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On the Interaction of Metal Extractant Reagents. Investigation of the Aggregation of *di*(2,4,4-Trimethylpentyl)phosphinic Acid and *di*(*n*-Octyl)phosphinic Acid in Toluene by Vapour-Pressure Osmometry

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Summary. The aggregation equilibria of *di*(2,4,4-trimethylpentyl)phosphinic acid (H*DTMPP*) and *di*(*n*-octyl)phosphinic acid (H*DOP*) dissolved in toluene have been investigated by vapour-pressure osmometry (VPO) at different temperatures. The experimental data have been treated both graphically and numerically, and the average aggregation number $\bar{n}$ as well as the aggregation constant have been determined. The results suggest that dimers are formed and that the dimerization constant decreases with temperature. Finally, the enthalpies for the aggregation of *di*(2,4,4-trimethylpentyl)phosphinic acid and *di*(*n*-octyl)phosphinic acid in toluene have been estimated using the *van't Hoff* equation.

Keywords. Aggregation; *di*(2,4,4-Trimethylpentyl)phosphinic acid; *di*(*n*-Octyl)phosphinic acid; Vapour-pressure osmometry.

Über die Wechselwirkung metallextrahierender Reagentien. Untersuchung der Aggregation von *di*-(2,2,4-Trimethylpentyl)-phosphinsäure und *di*-(*n*-Octyl)-phosphinsäure in Toluol mittels Dampfdruckosmometrie

Zusammenfassung. Die Aggregationsgleichgewichte von in Toluol gelöster *di*-(2,4,4-Trimethylphentyl)-phosphinsäure (H*DTMPP*) und *di*-(*n*-Octyl)-phosphinsäure (H*DOP*) wurden mittels Dampfdruckosmometrie (VPO) bei verschiedenen Temperaturen untersucht. Die experimentellen Daten wurden sowohl graphisch als auch numerisch ausgewertet; es wurden sowohl die mittlere Aggregationszahl $\bar{n}$ als auch die Aggregationskonstante bestimmt. Die Resultate lassen vermuten, daß Dimere gebildet werden und die Dimerisationskonstante mit der Temperatur abnimmt. Mit Hilfe der *van't Hoff*schen Gleichung wurden die Enthalpien der Aggregation von *di*-(2,4,4-Trimethylpentyl)-phosphinsäure und *di*-(*n*-Octyl)-phosphinsäure in Toluol abgeschätzt.

Introduction

This work is a part of a series dealing with the interaction of metal extractant reagents in organic solvents. Organophosphorus compounds have been used extensively as metal extractants in many processess [1–3]. Among these, alkylphos-

phinic acids have been reported to possess higher separation factors for successive members of chemically similar groups such as cobalt and nickel [4, 5], actinides [6], lanthanides [7, 8], and other transition metals [9, 10].

Earlier investigations using cryoscopic, isospiestic, and viscosity measurements [11, 12] for determining the average aggregation number of organophosphorus acids in different solvents have shown that these compounds are monomer in very polar solvents such as water and alcohol and form aggregates in non polar aromatic and aliphatic solvents [13]. In solvent extraction chemistry, the knowledge of the interaction of extractants in the organic phase is essential in order to clarify the processess taking place in solution and to ascertain the stoichiometry of the extracted species. With this information it is possible to design optimal conditions for separation or purification steps in various technical applications.

In the present work, the aggregation constants of *di*(2,4,4-trimethylpentyl)phosphinic acid and *di*(*n*-octyl)phosphinic acid dissolved in toluene have been determined at different temperatures by vapour-pressure osmometry. The influence of the temperature on the aggregation equilibria has also been considered.

