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## Study of the aggregation of Cyanex 272 and Ionquest 290 by Vapor Pressure Osmometry

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Yves Le Quesne<sup>2</sup>

### Summary

The extractant molecule bis-2,4,4-trimethylpentyl phosphoric acid (BTMPP), is the active component of Cyanex 272 and Ionquest 290. BTMPP is known to form aggregates, especially dimers, in nonpolar organic diluents. The aggregation results from strong intermolecular hydrogen bonding between the P=O and P-OH groups. The knowledge of this aggregation is important, as it influences solvent extraction equilibria by reducing the amount of extractant molecules available for the extraction.

In the present work, aggregation of BTMPP was studied by Vapor Pressure Osmometry (VPO). The average numbers of aggregation were calculated for several solutions containing various concentrations of extractant for both Cyanex 272 and Ionquest 290. The average numbers of aggregation are around 2 – 2.2 at 50°C, depending on the concentration of BTMPP. It was concluded that BTMPP forms monomers, dimers and trimers. Then the equilibrium constants of dimerization and trimerization were estimated by a numerical optimization procedure developed on Matlab. The logarithms of the constants of dimerization and trimerization are respectively estimated at  $3.0 \pm 0.2$  and  $4.8 \pm 0.2$  at 50°C (constants in L/mol and L<sup>2</sup>/mol<sup>2</sup> resp.). VPO measurements were also conducted at 43°C and 60°C. Only small differences were observed for the average numbers of aggregation and the equilibrium constants calculated at 43°C, 50°C and 60°C. It was concluded that the temperature dependence of the aggregation of BTMPP is low from 43°C to 60°C.

### Introduction

The extractant molecule bis-2,4,4-trimethylpentyl phosphoric acid (BTMPP), is the active component of Cyanex 272 and Ionquest 290 (CX272 and IQ290 resp.). BTMPP is widely studied for its hydrometallurgical applications of metals separation, especially cobalt and nickel. It is generally accepted that monobasic organophosphorus acid extractants like BTMPP form dimers in diluents of low polarity. The dimer arises from strong intermolecular hydrogen bonding between the P=O and P-OH groups as shown Figure 1. [1], [2].

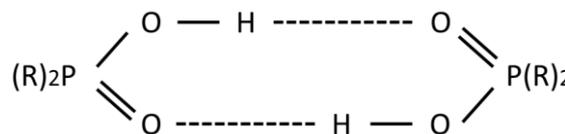


Figure 1: Schema of dimer BTMPP

The knowledge of the aggregation of an extractant is important, as it influences the extraction equilibria by reducing the amount of extractant molecules available for the extraction. Most of the studies on solvent extraction by BTMPP consider that BTMPP exists only as dimer in the organic phase. The predominance of the dimer form was demonstrated in toluene by Vapor Pressure Osmometry (VPO) [2], [3]. The existence of monomers and of other more aggregated forms such as

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trimer is also suggested [4]. Indirect methods involving biphasic equilibriums were used to estimate the value of the equilibrium constant of dimerization (Table 1). The dimerization constant is optimized together with the constants of the other equilibriums involved (distribution, dissociation...), in order to fit measured data such as pH, distribution of BTMPP or conductivity [5]–[9].

Authors/ ref	Experimental conditions	Log( $K_{dim}$ )	Method of determination
Biswas et al. [5]	Pure BTMPP in kerosene, 30°C	2.28	Biphasic distribution
Ke-An et al. [6]	CHCl <sub>3</sub> , 25°C	2.26	Biphasic distribution
	CDCl <sub>3</sub> , 25°C	2.31	
Fu et al. [7]	Pure BTMPP in Kerosene, 25°C	4.2	Conductivity measurement
Nagaosa et al. [8]	CX272 in kerosene, 25°C	4.56	Biphasic potentiometric titration
Sella et al. [9]	CX272 in Kerosene, 25°C	3	Biphasic potentiometric titration
Sastre et al. [10]	Pure BTMPP in toluene, 30°C	3.07	VPO
	37°C	2.92	
	50°C	2.57	

Table 1: review of the dimerization constants of CX272 or pure BTMPP available in the literature, with the conditions and the methods used for their estimation.

It was pointed out that dimerization constant cannot be determined precisely from these biphasic methods, because of the too low impact of the variation of the constant on the measured data [7], [9]. This could explain the dispersion observed between the constants reported in Table 2. Furthermore, some studies are conducted with BTMPP purified from CX272 whereas others use non-purified CX272. Sastre et al. estimated the dimerization constant of BTMPP by VPO [10].

