What is Aliquat® 336 and Adogen® 464 HF?
Let's Clear Up the Confusion

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Anyone who has read a fair amount of phase-transfer catalysis literature has undoubtedly encountered the catalysts with the tradenames Aliquat® 336 and Adogen® 464 HF. These catalysts are highly effective in thousands of PTC reactions and hundreds of PTC patents. If you have run several PTC reactions in the lab yourself, you probably used these catalysts. You may have even been frustrated trying to weigh out this viscous liquid since it's almost impossible to get it into a Pasteur pipette without carefully and safely breaking off the stem!

You may be wondering why would anyone write an article called "What is Aliquat® 336 and Adogen® 464 HF?" The answer is that there is so much confusion in the literature and even among the technical service people of the manufacturers, that few people actually know what its composition is supposed to be and fewer even know what its composition really is. In fact, at the time of this writing, I'm not sure of its EXACT composition.

However, I do know what the composition is not and what it's not is what most people think it is!

Before we get into the technical discussion, let's use a simple nomenclature for this article. We will refer to Aliquat 336 and Adogen 464 HF as "QCl." For the purposes of this article, we will treat the two materials as if they are the same. We will use the individual tradenames in this article only when we refer to information specifically relevant to BASF's Aliquat 336 or specifically relevant to Evonik's Adogen464 HF.

It is also worthwhile to note that Adogen 464 HF is the "high flash point" material since it does not contain isopropanol. Evonik also sells Adogen 464 85 which is a solution of 85% Adogen 464 in isopropanol.

What is QCl NOT?

Let's start the technical discussion by stating what QCl is not. This will come as a surprise to at least half of our readers and it will come as a surprise to the people who write MSDS's around the world and to the people who have blindly copied them. It will also come as a surprise to anyone who tries to reconcile the numerous identities shown for this compound on its Wikipedia page at the time of this writing (Sept 2012; this may be resolved by the time you look it up).

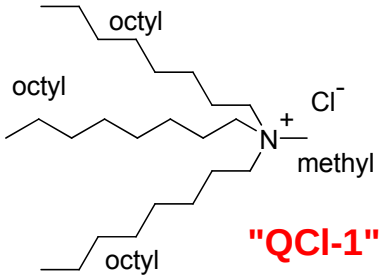
So, are you ready to hear the truth?

QCl is NOT methyl trioctyl ammonium chloride!!! We can even be semi-humorous and say that QCl NOT is trioctyl methyl ammonium chloride or even N-methyl-N,N-dioctyl-1-octanaminium chloride which are all obviously different names for the same thing.

So, the structure shown in Figure 1 below does NOT represent QCl.

At the moment, we believe (though not guaranteed) that the Chemical Abstracts Registry Number (CAS#) of QCl-1 is likely 5137-55-3. The United States EPA appears to believe that this is the CAS# of methyl trioctyl ammonium chloride. The molecular weight of QCl-1 is about 404 g/mole (404.16 g/mole shows more significant figures). To reiterate, this is NOT Aliquat 336 or Adogen 464.

Figure 1: Structure of Methyl Trioctyl Ammonium Chloride “QCl-1”; THIS IS NOT QCl



What Does the Aldrich Catalog and MSDS think of QCl?

When you look up Aliquat 336 in the Aldrich catalog you will see that the molecular weight is shown as 404.16 g/mole. If Aliquat 336 was indeed methyl trioctyl ammonium chloride, then the molecular weight would indeed be 404.16 g/mole. But since Aliquat 336 is not methyl trioctyl ammonium chloride, then the molecular weight of Aliquat 336 is not 404.16 g/mole.

Why is this important?

Because chemists in the lab, including me, often use the Aldrich catalog to determine molecular weights when we are too lazy to calculate them ourselves. When I ran my first PTC reaction in my youth using Aliquat 336 or Adogen464 HF in the late 1970’s, I relied on the Aldrich catalog to tell me the proper molecular weight so I can weigh out the right amount for my reaction based on mole%.

I’ll give you a hint and say that since the 1990’s, I have been using a molecular weight of 432 g/mole for Aliquat 336 and Adogen 464 HF which I think is closest to the true molecular weight. This MW is 6.9% higher than that shown in the Aldrich catalog.