Results and Discussion

The experimental data ΔR were plotted as a function of the total concentration $[HA]_{tot}$ in toluene at three different temperatures, and are given in Fig. 1. The dashed

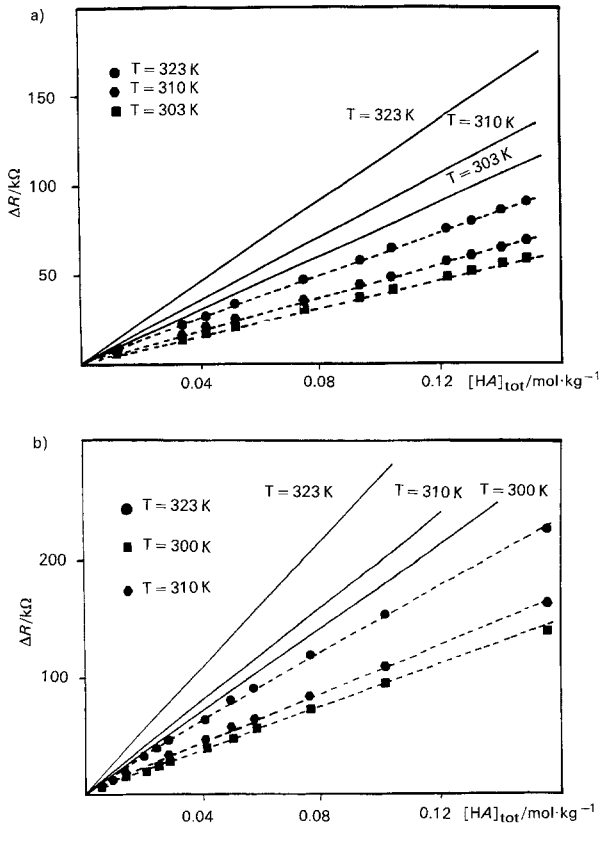

Fig. 1. ΔR plotted as a function of the total solute concentration for H*DTMPP*-toluene (a) and H*DOP*-toluene (b) at three different temperatures; the dashed and full drawn lines were calculated using the constant values given in Tables 1 and 2, respectively

lines were obtained from the experimental values of ΔR *vs.* the total benzil concentration in toluene and represent the behaviour of a monomeric system. As may be observed, the experimental points for the H*A*-toluene systems deviate from the monomeric behaviour of benzil in toluene. Thus, it can be assumed that deviations of the measured ΔR values from those of the standard solution are due to the presence of aggregates.

Determination of the average aggregation number

The aggregation of organophosphinic acids H*A* in toluene can be expressed as

$$\mathrm{n}HA = (HA)_\mathrm{n} \qquad 1$$

Assuming an ideal behaviour of the organophosphinic acids, the stoichiometric constant β_n can be written as

$$\beta_\mathrm{n} = \frac{[(HA)_\mathrm{n}]}{[HA]^\mathrm{n}} \qquad 2$$

Then, from the experimental data (ΔR, $[HA]_{tot}$) for each temperature and system, and using equation 11 with the calibration constants given in Table 1, values of S may be calculated. The average aggregation number $\tilde{n}$ of H*A* in toluene may be determined as

$$\tilde{n} = \frac{[HA]_{tot}}{S} \qquad 3$$

where $[HA]_{tot}$ and S are defined as

$$[HA]_{tot} = \Sigma n \beta_\mathrm{n} [HA]^\mathrm{n} \qquad 4$$

$$S = \Sigma \beta_\mathrm{n} [HA]^\mathrm{n} \qquad 5$$

and n varies from 1 to N.

In Fig. 2, the average aggregation number has been plotted as a function of the total concentration of H*A* for the systems H*DTMPP*-toluene and H*DOP*-toluene.