In the present work, the aggregation of BTMPP is studied by VPO at 50°C, temperature commonly chosen for industrial applications. The aggregation constants are calculated by least square optimization method. In order to know the impact of temperature, tests were also conducted at 43°C and 60°C.

## Material and methods

### Reagents

The extractants Cyanex 272 (Cytec) and Ionquest 290 (Rhodia) are used without further purification. The diluents chosen for the VPO tests are n-hexane (Sigma-Aldrich) for the measurements at 43°C and 50°C, and n-heptane (Panreac) at 60°C, because their boiling points (69°C and 98°C resp.) are adapted to VPO at such temperatures and they have dielectric properties similar to kerosene. We assumed that the length of chain of the alkane diluent does not modify the aggregation of BTMPP. Tri-octylamine (TOA) (Sigma-Aldrich) is used as standard because it is known to be monomeric and to dissolve well in alkane diluents [11]. All the solutions are prepared by weighting.

### VPO technique

VPO consists in measuring the difference of resistance  $\Delta R$  between two thermistors: one containing a drop of pure diluent suspended, and the other a drop of solution (diluent + solute). The two thermistors are located in an atmosphere saturated with

diluent vapor.  $\Delta R$  is directly proportional to the difference of temperature between the thermistors. It is also a function of the difference in vapor pressure of the two drops, and so directly related to the activity of the diluent, or to the apparent molar fraction of solutes in the solution ( $X_{app}$ ).  $X_{app}$  is the molar fraction of all the solute species present in the solution:

$$X_{app} = \frac{n_{monomer} + n_{dimer} + \dots}{n_{diluent} + n_{monomer} + n_{dimer} + \dots}$$

The simplification of the equation of Clausius Clapeyron leads to a proportional relation between  $\Delta R$  and  $X_{app}$  [12].

$$\Delta R = K \cdot X_{app} \quad (\text{constant } K \text{ determined by calibration})$$

This proportional relation, valid for low  $X_{app}$ , can also be used with molalities instead of molar fractions for solutions of low molalities. Although most of the VPO studies work with molalities for convenience, we chose to work with molar fractions that led to better calibrations than molalities because of the high concentrations of our solutions.

VPO experiments are carried out at 43°C, 50°C and 60°C using a Knauer K-7000 Vapor pressure osmometer. The drop size is kept as constant as possible. Due to the time dependence of the signal, the measurements are taken when the maximum of  $\Delta R$  is attained and stabilized for a short period of time. Three measurements are done for each sample showing a good repeatability. The average of the three measurements is calculated.

#### *Calculation method*

$\Delta R$  are measured by VPO for several solutions containing extractant at various analytical molar fractions, called  $X_{tot}$ .  $X_{tot} = \frac{n_{BTMPP} + n_{impurities}}{n_{diluent} + n_{BTMPP} + n_{impurities}}$

$X_{app}$  are calculated from the  $\Delta R$  and  $K$ . The average numbers of aggregation ( $N_{agg}$ ) are obtained from the couples  $X_{tot}$  and  $X_{app}$ :  $N_{agg} = X_{tot} / X_{app}$

Then an optimization procedure developed on Matlab based on the least square method is used to estimate the equilibrium constants of aggregation from the experimental average number of aggregation. For convenient use of the constants, the molar fractions are converted into molar concentrations.

## **Results and discussion**

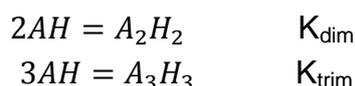
### *Presence of impurities*

CX272 and IQ290 are respectively 88% and 95% pure. The presence of impurities influences the estimation of  $N_{agg}$  obtained by VPO because they are included in  $X_{app}$  and  $X_{tot}$ . The main impurity is tri(2,4,4-trimethylpentyl) phosphine oxide. For simplification, we assumed that the phosphine oxide impurities are monomeric, although mixed aggregates phosphine-oxide / BTMPP could be formed, as it was suggested for TOPO and D2EHPA [13]. Other assumptions were tried: similar

aggregation behavior of the impurities and BTMPP, formation of mixed aggregates... However these assumptions (results not presented here) led to different values of aggregation constants between CX272 and IQ290.