So, if I am running a commercial PTC process that uses say 10 metric tons per year of QCl, it is possible that I am buying nearly a ton and a half too much every year! Do you think that will get the attention of your purchasing manager?

Anyway, let’s get back to the Aldrich catalog and their MSDS’s.

In September 2012, the MSDS for Aliquat 336 was available on the Sigma-Aldrich website at http://www.sigmaaldrich.com/catalog/product/aldrich/205613?lang=en&region=US. In September 2012, this MSDS showed a formula of $C_{25}H_{54}ClN$ and a molecular weight of 404.16 g/mole and all of this is consistent with methyl trioctyl ammonium chloride, QCl-1. But…the CAS# shown is 63393-96-4.

So what?

Well, if you go to the EPA website and type in this CAS# you don’t get methyl trioctyl ammonium chloride. What you get is “Quaternary ammonium compounds, tri-C8-10-alkylmethyl, chlorides” and the EPA shows the molecular weight to be unspecified.

Of course, you can say that methyl trioctyl ammonium chloride is INCLUDED in this description and you would be right. But when you are calculating phase-transfer catalyst loadings, or filing a PMN or being accurate when dealing with CAS#’s (as all scientists strive to do), then you need to be right, not close to right. But the fact is that you wouldn’t even be close to right.

As we will see shortly, if you assume that methyl trioctyl ammonium chloride (QCl-1) is the dominant chemical species in Aliquat 336 and Adogen 464 HF, then you would be mostly wrong. QCl-1 comprises only about 1/3 of QCl, not including any diluents or impurities that may be present.

Now back to the Aldrich MSDS.

When looking up Adogen 464 in the Aldrich catalog in September 2012, it showed the CAS# 72749-59-8. When you go to the EPA website, this shows a name of "Quaternary ammonium compounds, tri-C6-12-alkylmethyl, chlorides." Great…now the range of alkyl groups has been expanded to include C6 and C12, not just C8 and C10. Grrrrrr.

In September 2012, the Aldrich MSDS for Adogen 464 obtainable at http://www.sigmaaldrich.com/catalog/product/aldrich/856576?lang=en&region=US showed a CAS# of 63393-96-4 but it also showed that this is the CAS# for methyl trioctyl ammonium chloride. Are you sufficiently confused now?

Worse yet, the Aldrich MSDS in September 2012 shows a molecular weight of 1,338 g/mole. This must be a humongous typographical error.

Reliable Information about QCl is Available from the Producers!

Adogen 464 HF

The only reliable information on Adogen 464 HF is that provided directly by Evonik in their MSDS and their Technical Information Sheet. Evonik's Adogen 464 HF MSDS from October 2010 (this is the most recent version available at the time of writing) shows the CAS# to be 63393-96-4 and the component name shown is "Quaternary ammonium compounds, tri-C8-10-alkylmethyl, chlorides". ***We believe that this is the most accurate description***. The Aldrich MSDS dated July 2012 should be disregarded.

The Evonik Technical Information Sheet for Adogen 464 HF dated June 2010 clearly states that the composition is 60% C8 and 40% C10. It does not however disclose if that is the weight ratio or the mole ratio. This will be addressed below.

Aliquat 336

The only reliable information on Aliquat 336 is that provided directly by BASF in their MSDS and their Technical Data Sheet. BASF's Aliquat 336 MSDS from August 2011 (this is the most recent version available at the time of writing) also shows the CAS# to be 63393-96-4 and the component name shown is "tri-C8-10-alkylmethylammonium chlorides".

Other Historical Information about QCl

If you are a history buff and have the original article by Dr. Charles Starks that coined the term "phase-transfer catalysis" in 1971 (J. Amer. Chem. Soc., *93*, **1971**, 195) you will see that Aliquat 336 is mentioned by name in that historic landmark article and it is described as follows in the honorary spot at the very beginning of the Experimental Section: "***Tricaprylylmethylammonium chloride" or "aliquat 336" was obtained from General Mills Company, Chemical Division, Kankakee, Ill. The alkyl groups are a mixture of C_8-C_{12} straight chains with an average of ten carbon atoms. Molecular weight by titration of the chloride was 507***".