Determination of aggregation constants

The curve-fitting method of *Rossotti* [18] has been used for the analysis of experimental data. As a starting model, only one equilibrium monomer-polymer has been considered; thus, the stoichiometric concentration of H*A* can be written as

$$[HA]_{tot} = [HA] + \mathrm{n}[(HA)_\mathrm{n}] = [HA] + \mathrm{n}\beta_\mathrm{n}[HA]^\mathrm{n}. \qquad 6$$

Table 1. Calibration constant values obtained from $\Delta R = \mathrm{f}(B_{tot})$ for benzil-toluene solutions at different temperatures for different Knauer Vapor Osmometers (Mod. No. 0280 with an universal probe (a) and Mod. No. 11.00 with an organic probe (b))

a)	T	k_1	b)	T	k_1
	303	758 ± 1		300	1785 ± 1
	310	892 ± 2		310	2016 ± 2
	323	1138 ± 3		323	271 ± 1

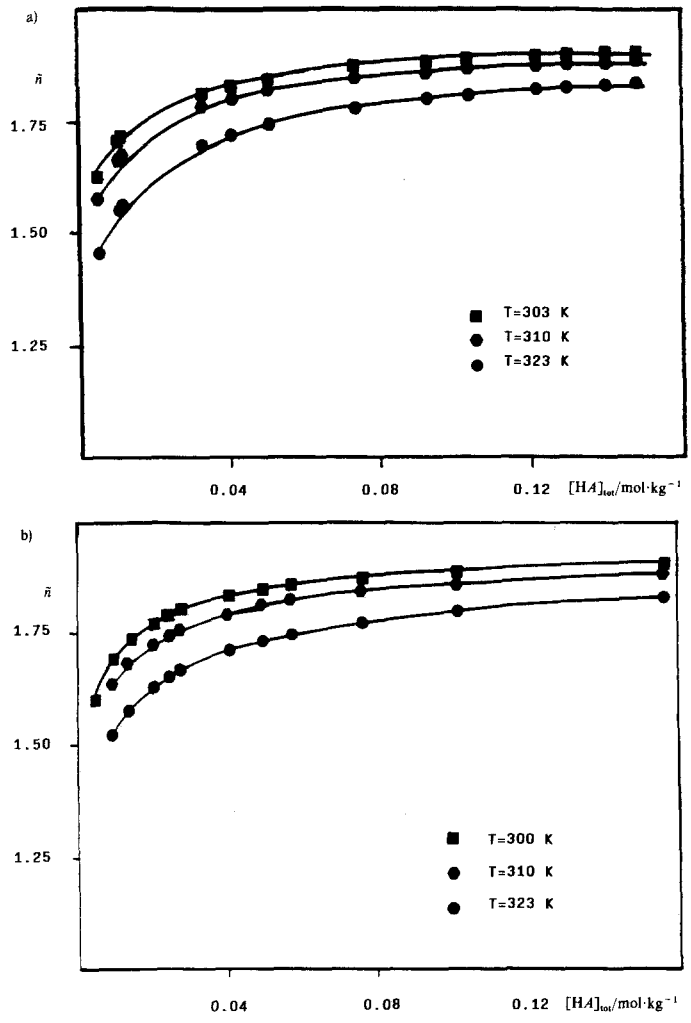

Fig. 2. Aggregation numbers as a function of the total organophosphinic acid concentration for H*DTMPP*-toluene (a) and H*DOP*-toluene (b); the full drawn lines were calculated using the constants given in Table 3

Rearranging, we obtain

$$\log\left(\frac{[HA]_{tot}}{[HA]} - 1\right) = \log n\beta_n + (n-1)\log[HA] \qquad 7$$

A plot of $\log(([HA]_{tot}/[HA]) - 1)$ *vs.* $\log[HA]$ should give a straight line with slope $n - 1$, and β_n may be obtained from the intercept.

Values for the free monomer concentration may be calculated from the values of $[HA]_{tot}$ and the experimental values of S using the *Bjerrum* relationship [19]:

$$[HA]\frac{dS}{d[HA]} = [HA]_{tot} = \tilde{n}S \qquad 8$$

$$\ln[HA] - \ln[HA]_o = \int 1/\tilde{n}\, d\ln S \qquad 9$$

The free monomer concentration [HA] may then be estimated by graphical integration of the curve $1/\tilde{n}$ *vs.* $\ln S$, assuming the association of HA to be negligible and thus $[HA]_o = S_o$.

