

Self-association and association of tri-*n*-butyl phosphate (TBP) in different diluents

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The interaction of tri-*n*-butyl phosphate (TBP) with diluents and its self-association have been investigated. The corresponding equilibrium constants were determined and used to calculate the concentration of TBP monomer. The calculated TBP monomer concentrations correspond to the TBP activities published in the literature.

Keywords: self-association, association, tri-*n*-butyl phosphate (TBP), extraction model, TBP activity.

Tri-*n*-butyl phosphate (TBP) is widely used in spent nuclear fuel reprocessing plants. It is the extractant of choice in the PUREX technology process, used for the recovery of uranium and the separation of plutonium from fission products. In the THOREX technology process, TBP is used for the separation of uranium from irradiated ^{232}Th . The basis of both technologies is the extraction of uranyl(thorium) nitrate from the aqueous phase with TBP.

TBP is usually diluted with an organic diluent to regulate the viscosity and density of the TBP-diluent system and to avoid criticality of ^{235}U . The choice of diluent aims at improving the solubility of the TBP-metal salt complex in the organic phase.

TBP, containing a phosphoryl group, can react with active diluents or it can self-associate if an inert diluent is used. The distribution of solutes between the aqueous and the TBP-diluent organic phase is greatly influenced by the diluent used.

The aim of this work was to examine the TBP-diluent interaction and the self-association of TBP and to determine the corresponding equilibrium constants. The equilibrium constants enable the free TBP concentration in the different diluents to be computed.

THEORETICAL

A decrease of the free (uncomplexed) TBP concentration leads to an increase of the TBP distribution ratio values. The TBP extraction power is lowered as a

consequence of self-association of TBP, Eq. (1), or of the interaction of the TBP with the diluent, Eq. (3), in the organic phase. The corresponding equilibrium constants are given by Eqs. (2) and (4), where, M, D, and S denote the monomer and dimer of TBP and the monomer of the diluent, respectively. The concentrations, c , of the species, denoted by the easily recognized subscripts, are given in mol dm^{-3} :



$$K_D = c_{D(\text{org})}/c_{M(\text{org})}^2 \quad (2)$$



$$K_{MS} = c_{MS(\text{org})}/c_{M(\text{org})}c_{S(\text{org})} \quad (4)$$

The study of TBP self-association in an inert diluent is based on the mass balance Eq. (5):

$$c_{\text{TBP}(\text{org})}^{\text{tot}} = c_{M(\text{org})} + 2c_{D(\text{org})} \quad (5)$$

Introducing the value of $c_{D(\text{org})}$, derived from Eq. (2), into Eq. (5), leads to Eq. (6):

$$c_{M(\text{org})} = \frac{c_{\text{TBP}(\text{org})}^{\text{tot}} + 8K_D c_{\text{TBP}(\text{org})}^{\text{tot}} - 1}{4K_D} \quad (6)$$

Using Eq. (6), the values of $c_{M(\text{org})}$ and K_D can be calculated as the best fit of experimental data to $c_{\text{TBP}(\text{org})}^{\text{tot}}$.

The interaction of TBP with active diluents is presented by Eqs. (3) and (4) and corresponding mass balance Eq. (7):

$$c_{\text{TBP}(\text{org})}^{\text{tot}} = c_{M(\text{org})} + c_{MS(\text{org})} \quad (7)$$

The introduction of the $c_{MS(\text{org})}$ value, derived from Eq. (4), into Eq. (7) leads to Eq. (8).

$$c_{\text{TBP}(\text{org})}^{\text{tot}} = c_{M(\text{org})} + K_{MS} c_{M(\text{org})} c_{S(\text{org})} \quad (8)$$

Eq. (8) together with Eq. (9) and (10) gives rise to Eq. (11):

$$c_{S(\text{org})}^{\text{tot}} = c_{S(\text{org})} + c_{MS(\text{org})} \quad (9)$$

$$K_d = c_{M(\text{org})}/c_{M(\text{aq})} \quad (10)$$

$$c_{\text{TBP}(\text{org})}^{\text{tot}} = K_d c_{\text{TBP}(\text{aq})}^{\text{tot}} + K_d K_{MS} \frac{c_{\text{TBP}(\text{aq})}^{\text{tot}} c_{\text{TBP}(\text{org})}^{\text{tot}}}{1 + K_d K_{MS} c_{\text{TBP}(\text{aq})}^{\text{tot}}} \quad (11)$$

From Eq. (11), the values of $c_{M(\text{org})}$ and $c_{MS(\text{org})}$, as well as of K_d and K_{MS} , can be calculated as the best fit of experimental data to $c_{\text{TBP}(\text{org})}^{\text{tot}}$ and $c_{S(\text{org})}$.

