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Dissociation, Distribution and Polymerization Constants for Dibutylphenacylphosphonate (HDBPP)

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The distribution of dibutylphenacylphosphonate between 1 M $(Na,H)ClO_4$ and organic diluents (n-hexane, n-heptane, benzene, toluene) has been studied by a spectrophotometric method, as well as the dissociation in the aqueous phase and the di- and trimerization in the organic phase. The following constants (25 °C) were obtained: Dissociation ($K_a = [H^+][A^-]/[HA]$): 12.30 ± 0.03; distribution ($K_d = [\overline{HA}/[HA]$): 29.8 ($\Delta H° = 16.8$ kJ/mol, $T\Delta S° = 25.2$ kJ/mol; n-heptane), 35.0 (n-hexane), 1200 ± 200 (benzene) and 1400 ± 200 (toluene); dimerization ($K_n = [(\overline{HA})_n]/[\overline{HA}]^n$, n = 2): 7.95 ($\Delta H° = -11.8$ kJ/mol, $T\Delta S° = -6.6$ kJ/mol; n-heptane), 6.7 (n-hexane), and trimerization (n = 3): 210 (n-heptane), 150 (n-hexane).

Although some metal complexes and metal extraction system using β-ketophosphonates as ligands or extractants have been studied[1-12], very little information is available concerning the properties of these complexing agents in two-phase systems, *i.e.* distribution constants (K_d), dissociation constants (K_a) and possible polymerization constants (K_n). These parameters are required for the interpretation of metal extraction processes. This paper describes a determination of these constants for dibutylphenacylphosphonate [HDBPP; composition $C_6H_5C(O)CH_2P(O)(OC_4H_9)_2$] in aqueous 1 M $NaClO_4$ – n-hexane, n-heptane, benzene and toluene systems.

EVALUATION METHODS

Neglecting any aggregation in the aqueous phase and any dissociation in the organic phase, an acidic extractant HA in a two-phase liquid system can generally be described by the following equilibria:

$$HA \rightleftharpoons H^+ + A^- \quad (K_a\text{, dissociation constant})$$
$$HA \rightleftharpoons \overline{HA} \quad (K_d\text{, distribution constant})$$
$$n\overline{HA} \rightleftharpoons (\overline{HA})_n \quad (K_n\text{, polymerization constant})$$

(overlined symbols refer to species in the organic phase).

The distribution ratio D is defined by

$$D = [\overline{HA}]_{tot}/[HA]_{tot}$$

giving eqn. (1).

$$D = (K_d + \sum_2^n nK_nK_d^n[HA]^{n-1})/(1 + K_a[H^+]^{-1}) \quad (1)$$

K_d *and* K_n *determination.* For $pH \ll pK_a$, D is independent of pH and eqn. (1) can be written as eqn. (2). A plot of D *vs.* [HA] permits a determination

$$D = K_d + \sum_2^n nK_nK_d^n[HA]^{n-1} \quad (2)$$

of the constants K_d and K_n with $K_d = D([HA] = 0)$, assuming that K_d is constant, independently of [HA].

K_a *determination.* For $[HA] \rightarrow 0$, the aggregation of HA in the organic phase can generally be neglected and eqn. (1) can be written as

$$D = K_d(1 + K_a[H^+]^{-1})^{-1}$$

or eqn. (3). Thus, pH *vs.* $\log(K_dD^{-1} - 1)$ is a straight line with slope 1 and intercepts pK_a. (It is assumed that K_d is constant in the pH range studied.)

$$pH = \log(K_dD^{-1} - 1) + pK_a \quad (3)$$

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EXPERIMENTAL

Chemicals. Sodium perchlorate was prepared and purified according to conventional methods. HDBPP was prepared, purified and checked as described previously.[9] All other chemicals were of *p.a.* quality and used without further purification.

Distribution measurements. The distribution of HDBPP between an aqueous sodium perchlorate solution and organic phases was studied in a thermostated vessel (± 0.1 °C). The two phases (with an initial HDBPP concentration in the organic phase between 10^{-4} and 1.7×10^{-3} M) were vigorously stirred for one hour and then allowed to separate by gravity. For each distribution ratio determination, an aliquot of each phase was withdrawn and diluted with ethanol and the UV spectrum recorded. The UV absorption spectrum of HDBPP in ethanol contains a strong absorption band at 246 nm with a maximum extinction coefficient (ε_{max}) of 13 000 M^{-1} cm^{-1} and a shoulder at 280 nm with $\varepsilon_{max} \sim 1200$ M^{-1} cm^{-1}. The Beer-Lambert law was checked and the 246 nm band used to determine HDBPP concentrations in the two phases. When benzene and toluene were used as solvents, the measurements had to be corrected taking into account the absorption of the solvents themselves (this explains the low relative precision of the corresponding measurements).