In Fig. 3, $\log(([HA]_{tot}/[HA]) - 1)$ is plotted against $\log[HA]$ for both systems. The data may be fitted to a straight line with a slope of 1, which indicates that a monomer-dimer equilibrium exists; $\log\beta_2$ values are given in Table 2.

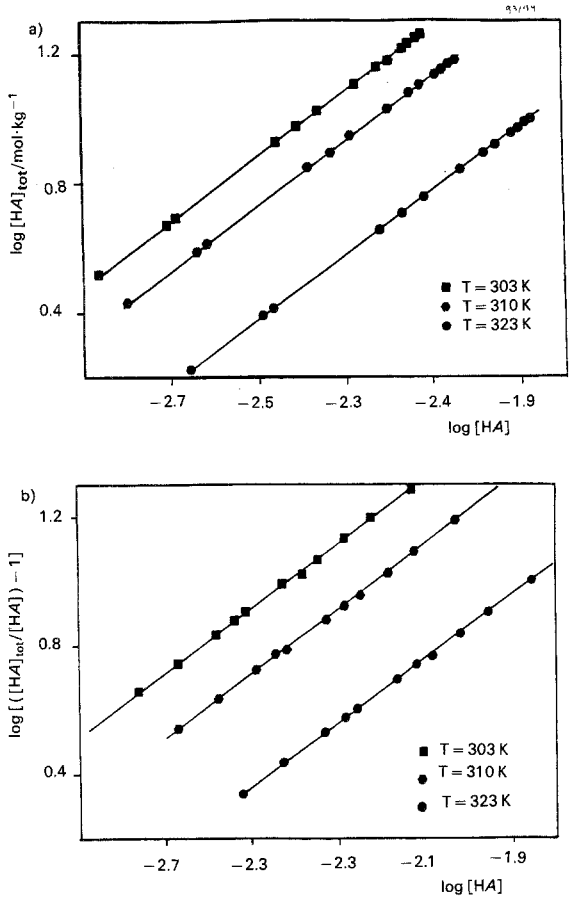

Fig. 3. $\log(([HA]_{tot}/[HA]) - 1)$ plotted as a function of the free organophosphinic acid concentration in toluene; H*DTMPP*-toluene (a) and H*DOP*-toluene (b)

Table 2. Aggregation constant values for H*DTMPP*-toluene (a) and H*DOP*-toluene (b) calculated using graphical methods

a)	T	$\log\beta_2$	b)	T	$\log\beta_2$
	300	3.07		300	3.13
	310	2.92		310	2.94
	323	2.57		323	2.56

Finally, the data (ΔR, $[HA]_{tot}$) have been treated with the CPLET program [20]. The program uses several minimizing routines to calculate the equilibrium constants β_n, the calibration constant k_i, and the stoichiometric coefficient n, and affords the minimum squares-sum error U defined as $U = \Sigma(\Delta R_{calculated} - \Delta R_{experimental})^2$. The best set of parameters are obtained when only one calibration constant is used. The results are given in Table 3.

In order to verify the proposed constants, ΔR was recalculated theoretically. Taking into account equation 11 and 5, for n = 2, ΔR can be written as

$$\Delta R = k_1[HA] + k_1\beta_2[HA]^2 \qquad 10$$

where k_1 is the calibration constants given in Table 1, β_2 the formation constants given in Table 2, and $[HA]$ the free monomer concentration estimated graphically.

Table 3. Results obtained from numerical calculations for H*DTMPP*-toluene (a) and H*DOP*-toluene (b) using the CPLET program

a)	T	$\tilde{n}$	$\log \beta_2$	K_1	U	σ
	303	1.999 ± 0.002	3.08 ± 0.02	757 ± 1	0.0112	0.0293
	310	2.001 ± 0.002	2.93 ± 0.01	894 ± 1	0.0126	0.0312
	323	1.997 ± 0.002	2.57 ± 0.01	1135 ± 2	0.0092	0.0266
b)	T	$\tilde{n}$	$\log \beta_2$	K_1	U	σ
	300	2.003 ± 0.008	3.13 ± 0.09	1789 ± 4	0.0082	0.0263
	310	2.008 ± 0.012	2.93 ± 0.05	2016 ± 12	0.0988	0.0947
	323	1.999 ± 0.002	2.56 ± 0.02	2714 ± 3	0.0154	0.0037

The results are presented in Fig. 1 as full drawn lines. The good agreement obtained between both experimental and calculated values gives great confidence in the proposed constants.