### Comparison of Cyanex 272 and Ionquest 290 at 50°C

Depending on the concentration of BTMPP, its average number of aggregation varies from 1.8 to 2.2 (Figure 2), so it was concluded that BTMPP forms monomers (AH), dimers ( $A_2H_2$ ) and trimmers ( $A_3H_3$ ):



The procedure of optimization developed on Matlab is used to estimate the aggregation constants (for calculations in concentrations):

$$\begin{array}{lll} \text{CX272:} & \text{Log}(K_{\text{dim}}) = 3.1 \pm 0.2 & \text{Log}(K_{\text{trim}}) = 4.9 \pm 0.2 \quad (\text{at } 50^\circ\text{C}) \\ \text{IQ290:} & \text{Log}(K_{\text{dim}}) = 3.3 \pm 0.2 & \text{Log}(K_{\text{trim}}) = 4.9 \pm 0.2 \quad (\text{at } 50^\circ\text{C}) \end{array}$$

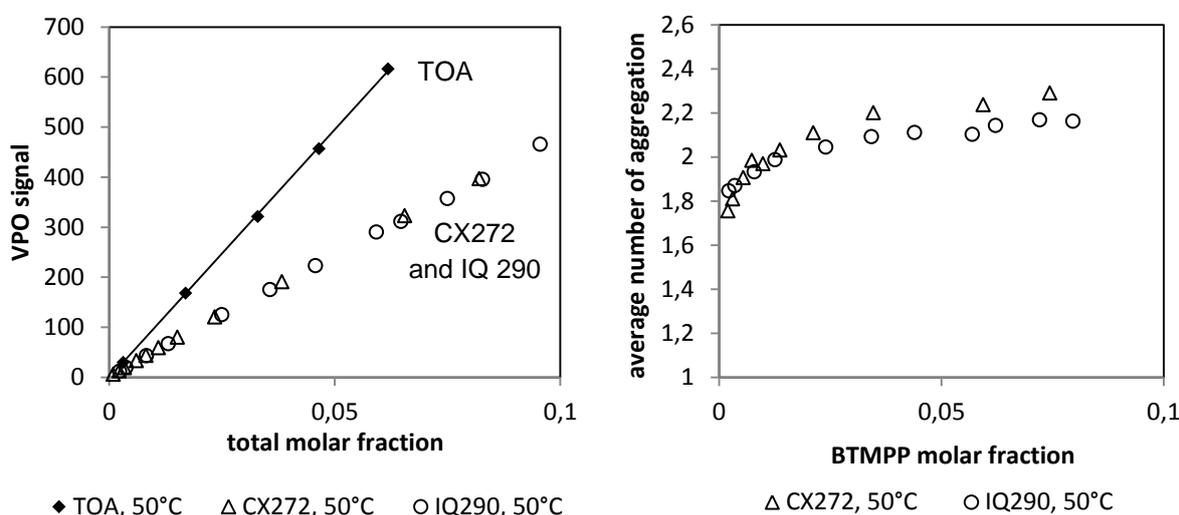


Figure 2: Calibration curve with TOA, VPO signals and average numbers of aggregation obtained at 50°C with CX272 and IQ290 at various concentration of extractant

The optimized aggregation constants allow calculating the experimental average numbers of aggregation with good agreement. However, we observe that the method is very sensitive to small variations of the experimental average numbers of aggregation. Moreover, the aggregation constants are only approximations due to the presence of impurities and the assumption on their aggregation. Therefore the incertitude on the logarithm of the optimized aggregation constant is around 0.2.

### Influence of temperature

Experimental tests were also conducted at 43°C (in n-hexane) and 60°C (in n-heptane) with CX272, in order to see the influence of such temperature variations (Figure 3). The differences obtained between the three couples of constants are low, comparable to the incertitude

CX272	Log( $K_{\text{dim}}$ )	Log( $K_{\text{trim}}$ )
43°C	2.8	4.8
50°C	3.1	4.9
60°C	3.0	4.8

Table 2: Logarithm of BTMPP equilibrium constants of aggregation estimated with CX272 at 43°C, 50°C and 60°C.

of the method (Table 2). So it is concluded that temperature variations from 43 to 60°C have small influence on the aggregation. At first approximation, it can be considered that aggregation is independent on temperature from 43°C to 60°C, taking the average of the constants calculated at each temperature:

