCMAC, Aliquat 336).

## Experimental

Analar grade sodium hypochlorite (SRL, Mumbai) was used for the preparation of hypochlorite solution in doubly distilled water. All the solvents, ethyl acetate, toluene and dichloromethane (Merck, India) were purified further by distillation under reduced pressure. The PT catalysts tetrabutylphosphonium bromide (Merck KGaA, Germany), tetrabutylammonium bromide, tetrabutylammonium hydrogen sulphate, cetyltrimethylammonium bromide (Spectrochem, India) and tricapyrylmethylammonium chloride (SRL, Mumbai) were used as such.

The extraction of hypochlorite ion from aqueous to organic phase with the assistance of PT catalyst was carried out and the effect of concentration of PT catalyst, effect of structure of PT catalyst and effect of solvent have been studied.

A known concentration of aqueous hypochlorite (20 mL) was shaken with 20 mL organic solvent containing varying amount of PT catalyst for about one hour at room temperature. The amount of hypochlorite extracted to organic phase was determined by titration of the aqueous layer against standard sodium thiosulphate solution and from the obtained results the percentage of extraction of hypochlorite from aqueous to organic phase was determined from the ratio of hypochlorite in organic phase to aqueous phase.

## Results and Discussion

The experimental results on the extraction of hypochlorite ions from aqueous to organic phase in presence of PT catalyst were carried out and the effect of catalyst and solvent with various concentrations of PT catalyst are given in **Tables 1-5**.

**Table 1** Effect of PT catalyst and solvent on extraction of hypochlorite

PT catalyst	Percentage of extraction		
	Toluene	Ethyl acetate	Dichloromethane
TBPB	23.2	31.6	29.8
TBAB	20.6	26.4	25.2
TBAHS	21.0	26.6	25.4
CTMAB	20.2	24.8	23.7
TCMAC	26.8	37.4	35.8

[OCl<sup>-</sup>] × 10<sup>2</sup> = 2.0 mol dm<sup>-3</sup>; Temperature - 300 K;  
Time - 60 minute; [PT catalyst] = 1.0 × 10<sup>2</sup> mol dm<sup>-3</sup>

**Table 2** Effect of PT catalyst and solvent on extraction of hypochlorite

PT catalyst	Percentage of extraction		
	Toluene	Ethyl acetate	Dichloromethane
TBPB	38.0	42.2	40.4
TBAB	31.8	40.5	39.7
TBAHS	32.0	39.2	38.3
CTMAB	30.1	33.5	32.8
TCMAC	42.2	44.5	43.9

[OCl<sup>-</sup>] × 10<sup>2</sup> = 2.0 mol dm<sup>-3</sup>; Temperature - 300 K  
Time - 60 minute; [PT catalyst] = 2.0 × 10<sup>2</sup> mol dm<sup>-3</sup>

**Table 3** Effect of PT catalyst and solvent on extraction of hypochlorite

PT catalyst	Percentage of extraction		
	Toluene	Ethyl acetate	Dichloromethane
TBPB	42.0	47.4	45.7
TBAB	34.2	37.3	35.6
TBAHS	33.6	38.8	35.2
CTMAB	31.8	34.2	33.7
TCMAC	47.8	52.2	50.2

[OCl<sup>-</sup>] × 10<sup>2</sup> = 2.0 mol dm<sup>-3</sup>; Temperature - 300 K  
Time - 60 minute; [PT catalyst] = 3.0 × 10<sup>2</sup> mol dm<sup>-3</sup>

**Table 4** Effect of PT catalyst and solvent on extraction of hypochlorite

PT catalyst	Percentage of extraction		
	Toluene	Ethyl acetate	Dichloromethane
TBPB	52.8	57.4	55.9
TBAB	46.3	52.7	50.8
TBAHS	46.8	54.2	52.0
CTMAB	43.8	49.6	47.5
TCMAC	57.2	68.8	66.2

[OCI] x 10<sup>2</sup> = 2.0 mol dm<sup>-3</sup>; Temperature - 300 K  
Time - 60 minute; [PT catalyst] = 4.0 x 10<sup>2</sup> mol dm<sup>-3</sup>

**Table 5** Effect of PT catalyst and solvent on extraction of hypochlorite

PT catalyst	Percentage of extraction		
	Toluene	Ethyl acetate	Dichloromethane
TBPB	54.6	58.9	56.6
TBAB	48.5	54.6	53.2
TBAHS	48.8	54.2	52.6
CTMAB	44.4	50.4	48.5
TCMAC	59.4	70.5	68.8

[OCI] x 10<sup>2</sup> = 2.0 mol dm<sup>-3</sup>; Temperature - 300 K  
Time - 60 minute; [PT catalyst] = 5.0 x 10<sup>2</sup> mol dm<sup>-3</sup>

The above results show that the percentage of extraction of hypochlorite ion from aqueous phase to organic phase in a given solvent increased with increase in concentration of PT catalyst. The extraction reaches maximum value and attains almost steady state when the PT catalyst concentration becomes twice that of hypochlorite concentration.