In order to check the direct measurements of low HDBPP concentrations in highly dissociated systems, the total aqueous HDBPP concentration was calculated from the difference between the added HDBPP and the measured organic HDBPP concentration. The calculated $[HDBPP]_{tot}$-values were verified by direct UV measurements on the aqueous solutions which were pH adjusted after separation of the phases to suppress the HDBPP dissociation effect.

All UV measurements were performed on a Perkin-Elmer 551 spectrophotometer using 1 cm quartz cells.

Table 1. Distribution and polymerization constants.

Diluent	t, °C	K_d	K_2	K_3
	10.0	19.0	10.1	215
n-Heptane	24.9	29.8	7.95	210
	39.4	37.3	6.3	230
n-Hexane	25.0	35.0	6.7	150
Benzene	25.0	1200 ± 200	–	–
Toluene	25.0	1400 ± 200	–	–

RESULTS AND DISCUSSIONS

K_d and K_n determinations. The determinations of distribution constants and polymerization constants were performed using an aqueous phase of 1 M $(Na,H)ClO_4$ at pH 4, and n-hexane, n-heptane, benzene and toluene as organic diluents. Fig. 1 shows a plot of *D vs.* [HDBPP] at different temperatures for n-heptane and n-hexane. According to

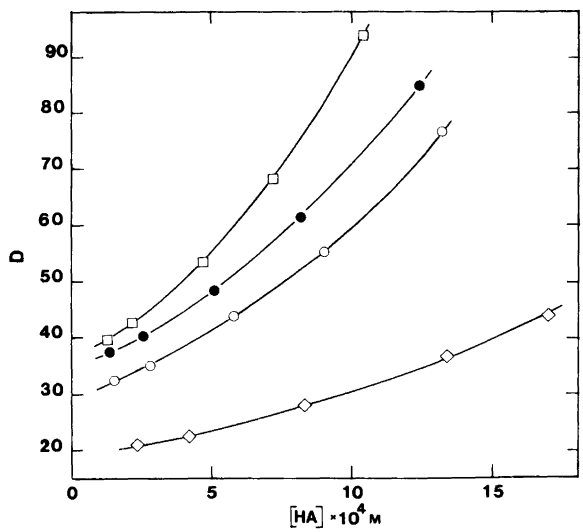

Fig. 1. Distribution ratios of HDBPP in 1 M $(Na,H)ClO_4$ – n-heptane and n-hexane. □, 39.4 °C; ○, 24,9 °C; ◇, 10.0 °C – n-heptane; ●, 25.0 °C – n-hexane.

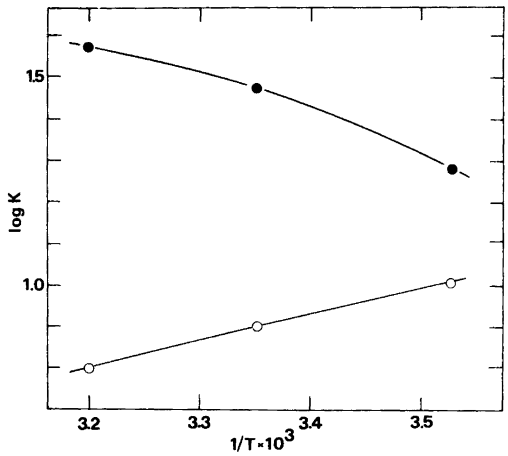

Fig. 2. log K_2 and log K_d *vs.* $1/T$. ○, log K_2; ●, log K_d – n-heptane.

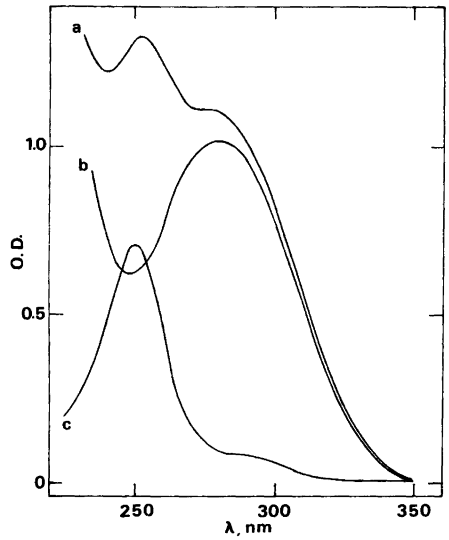

Fig. 3. UV spectra of HDBPP – $DBPP^-$ (optical density, O. D., *vs.* wave length, λ). a. Aqueous phase 1 M (Na,H)ClO_4, pH 12.66, after shaking with a 0.00205 M HDBPP – n-heptane solution. b. $DBPP^-$ in aq, 14.0×10^{-5} M; $\varepsilon_{280} = 7000$ M^{-1} cm^{-1}. c. HDBPP in n-heptane, 6.1×10^{-5} M; $\varepsilon_{250} = 11200$ M^{-1} cm^{-1}.