This paper by Starks remains the definitive text on the innovation of phase-transfer catalysis. This paper states that the range of alkyl groups was C_8 to C_{12}. Of course, that was in 1971 and the composition may have changed since then.

By the way, BASF still produces Aliquat 336 at that same site in Kankakee in 2012 that was mentioned in Starks' 1971 paper. I visited that site in the late 1990's.

If you read this carefully, you may ask what is "capr**ylyl**?" If you don't read this carefully, you may ask what is "capr**yl**" figuring that the word "capr**ylyl**" is a typographical error. In fact, to add to the confusion, dozens of articles and MSDS's incorrectly use the term "capr**yl**" instead of "capr**ylyl**" when describing Aliquat 336.

So, what is capr**ylyl**? Well, capr**yl** is an old common name for octyl, just like cetyl is for hexadecyl. Since Aliquat 336 contained a mixture of octyl groups and other long alkyl chains, someone in the 1960's or earlier (probably at General Mills that sold the business to Henkel) thought it would be a good idea to include the term "capr**ylyl**" to mean "**like capryl**". This is a cruel joke that became convention, sort of like wearing a necktie which really doesn't make any sense either, but everyone does it anyway. In any case, there are numerous citations in the academic literature and commercial literature to the incorrect term tricapr**yl**methyl ammonium chloride not tricapr**ylyl**methyl ammonium chloride.

In 2006, the MSDS from Cognis (now BASF) that produces Aliquat 336, stated that the molecular weight was 442 g/mole. This is still shown on the BASF Technical Data Sheet for Aliquat 336 in 2012. The BASF Aliquat 336 MSDS from Aug 2011 does not show a molecular weight and does not use the word "caprylyl" any longer.

Marketing literature in 1990 from Sherex (a precursor to Witco which was a precursor to Degussa Goldschmidt which was a precursor to Evonik Goldschmidt) cited the phase-transfer catalyst Arosurf® 64, which was the same tri-C8-C10-alkylmethyl ammonium chloride as Adogen 464 HF, to have a molecular weight of 439.

I'm sure that if I can dig up more product literature in my files from the precursor companies of BASF and Evonik, it will probably produce additional contradictory information about what Aliquat 336 and Adogen 464 HF may really be or have been at various times in history.

No wonder there is confusion about what really is Aliquat 336 and Adogen 464 HF.

So what is the Real Composition of QCl?

In order to answer this question, we need to look at how QCl is made by BASF and Evonik. In the June 2012 Technical Information Sheet published by BASF for Aliquat 336, it notes "***Aliquat 336 is a water insoluble quaternary ammonium salt made by the methylation of mixed tri octyl/decyl amine***". This is a definitive and reliable statement by the manufacturer.

Among other things, this statement clearly suggests that the Aliquat 336 is NOT methyl trioctyl ammonium chloride (QCl-1). ***Since the most frequent incorrect statement about Aliquat 336 is that it is methyl trioctyl ammonium chloride, this myth must right now be put to rest though it will likely continue to be perpetuated in the literature for decades to come***. This means that importers, exporters and manufacturers may technically be non-compliant with EPA and FDA regulations.

So, if we knew how QCl is made, we could know the composition of QCl. Based on public and private communications in recent years by the companies that preceded BASF and Evonik that produced Aliquat 336 and Adogen 464 HF, QCl, is likely produced by the following two steps:

1. Reaction of a mixture of octanol and decanol with a nitrogen compound to form a trialkylamine that has a weight ratio of octyl groups to decyl groups of 1.5:1 which is equivalent to a molar ratio of 2:1. This trialkylamine is sometimes called tricaprylylamine and is sometimes represented by $(C_8H_{17}\text{-}C_{10}H_{21})_3N$.
2. Reaction of this trialkylamine with methyl chloride to produce QCl

Therefore, in order to understand the true composition of QCl, we must understand the composition of the trialkylamine. A descriptive name for this trialkylamine could be "tri-C8-10-alkylamine", at least since the mid-1990's

The trialkylamine produced by BASF is called Alamine® 336 (trademark of BASF SE) and it is the precursor of Aliquat 336. The trialkylamine produced by Evonik is called Adogen® 364 (trademark of Evonik Goldschmidt Corporation) and it is the precursor of Adogen 464 HF.