All the PT catalysts were found to be very effective in transferring hypochlorite ions from aqueous phase to organic phase which will not take place in the absence of catalyst. The reactivity of PT catalysts are in the order TCMAC > TBPB > TBAHS > TBAB > CTMAB. It is already established that the alkyl groups of PT catalyst should be sufficiently organic to transfer the desired anion into the organic phase. TCMAC shows more reactivity since it is having bigger alkyl groups compared to other catalysts. TBPB also shows higher reactivity because of the presence of phosphonium as the central onium atom whereas all other PT catalysts are having ammonium as the central onium atom. It is found that phosphonium is more reactive to make ion pair with hypochlorite than ammonium in a PT catalyst. The anions present in the PT catalysts are chloride, bromide and hydrogen sulphate. All these anions in the PT catalyst are able to exchange with hypochlorite ions in the aqueous phase in a similar fashion.

The extraction of hypochlorite from aqueous to organic phase in various organic solvents is in the order ethyl acetate > dichloromethane > toluene. The solubility and partitioning behaviour of quaternary salts are affected by slight changes in the nature of organic phase. Solubility and partitioning of quaternary salts are increased by increasing the polarity of the aprotic organic phase. Since the dipole moment of solvents is in the order ethyl acetate > dichloromethane > toluene the extraction also higher in ethyl acetate than in dichloromethane and toluene.

## Conclusion

The extraction of hypochlorite ion from aqueous phase to various organic phase was conveniently carried at room temperature with the help of a PT catalyst. The effect of various PT catalysts, their concentration and the effect of various solvents on extraction were studied. The extracted hypochlorite in organic medium is found to be fairly stable for about ten hours. This can be used for the oxidation of various organic substrates in organic medium and kinetics of such reactions can be easily studied.

## References

- [1] A. J. Parker, Chem. Rev., 1969, 69 (1), 1-32.
- [2] M. A. Lapitskaya, L. L. Vasiljeva, K. K. Pivnitsky, Mendeleev Commun., 2008, 18(6), 309-311.
- [3] V. K. Ahluwalia, R. Aggarwal, Organic Synthesis: Special Techniques, Alpha Science International Limited, Pangbourne, 2001.
- [4] K. B. Wiberg, Oxidation in organic chemistry, Academic Press, London and New York, 1965.

- [5] D. G. Lee, Oxidation of organic compounds by permanganate ion and hexavalent chromium, Open Court: La Salle, 1980.
- [6] C. M. Starks, C. Liotta, Phase transfer catalysis, Principles and Techniques, Academic Press, New York, 1978.
- [7] E. V. Dehmlow, S. S. Dehmlow, Phase transfer catalysis, VCH:Weinheim, Germany, 1993.
- [8] Y. Sasson, R. Neumann, Handbook of Phase Transfer Catalysis, Kluwer Academic Publishers; Dordrecht, 1997.
- [9] M. Makosza, M. Ludwickow, Angewandte. Chemie, 1974, 86 (20), 744-745.
- [10] A. Brandstrom, K. Gustavii, Acta. Chem. Scand., 1969, 23, 1215-1218.
- [11] G. A. Lee, H. H. Freedman, Isr. J. Chem., 1985, 26 (3), 229-234.
- [12] S. Asai, H. Nakamura, T. Sumita, AIChE J., 1994, 40 (12), 2028-2033.
- [13] J. S. Do, T. C. Chou, Ind. Eng. Chem. Res., 1990, 29, 1095-1103.
- [14] R. O. Hutchins, N. R. Natale, W. J. Cook, J. Ohr, Tetrahedron Lett., 1977, 18 (48), 4167-4169.
- [15] T. D. Radhakrishnan Nair, P. Rajendran, Indian J. Chem., 2003, 42A, 64-67.
- [16] K. M. Basheer, J. Joseph, T. D. Radhakrishnan Nair, Modern Res. Catal., 2013, 2, 35-38.
- [17] K. Bijudas, P. Bashpa, IRA Int. J. App. Sci., 2016, 5(3), 110-114.
- [18] P. S. Sheeba, T. D. Radhakrishnan Nair, Asian J. Chem., 2003, 16(3-4), 1327-1333.
- [19] K. Bijudas, P. Bashpa, T. D. Radhakrishnan Nair, Bull. Chem. React. Engg. Catal, 2014, 9(2), 142-147.
- [20] K. Bijudas, T. D. Radhakrishnan Nair, Curr. Chem. Lett., 2014, 3(2), 109-114.
- [21] K. Bijudas, P. Bashpa, K. P. Ayisha Nasrin, K. Krishnapriya, Reshma Krishnan, Chem. Sci. Rev. Lett. 2014, 3 (10), 123-126.
- [22] D. Pletcher, S. J. D. Tait, J. Chem. Soc, Perkins Trans., 1979, 2 (6), 788-791.
- [23] S. Abramovici, R. Neumann, Y. Sasson, J. Mol. Catal. 1985, 29, 299-303.
- [24] G. A. Mirafzal, A. M. Lozeva, Tetrahedron Lett., 1998, 39 (40), 7263-7266.
- [25] K. Bijudas, P. Bashpa, V. P. Bibin, Lakshmi Nair, A. P. Priya, M. Aswathy, C. Krishnendu, P. Lisha, Bull. Chem. React. Engg. Catal., 2015, 10 (1), 38-42.

## Publication History

Received 15<sup>th</sup> Nov 2017  
Revised 24<sup>th</sup> Nov 2017  
Accepted 25<sup>th</sup> Nov 2017  
Online 30<sup>th</sup> Nov 2017

© 2017, by the Authors. The articles published from this journal are distributed to the public under “**Creative Commons Attribution License**” (<http://creativecommons.org/licenses/by/3.0/>). Therefore, upon proper citation of the original work, all the articles can be used without any restriction or can be distributed in any medium in any form.