eqn. (2), the non-linearity of the curves is consistent with a polymerization ($n > 2$). Assuming a trimerization of HDBPP in n-heptane, the experimental results can be well described by eqns. (4)–(6). A similar result is obtained for n-hexane;

$$D(10\,°C) = 19.0 + 7330[HDBPP] + 4.38 \times 10^6[HDBPP]^2 \quad (4)$$

$$D(24.9\,°C) = 29.8 + 13800[HDBPP] + 16.3 \times 10^6[HDBPP]^2 \quad (5)$$

$$D(39.4\,°C) = 37.3 + 17500[HDBPP] + 35.8 \times 10^6[HDBPP]^2 \quad (6)$$

$$D(25.0\,°C) = 35.0 + 16400[HDBPP] + 19.5 \times 10^6[HDBPP]^2 \quad (7)$$

eqn. (7). Using eqns. 2, 4, 5, 6 and 7, K_d, K_2 and K_3 were calculated, Table 1, Fig. 2. For the benzene and toluene systems, the distribution constants were independent of [HDBPP] (in the concentration range $0 < [HDBPP] < 0.6$ M), which shows that HDBPP is not aggregated in these dilutents. This result is consistent with previous observations from cryoscopic measurements[9] that HDBPP is monomeric in benzene.

The influence of pH on the distribution constant (in the 1 M (Na,H)ClO_4 – n-heptane system, 25 °C) has also been investigated. For $2 < pH < 10$, other parameters kept constant, the distribution ratio is independent of pH. (The UV spectra of the two phases are constant). For the studied pH range no detectable dissociation of HDBPP occurs.

The hypothesis of extraction of $HClO_4$ by HDBPP as an explanation of the non-linearity of the curves D *vs.* [HDBPP] (Fig. 1) can be eliminated ($HClO_4$ extraction would only occur at lower pH).

pK_a *determination.* When pH is increased over 10, the UV spectra of the aqueous phases are progressively changed as an effect of HDBPP dissociation. Each spectrum can be decomposed into two spectra corresponding to HDBPP and $DBPP^-$ (Fig. 3). The UV spectrum of $DBPP^-$ has a broad adsorption band at 280 nm with an ε_{max} of 7000 M^{-1} cm^{-1}. If pH is adjusted back to $pH < 10$, the spectrum of undissociated HDBPP is quantitatively recovered which shows the reversibility of the dissociation and permits quantitatively measurements of aqueous $[HDBPP]_{tot}$.

The curve pH *vs.* $\log(K_d D^{-1} - 1)$ is given in Fig. 4. The observed slope of 1.03 is close to the theoretical value of 1. The pK_a-value from the intercept is 12.30 ± 0.03, which is higher than for most of the β-diketones (*e.g.* for acetylacetone).[13] Thus, HDBPP would be expected to act as a chelating

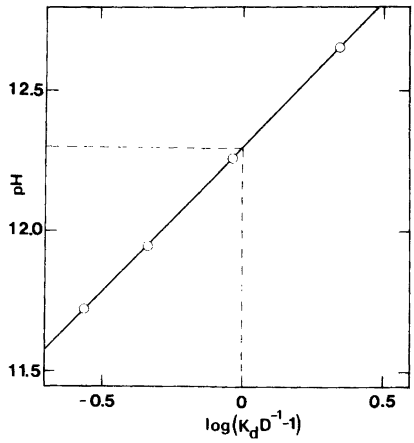

Fig. 4. Dissociation constant of HDBPP at 25 °C. (pH *vs.* $\log(K_d D^{-1} - 1)$. Aqueous phase: 1 M (Na,H)-ClO_4; organic phase n-heptane.

extractant in a higher pH-range than *e.g.* acetylacetone.

Temperature effects. From the temperature dependence of K_d and K_2 in the n-heptane system (*cf.* Table 1 and Fig. 2) and according to the relationship $\Delta G° = \Delta H° - T\Delta S° = -RT\ln K$, the following thermodynamic constants were calculated (25 °C):

Distribution: $\Delta H° = 16.8 \pm 1.2$ kJ/mol, $T\Delta S° = 25.2 \pm 1.2$ kJ/mol.

Dimerization: $\Delta H° = -11.8 \pm 1.0$ kJ/mol, $T\Delta S° = -6.6 \pm 1.0$ kJ/mol.

(The uncertainty in the K_3-values is too large to allow any calculation of $\Delta H°$- and $T\Delta S°$-values for the trimerization.) Thus, it is evident that a temperature increase favours a transfer of HDBPP from the aqueous phase to the n-heptane phase, which would be expected, considering the similarity with the β-diketones,[13] but disfavours the dimerization in the organic phase.

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