

Trifluoroacetic acid Recovery from Industrial Aqueous Effluent

Niraj Kumar Tripathi, Brij kishor Mishra, Arunkant Tiwari, Dr. O.N. Choubey
Chemistry Department, Govt. Narmada P.G. College, Hoshangabad (M.P.) India 461002

Abstract: Miscibility of Trifluoroacetic acid (TFA) in water is very high & therefore its recovery is very difficult from its dilute aqueous solutions by conventional techniques. To address this limitation and facilitate TFA recovery, insoluble salt formation has proven to be an effective approach. This work expands to prepare ester in-situ or with recovered TFA from its adduct & alcohol. The objective of this work is to provide a different technology options for quantitatively recovery from most environmental waters using water insoluble adduct formation and process configurations to this end, highlighting notable achievements and recent developments. In this approach, water insoluble adduct is prepared by reaction of base dicyclohexyl amine with industrial aqueous effluent containing trifluoroacetic acid moiety followed by fractional distillation in presence of sulphuric acid. Gas Chromatography(GC)analysis tools also developed for conformation and purity of isolated content.

Keywords: Trifluoroacetic acid; Isopropyl trifluoroacetate; Dicyclohexyl amine (DCHA), Sulphuric acid

I. Introduction

Trifluoroacetic acid is a very strong halogenated derivative of acetic acid. A mildly phytotoxic compound Trifluoroacetic acid is an analogue of acetic acid with the three hydrogen atoms replaced by three fluorine atoms. The acidity of TFA is approximately 34,000 times stronger than that of acetic acid due to the high electronegative character of the trifluoromethyl group. TFA is widely used in organic chemistry for various purposes.

The research work relates to a method for recovery trifluoroacetic acid from aqueous compositions containing said acids. The invention more particularly relates to the recovery of trifluoroacetic (or trifluorocarboxylic acid) forming practically water insoluble adduct with organic base and makes ester with alcohol in presence of catalyst. The chemical industry uses trifluorocarboxylic acids in many field of activity for the most part they are soluble in water and are often present in varying amounts in industrial effluents, notably waste water.

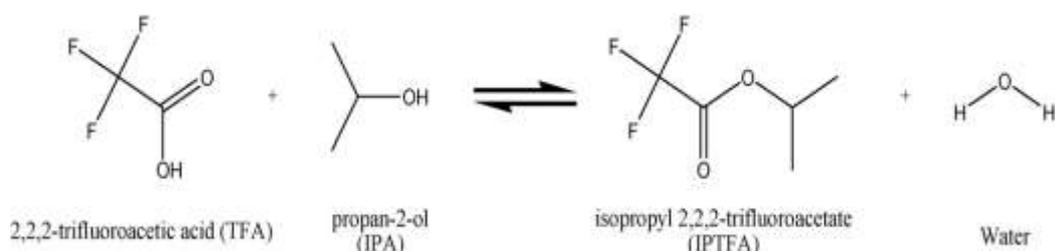
In view of the costs of this trifluorocarboxylic acid, it can prove useful and profitable to treat the aqueous effluents containing said acid, in order to recover them.

Moreover, the presence of trifluorocarboxylic acid in industrial aqueous effluents may be harmful to the environment and as environmental requirements are becoming increasingly stringent, the recovery of trifluorocarboxylic acid is now becoming a problem for which no acceptable solution is yet available on an industrial scale. A simple and effective means might comprise distillation of the aqueous waste containing the trifluorocarboxylic acid. However, this acid generally forms azeotrope with water, so that their distillation to a satisfactory degree of purity is impossible. For example, trifluoroacetic acid (TEA) forms an azeotrope with water, with boiling point of about 103° C. This temperature, which is very close to the boiling point of water, makes simple TFA/water distillation even less effective, and it cannot be used.