RESULTS AND DISCUSSION

Earlier investigations on TBP self-association and its interaction with diluents have been reported elsewhere.¹⁻⁶

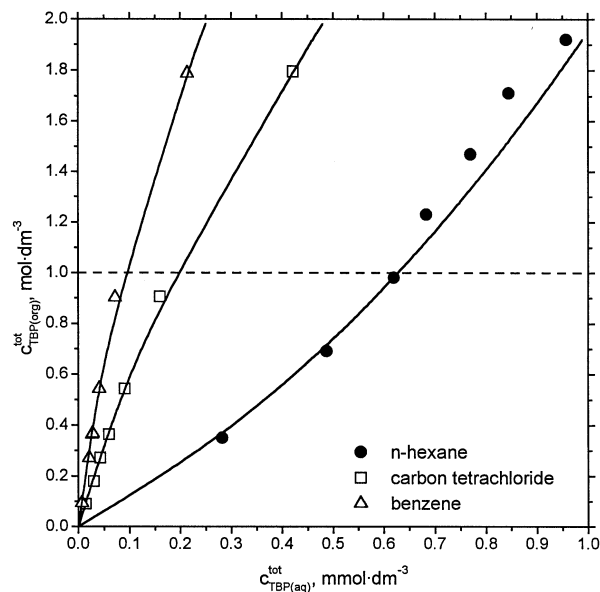


Fig. 1. The distribution of TBP between different organic diluents and the aqueous phase. The lines are the best fit of the experimental data,² with Eq. (11).

The distribution ratio of TBP between the organic and aqueous phase is rather high and is difficult to measure accurately, hence of that, we made use of the very good TBP distribution data obtained by Johnson and Dillon,² determined at room

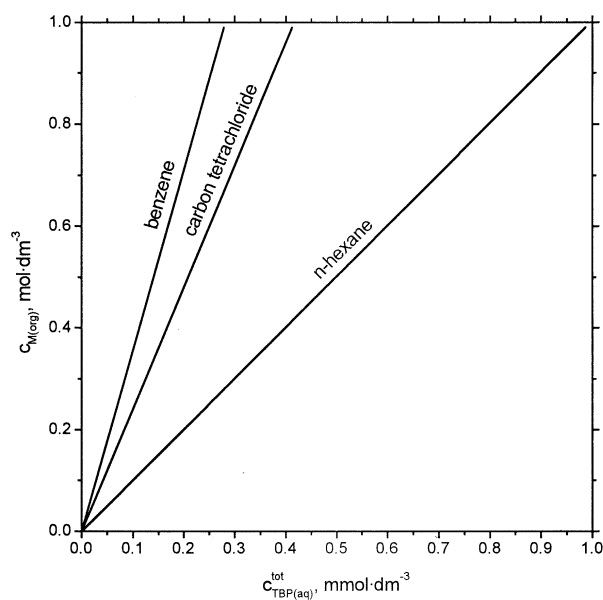


Fig. 2. The concentration of TBP monomer in the organic phase, calculated using Eq. (6) and $K_D = 0.57$ using data from the literature.²

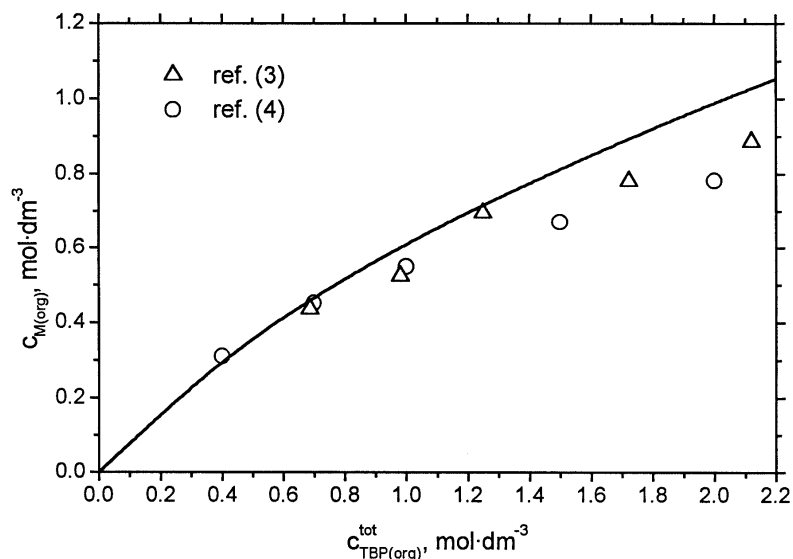


Fig. 3. The TBP monomer concentrations (line) calculated for $K_D = 0.57$ using Eq. (6). The circles and triangles are chemical activities taken from the literature,^{3,4} respectively.

temperature and atmospheric pressure. When *n*-hexane, as the most inert diluent, is used, TBP dimers exist in the organic phase. Due to the low solubility of TBP in water (about $0.0015 \text{ mol dm}^{-3}$), the self-association of TBP in the aqueous phase can be neglected. The TBP dimerization constant, K_D , defined by Eq. (2), was calculated for the organic phase as the best fit of the experimental data on $c_{\text{TBP}(\text{org})}^{\text{tot}}$ and $c_{\text{TBP}(\text{aq})}^{\text{tot}}$ using Eq. (11). The curves in Fig. 1 were drawn for $K_D = 0.52$ and $K_d = 973$.