The results reported in this work for the aggregation of H*DTMPP* and H*DOP* in toluene indicate the existence of monomer-dimer equilibria at the experimental conditions used. As may be seen from Fig. 2, the average aggregation number increases with the total concentration of organophosphinic acid up to 0.05 $mol \cdot kg^{-1}$, but remains almost constant at higher concentrations. Similar $\tilde{n}$ values have been found for the aggregation of H*DTMPP* in chloroform [21] and for H*DOP* in benzene using cryoscopic methods [22]. The constant values show the strong tendency of organophosphinic acids to associate in the organic phase, and this trend decreases when the temperature is increased. This may be corroborated from the distribution diagrams (Fig. 4), calculated with the program CPLET using the proposed constants, where the dimer is the predominant species for concentrations above 0.010 $mol \cdot kg^{-1}$. Comparing the aggregation constant values obtained for H*DTMPP* ($\log \beta_2 = 3.08$) or H*DOP* ($\log \beta_2 = 3.13$) in toluene with those obtained for *di*-2-ethylhexylphosphoric acid ($\log \beta_2 = 3.68$) and 2-ethylhexylethylhexyl phosphonic acid ($\log \beta_2 = 3.37$) in toluene [23] at similar temperatures, it can be seen that a progressive replacement of an electron-acceptor group (alkoxy) by an electron-donor group (alkyl) attached to the phosphorus causes a decreasing tendency with respect to aggregation.

The aggregation constants for H*DTMPP* given in the present work are similar to those obtained in kerosene ($\log \beta_2 = 3.0$) [24] and higher than those obtained in chloroform ($\log \beta_2 = 2.2$) [25] which is a more polar solvent. This seems to agree with the tendency of decreasing the dimerization constants of organophosphinic acid compounds when increasing the polarity of the solvent.

The value of the aggregation constant of H*DOP* is slightly higher than the value found by the same authors ($\log \beta_2 = 2.74 \pm 0.21$) using two phase systems [26]. In a two phase system, toluene is water saturated and becomes slightly more polar; thus the tendency to aggregation decreases.

In order to obtain approximate values of the enthalpies of aggregation of H*DTMPP* and H*DOP*, the *van't Hoff* equation was used. From the slope of the function $\log \beta_2$ *vs.* $1/T$ (Fig. 5), the ΔH value of dimerization was calculated and found to be $-47.4\ kJ \cdot mol^{-1}$ and $-46{,}2\ kJ \cdot mol^{-1}$ respectively, which corresponds to the energy of two hydrogen bonds.