II. Experimentation

Prior methods for recovery of substantially anhydrous trifluoroacetic acid are cumbersome and uneconomical. A representative proposed procedure involves alcohol extraction of sodium trifluoroacetate from a reaction mixture which had been evaporated to dryness. After removal of the alcohol, the residue of the extract is treated with sulfuric acid, and the mixture is then distilled in the presence of strong sulfuric acid to effect recovery of trifluoroacetic acid as overhead. Most prior art processes for recovery of substantially anhydrous trifluoroacetic acid require distillation of CF₃COOH out of a concentrated sulfuric acid solution.

In our proposed way, take industrial effluent containing trifluoroacetic acid (TFA) or its constituents amide or ester form in a well-equipped 4-necked round bottom flask (or reactor) assembly, distill to remove organic solvent, add caustic soda solution to adjust pH basic, heat & stir, cool and adjust pH acidic by use of mineral acid like aqueous hydrochloric acid, further add Dicyclohexyl amine organic base. Filter off precipitated material; thoroughly wash with water and dry material under reduced pressure. Obtained yield is 98% of total TFA content present in industrial effluent. Take solid obtained as above, in sulphuric acid at ambient temperature, add alcohol (1-6 carbon length) like methanol, ethanol Propanol etc and stir. Collect ester of acid & with Gas Chromatographic purity NLT 99% (yield 93%).



III. Result & Discussion

Aim of this study to propose a simple and effective method permitting the recovery of trifluoroacetic acid from aqueous effluents, with efficiency and a degree of purity that are satisfactory and economically profitable, notably on an industrial scale. Other aims will become clear from the following account of the present research. As already mentioned, a conventional method of distillation does not allow the recovery of a trifluoroacetic acid of high purity, because of the azeotrope that said forms with water. In this research work, now discovered a method, which is the object of the invention, which permits the recovery of trifluoroacetic acid present in aqueous effluents (or more simply aqueous solutions). During development work resulting in the present improvements involves to make water insoluble adduct trifluoroacetic acid from aqueous effluent. Water insoluble adduct is used as with sulphuric acid followed to distillation. Dicyclohexylamine is a secondary amine which is used for making water insoluble salt with trifluoroacetic acid content. It is a colorless liquid, although commercial samples can appear yellow. It has a fishy odor, typical for amines. Since this organic base is sparingly soluble in water, easily recovered from residue left behind after trifluoroacetic acid / ester recovery.

IV. Conclusion

Trifluoroacetic acid water insoluble salt formation technique is a promising tool for the recovery of TFA from its dilute aqueous solution or industrial effluent. This research is providing highly efficient TFA recovery process with yield & quality. Advantage are-

1. An economically convenient method to preparation of TFADCHA salt from aqueous /organic effluent containing trifluoroacetic acid content (TFA free acid or its salt with organic or inorganic base, ester, amide etc.) of any concentration.
2. A method for recovery of trifluoroacetic acid from an aqueous effluent, comprising (a) contacting said aqueous effluent comprising Trifluoroacetic acid content (b) form water insoluble TFADCHA salt by use of organic base DCHA (c) recovering TFA as distillate from step (b) salt by treatment with sulphuric acid (d) Process for preparation of TFAE (trifluoroacetic acid isopropyl ester) from salt of step (b) with IPA in presence of sulphuric acid or other strong acid having pKa value less than -0.3 (e) process for Dicyclohexylamine (DCHA) recovery from residue of industrial waste or residue obtained in a, b or c.