$$\text{Log}(K_{\text{dim}}) = 3.0 \pm 0.2$$

$$\text{Log}(K_{\text{trim}}) = 4.8 \pm 0.2$$

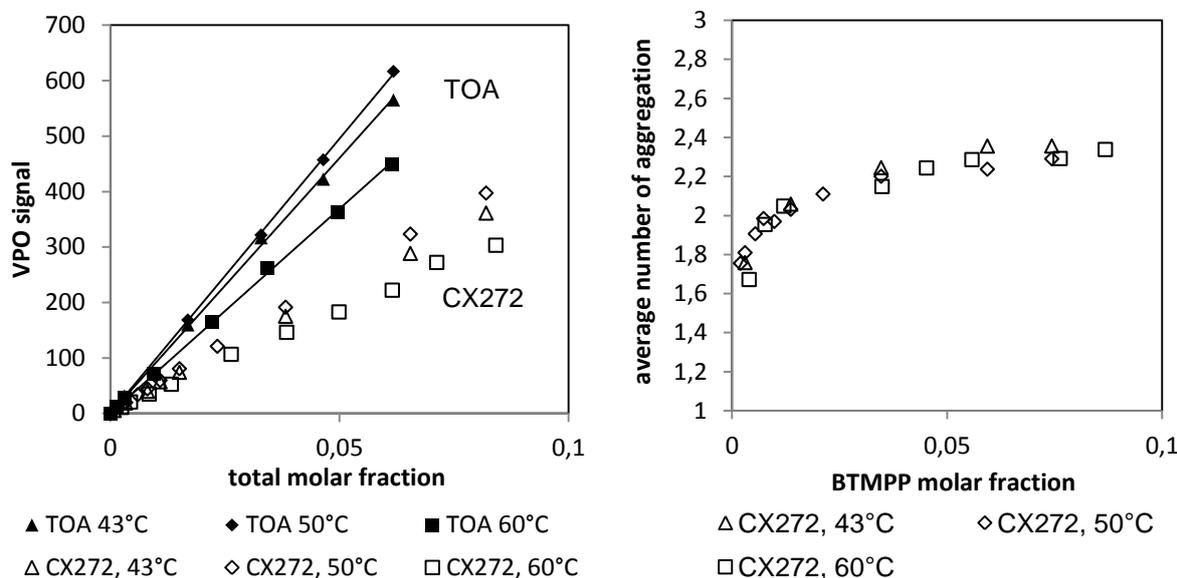


Figure 3: Calibration curves with TOA, VPO signals and average numbers of aggregation obtained at 43°C, 50°C and 60°C with CX272 at various concentration of extractant

Knowing the equilibrium constants of dimerization and trimerization, the distribution of BTMPP between monomers, dimers and trimers can be calculated at various analytical concentrations of BTMPP (Figure 4).

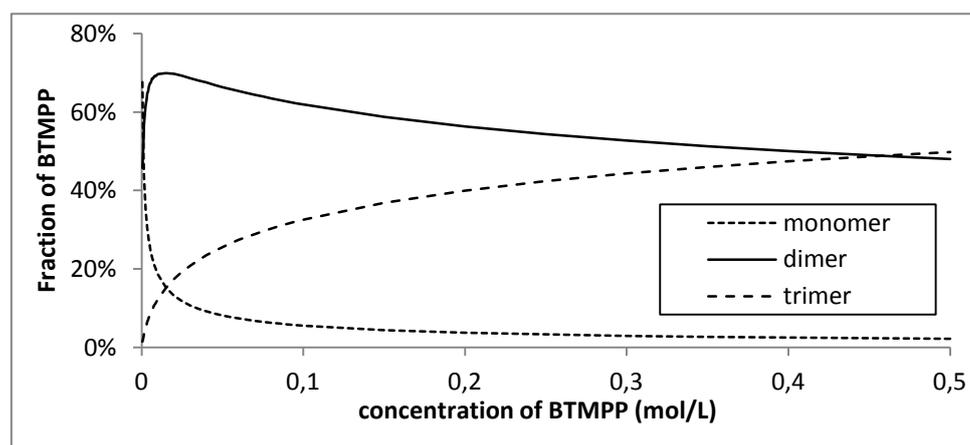


Figure 4: fraction of BTMPP that is present in the form of monomer, dimer or trimer, as a function of the analytical concentration of BTMPP.

Contrarily to the common assumption that BTMPP is only dimeric, the proportion of BTMPP present in the form of monomer or trimer can be elevated. For concentrations higher than 0.15 mol/L, the proportion of BTMPP present in the dimers is lower than 60%, and higher than 35% in the trimers.

## Conclusion

The aggregation of BTMPP has been studied by VPO. The average numbers of aggregation of CX272 and IQ290 are measured for various concentrations of extractant at 43°C, 50°C, 60°C. As the average number of aggregation reaches 2-2.2, it was concluded that BTMPP exists as monomer, dimers and trimers. The equilibrium constants of dimerization and trimerization are estimated by least square optimization method. Nearly similar values of equilibrium constants were obtained for both CX272 and IQ290 when assuming impurities of the commercial extractants are monomeric. No significant influence of temperature has been detected on the average aggregation number in the range 43 - 60°C.  $\text{Log}(K_{\text{dim}})$  and  $\text{Log}(K_{\text{trim}})$  are respectively estimated at  $3.0 \pm 0.2$  and  $4.8 \pm 0.2$ . At low concentrations of BTMPP (0.005-0.1mol/L), the extractant is mainly present as dimer. However at higher concentrations the fraction of BTMPP that is present as trimer becomes elevated.

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