Alamine 336 ➔ Aliquat 336
Adogen 364 ➔Adogen 464 HF

The question of the composition of QCl boils down to the question, "what is the ratio of C8-alcohol to C10-slcohol used in the manufacturing process for the precursor amines called Alamine 336 and Adogen 364?"

As noted above, Evonik's Technical Information Sheet from June 2010 states that the "approximate distribution" of the alkyl groups is 60% C_8 and 40% C_{10}. If this is a weight ratio, then the mole ratio of octyl to decyl is 2:1.

The technical service department at Cognis (the precursor company to BASF) once communicated that the 2:1 ratio of C8-alcohol to C10-alcohol was a weight ratio. Accordingly, they concluded that the molecular weight of Aliquat 336 was 442 g/mole. In a private conversation with the technical staff in 2006, I asked them to review their production process and they discovered that the 2:1 ratio was a molar ratio and not a weight ratio. The 2:1 molar ratio of octyl groups to decyl groups was consistent with my private communications with Henkel and Cognis (both precursors to BASF) since the 1980's. However, their June 2012 Technical Data Sheet for Aliquat 336 continues to show an "average molecular weight" of 442 g/mole. The Aug 2011 MSDS for Aliquat 336 does not mention a molecular weight.

If the molar ratio of octyl groups to decyl groups is indeed 2:1, then the composition of the quaternary ammonium salts of QCl (not including other components such as water, alcohol, etc.) would be as follows according to random statistical distribution:

methyltrioctyl ammonium chloride (about 33%)
methyldioctyldecyl ammonium chloride (about 28%)
methyloctyldidecyl ammonium chloride and (about 22%)
methyltridecyl ammonium chloride (about 17%)

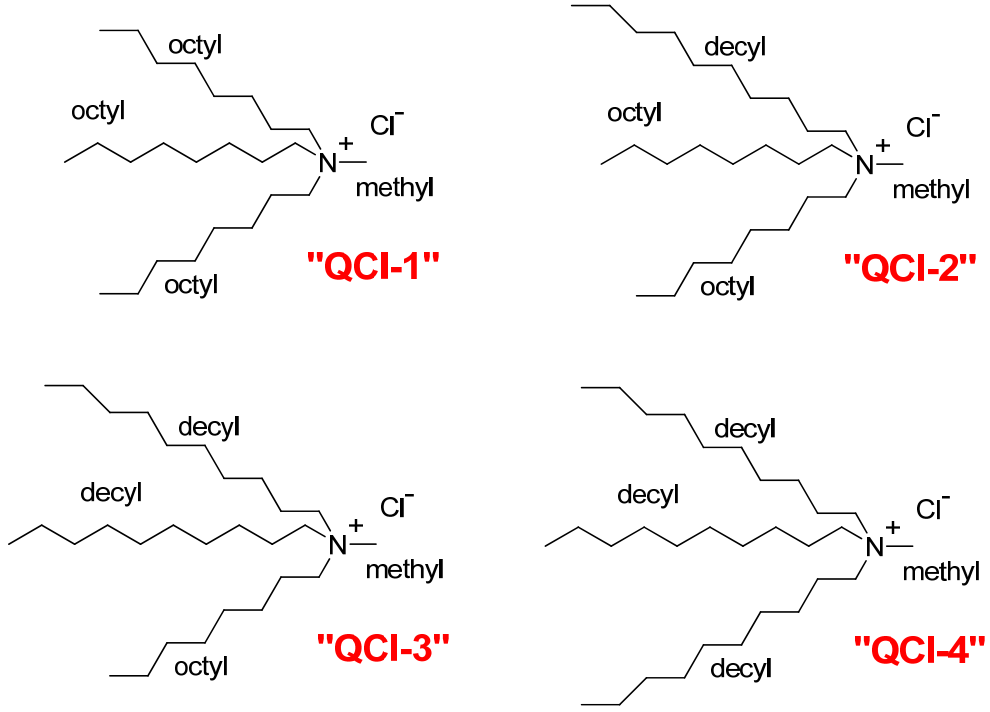
The structures are shown in Figure 2.