References

- [1] B. Saha B, S.P. Chopade, S. Mahajani, Recovery of dilute acetic acid through esterification in a reactive distillation column, *Catal. Today* 60(2000) 147–157.
- [2] Bhide, R.S., Levison, B.S., Sharma, R.B., Ghosh, S., and Salomon, R.G. (1986) *Tetrahedron Letters*, 27, 671–674.
- [3] Brown, T., Jones, J.H., and Richards, J.D. (1982) *Journal of the Chemical Society, Perkin Transactions I*, 1553–1561.
- [4] C. Chen, L. Tan, R. Larsen, US Patent 6,140,515, 2000.
- [5] Fukase, Y., Fukase, K., and Kusumoto, S. (1999) *Tetrahedron Letters*, 40, 1169–1170.
- [6] I. Dorziotis, I. Houppis, K.K. Eng, US Patent 6,080,876, 2000.
- [7] Isidro-Llobet, A., Alvarez, M., and Albericio, F. (2008) *Tetrahedron Letters*, 49, 3304–3307.
- [8] J.A. Chong, F. Abdesaken, L. A. Spangler, US Patent 4,701,551, 2001.
- [9] J.D. Raal and A.L. Muhlbauer, *Phase equilibria: Measurement and Computations*, Taylor and Francis Publication, London, 1998.
- [10] J. Peng, S. Lextrait, T. Edgar, R. Eldridge, A comparison of steady-state equilibrium and rate-based models for packed reactive distillation columns, *B. (1991) Tetrahedron Letters*, 32, 739–742.
- [11] Jetten, M., Peters, C.A.M., van Nispen, JanW.F.M., and Ottenheijm, H.C.J. (1991) *Tetrahedron Letters*, 32 6025–6028.
- [12] K. Rossen, R. Volante, G. Ho, R. Farr, D. Mathre, US Patent 5,883,267, 1999.
- [13] K. Rossen, G. Ho, R.P. Volante, R.N. Farr, D. Mathre, US Patent 6,153,787, 2000.
- [14] Kenner, G.W. and Seely, J.H. (1972) *Journal of the American Chemical Society*, 94, 3259–3260.
- [15] L.A. Spangler, F. Abdesaken, J.A. Chong, US Patent 6,278,015, 2001.
- [16] M. Sharma, S. Mahajani, Industrial application of reactive distillation (a review), in: K. Sundmacher, A. Kienle (Eds.), *Reactive Distillation Status and Future Trends*, Wiley–VCH, 2003, pp. 1–29.
- [17] Morton, D.R. and Thompson, J.L. (1978), *The Journal of Organic Chemistry*, 43, 2102–2106.
- [18] R. Taylor, R. Krishna, Modeling reactive distillation, *Chem. Eng. Sci.* 55 (2000) 5183–5229.
- [19] Ramachandran, J. and Li, C.H. (1962) *The Journal of Organic Chemistry*, 27, 4006–4009.

- [20] R.S. Hiwale, N.V. Bhate, Y. Mahajan, S.M. Mahajani, Industrial applications of reactive distillation: recent trends, *Int. J. Chem. React. Eng.* (2004) (review R1). Ref 1 in Milne, J. B.; Parker, T. J. (1981). "Dissociation constant of aqueous trifluoroacetic acid by cryoscopy and conductivity". *Journal of Solution Chemistry* 10 (7): 479.
- [21] S. Grego, A. Checchin, G. Guglielmo, US Patent 4,916,256, 2001.
- [22] Schallenberg, E.E. and Calvin, M. (1955) *Journal of the American Chemical Society*, 77, 2779–2783.
- [23] Schwyzer, R. and Rittel, W. (1961) *Helvetica Chimica Acta*, 44, 159–169.
- [24] Webref 1: <http://www.solvaychemicals.com/product/datasheet/0,0,-EN-1000769,00>. Html, last accessed July 2006.
- [25] Y. Mahajan, PhD. Thesis, Department of Chemical Engineering, IIT Bombay, India, 2006.
- [26] Z. Xu, A. Afacan, K. Chuang, Removal of acetic acid from water by catalytic distillation. Part 1. Experimental studies, *Can. J. Chem. Eng.* 77(1999) 676–681. Wujcik CE1, Cahill TM, Seiber JN. Extraction and analysis of trifluoroacetic Acid in environmental waters; *Anal Chem.* 1998 Oct 1;70(19):4074-80.