When benzene and carbon tetrachloride are used as diluents, the TBP distribution is higher than when *n*-hexane is employed (*cf.* Fig. 1). This is a consequence of the interaction of TBP with benzene or carbon tetrachloride, described by Eq. (3) and the corresponding equilibrium constant Eq. (4).

One can see from Fig. 1 that for a constant TBP concentration in the organic phase, *e.g.*, 1 mol dm^{-3} TBP, or 30%, as in the PUREX process (dashed line), the TBP concentration in the aqueous phase increases in the following order of diluents used: benzene < carbon tetrachloride < *n*-hexane. This is in agreement with Fig. 2, which shows the dependence of the TBP monomer concentration in the organic phase on the TBP concentration in the aqueous phase for the different diluents. This suggests that the TBP monomer, responsible for extraction of different materials, can be a measure of the TBP activity. This is illustrated in Fig. 3, which shows an agreement between the calculated TBP monomer concentrations and corresponding TBP activities. These activities were originally given on the mole fraction concentration scale with pure TBP as the standard state, but they were recalculated to the mol dm^{-3} concentration scale with infinite dilution as the standard state.

TABLE I. The determined dimerization (K_D) and association (K_{MS}) constant values of TBP, defined by Eqs. (2) and (4), respectively, in different diluents. Some literature values are also included.

Diluent	Experimental technique	$K_D/\text{mol}^{-1} \text{dm}^3$	$K_{MS}/\text{mol}^{-1} \text{dm}^3$	Source
<i>n</i> -Hexane	distribution (wet)	0.57	-	this work
	IR spectroscopy (dry)	2.9	-	ref. (5)
Carbon tetrachloride	distribution (wet)	-	0.18	this work
	dielectric constant (dry)	-	1.1	Ref. (1)
	IR spectroscopy (dry)	-	0.9	Ref. (6)
Benzene	distribution (wet)	-	0.30	this work
	dielectric constant (dry)	-	0.1	Ref. (1)
	IR spectroscopy (dry)	-	0.9	Ref. 6
Chloroform	dielectric constant (dry)	-	6.1	Ref. (1)
	NMR (dry)	-	5.2	Ref. (6)
Pure TBP	NMR (dry)	2.9	-	Ref. (6)
	IR spectroscopy (dry)	2.4	-	Ref. (6)

The calculated values of the equilibrium constant of the self-association and association of TBP in different diluents are listed in Table I, together with some literature values. One can notice that the K_D and K_{MS} values determined in dry systems are higher than the values calculated for wet systems. This can be a consequence of the interaction of TBP with water, as shown in our previous paper.⁶

ИЗВОД

САМОАСОЦИЈАЦИЈА И АСОЦИЈАЦИЈА ТРИБУТИЛФОСФАТА (ТБФ) У РАЗНИМ РАСТВОРАЧИМА

ЈОЖЕФ Ј. ЧОМОР, МИРОСЛАВ М. КОПЕЧНИ И ЂОРЂЕ М. ПЕТКОВИЋ

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Испитивана је интеракција трибутилфосфата (ТБФ) са разним растварачима, као и самоасоцијација ТБФ-а. Одређене су одговарајуће равнотежне константе интеракције, које су искоришћене за израчунавање равнотежне концентрације мономера ТБФ. Израчуната концентрација мономера ТБФ се слаже са измереним активностима ТБФ-а, објављеним у литератури.

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REFERENCES

1. Dj. M. Petković, Z. B. Maksimović, *J. Inorg. Nucl. Chem.* **38** (1976) 297
2. W. F. Johnson, R. L. Dillon, US AEC Report, HW-29086 (1953). Also L. L. Burger in *Science and Technology of Tributyl Phosphate*, Vol. I, W. W. Shulz and J. D. Navratil, Eds., CRC Press, Boca Raton, Florida, USA, p. 25 (Figure 2)
3. M. F. Pushlenkov, O. N. Schuvalov, *Radiokhimiya* **5** (1963) 536
4. A. M. Rozen, L. P. Khorklorina, V. G. Yurkin, N. M. Novikova, *Dokl. Akad. Nauk SSSR* **153** (1963) 1387
5. Dj. M. Petković, *J. Inorg. Nucl. Chem.* **30** (1968) 603
6. Dj. M. Petković, Z. B. Maksimović, *J. Inorg. Nucl. Chem.* **39** (1977) 2031.