By the way, it is possible that the ratio of octyl to decyl has varied over the years, though it is not known if it did. In the late 2000's a fire at a vegetable oil plant in Southeast Asia caused a temporary disruption in the supply of C8-alcohol and C10-alcohol and this affected the prices of Aliquat 336 and Adogen 464 HF. However, we assume that the ratio of octyl groups to decyl groups did not change in the past few years.

What is the Average Molecular Weight of QCl?

The following discussion will be valid only if the molar ratio of C_8 to C_{10} in QCl is 2:1.

Figure 2: Structures of Components of QCl



Octyl is the C_8H_{17} alkyl group and has a molecular mass of 113. Decyl is the $C_{10}H_{21}$ alkyl group and has a molecular mass of 141. A molar ratio of 2:1 for octyl:decyl would give an effective molecular mass for the tri-C_8-C_{10}-alkylamine of about 381 (Alamine 336 or Adogen 364).

When quaternized with methyl chloride, the average molecular weight of QCl would be rounded to 432 g/mole. Again, this would be valid only of the molar ratio of C_8 to C_{10} in the amine precursor is 2:1.

What Else is Present in QCl?

Following is the information provided recently by BASF for Aliquat 336 and by Evonik for Adogen464 HF.

The June 2012 Aliquat 336 Technical Data Sheet obtained from BASF shows the following:

% quaternary salt content	88.2 – 90.6
% water	≤ 5
Acid value + amine value	≤ 3.0

The August 2011 MSDS of Aliquat 336 from BASF shows the following:

CAS-No.	Content [W/W]	Chemical Name
112-30-1	≤ 6%	1-Decanol
111-87-5	≤ 5%	1-Octanol
63393-96-4	≥85% - ≤ 95%	tri-C8-10-alkylmethylammonium chlorides

The June 2009 Adogen 464 HF specification sheet obtained from Evonik shows the following:

Quaternary Corrected	≥ 90.00%
% water	3.00 – 5.00%
Amine + Amine salt	≤ 4.0

The June 2010 Adogen 464 HF Technical Information sheet shows the following:

Quat Weight %	85-89
Quat Content Meg/gram	2.10
Moisture %, Max.	3.5

The October 2010 MSDS of Adogen 464 HF from Evonik shows the following:

Components	CAS-No.	Concentration [%]
1-Decanol	112-30-1	< 5
Quaternary ammonium compounds, tri-C8-10-alkylmethyl, chlorides		
	63393-96-4	> 85
Methane, chloro-	74-87-3	< 0.05
1-Octanol	111-87-5	< 5
1-Hexanol	111-27-3	< 0.0001

Some MSDS's also show the presence of isopropanol.

Summary

According to our best understanding in September 2012, we think that the following statements are likely true:

- Aliquat 336 and Adogen 464 HF are similar materials
- Aliquat 336 and Adogen 464 HF are NOT methyl trioctyl ammonium chloride
- Aliquat 336 and Adogen 464 HF likely contain a MIXTURE of four quaternary ammonium salts that are likely methyl trioctyl ammonium chloride, methyl dioctyldecyl ammonium chloride, methyl octyldidecyl ammonium chloride and methyl tridecyl ammonium chloride (note that didecyl = two decyls, not one dodecyl).
- The total amount of quaternary ammonium chlorides in Aliquat 336 and Adogen 464 HF is likely close to about 90%
- The molar ratio of the octyl groups to decyl groups in Aliquat 336 and Adogen 464 HF is likely about 2:1
- The average molecular weight of Aliquat 336 and Adogen 464 HF is likely about 432 g/mole.
- Aliquat 336 and Adogen 464 HF appear to contain small amounts of the following materials:
    - a few percent water (likely 3-5%); this may also help prevent freezing during the winter in colder locations
    - some trialkylamine (likely 1-2%) with the same octyl/decyl ratio as the quaternary ammonium salt
    - some amount of alcohol, from about 0% to about 10% (does not apply to Adogen 464 85 which may contain 15% isopropanol) which likely includes octanol and decanol.

If you have questions or comments about this article, feel free to contact the author at marchalpern@phasetransfer.com.