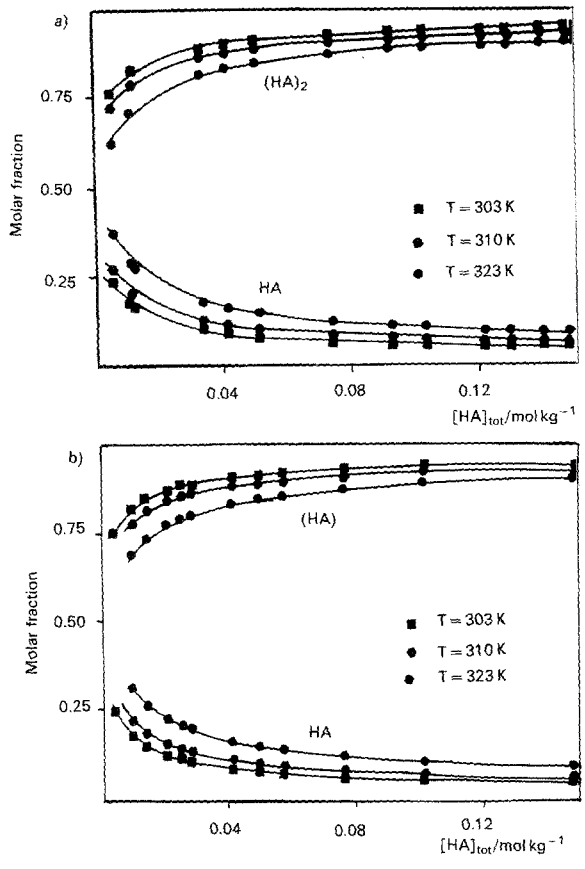

Fig. 4. Aggregation distribution diagrams as a function of the total concentration for *HDTMPP*-toluene (a) and *HDOP*-toluene (b) at three different temperatures

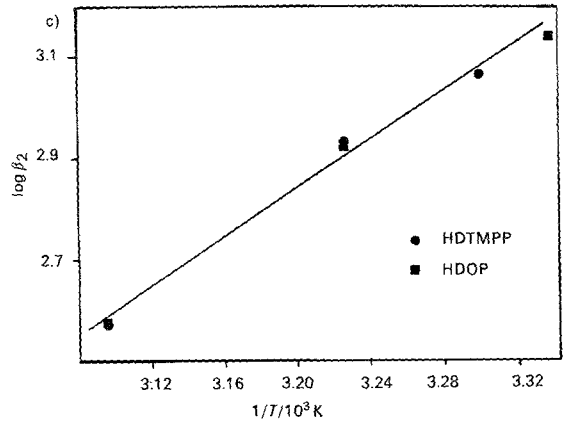

Fig. 5. $\log \beta_2$ plotted as a function of $1/T$ for *HDTMPP*-toluene and *HDOP*-toluene

Experimental

Reagents and solutions

Di(2,4,4-trimethylpentyl)phosphinic acid (*HDTMPP* = *HA*) supplied by Cyanamid Co. as Cyanex 272 was purified as described elsewhere [14]. *Di*(*n*-octyl)phosphinic acid (*HDOP* = *HA*) was synthesized by reaction of *n*-octene with sodium hypohosphite in the presence of *t*-butyl perbenzoate as iniator in a water-ethanol medium and was purified as described elsewhere [15]. The purities were determined

by potentiometric titration of acid in an 80% ethanol-water solution with 0.1 *M* NaOH using *Gran* plots [16]. A purity of 99% for H*DTMPP* and 95.3% for H*DOP* was found. Toluene (Merck, AR) was used without further purification; benzil (Merck, AR) was recrystallized twice from dried methanol. Solutions of benzil, H*DTMPP*, and H*DOP* were prepared by weight. The concentration range used was up to 0.150 mol·kg^{-1}.

Experimental technique

The osmometric measurements were carried out using a Knauer Vapour Pressure Osmometer (H*DTMPP*: Mod. No. A 0280; 303, 310, and 323 K; H*DOP*: Mod. No. 11.00; 300, 310, and 323 K). For the H*DTMPP*-toluene system a universal probe and for the H*DOP*-toluene system an organic probe were used; both were previously calibrated with benzil in toluene. Benzil was used as the standard because it is expected to be monomeric in toluene in the concentration range of interest [17].

The difference of resistance ΔR was measured as a function of the solute concentration. The measured property ΔR may be expressed as a function of the sum of the concentrations of all species, S:

$$\Delta R = k_1 S \qquad 11$$

(k_1: calibration constant; may be obtained by measuring ΔR for different monomeric benzil solutions in toluene [17]). The values of the calibration constants at different temperatures are given in Table 1.

In order to obtain reliable ΔR values, the drop size was kept as constant as possible and equal in both thermistors, and the measurements were performed by reading ΔR five minutes after placing the drops on the thermistors. In this manner the precision of ΔR was maintained within $\pm 0.02\ \Delta R$.

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