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Ultraviolet Absorption, Aqueous Solubility, and Octanol-Water Partition for Several Phthalates

F. Leyder and P. Boulanger

Department of Environmental Toxicology, University of Liege, Sart Tilman, Belgium

We drew our attention to phthalates when their toxicity became questioned since they are relatively resistant to biodegradation and probably accumulate in the environment.

Literature data on aqueous solubility and octanol-water partition are scarce and sometimes differ by several orders of magnitude (Table 1). Ultraviolet (UV) spectra of phthalates were mostly recorded using ethanol as solvent (Table 2).

In the course of a study on the physico-chemical properties of chemicals, we determined the above properties on eight phthalate (listed, along with their abbreviations, in Table 3).

MATERIALS AND METHODS

Reagents : Water was deionized and distilled from $KMnO_4$. The following reagents were used as received : n-hexane (Baker "Analyzed", 95%), dichloromethane (Aldrich, A.C.S. reagent 99.9 + %), 1-octanol (Merck, extra pure 97%), DMP (Fluka > 99%), DEP (Merck, 99%), D3P and D13P (Chrompack, stationary phases for gas chromatography), DBP (Fluka ≥98%), DIBP (BASF "Palatinol IC"), D5P (Kodak, practical grade > 90%) and DAP (CEPEA), BBP (Bayer Unimoll BB) and DEHP (Essochem DOP).

Apparatus : All UV measurements were made by using 1-cm cells in a Perkin-Elmer model 552 uv-Visible spectrophotometer.

Gas chromatography (GC) experiments were conducted on a Girdel type 3000 FFLE apparatus with flame-ionization detection. A 4 mm i.d. x 180 m stainless steel column packed with 3% OV-1 on 80-100 mesh Chromosorb W-AW-DMCS was used. The carrier gas was helium at a 20 mL/min flow rate. Teflon-lined silicone rubber septa (Microsep F-174) were used.

Procedures : OECD Guidelines for Testing of Chemicals (KAMLET 1960) were followed throughout this work : method 101 : UV-Visible absorption spectra; method 105 : water solubility;method

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Table 1 : Literature data on aqueous solubility and octanol-water partition of phthalates.

	Temperature (°C)	Aqueous Solubility			Calculated log p
		Original Units		µg/mL	
DMP	25	45000	ppm	45000	
	25	23.3	mM	4520	
		0.4	%	4000	2.34
		0.5	%w/w	5000	
DEP	25	1200	ppm	1200	
	25	4.6	mM	1020	
		0.1	%	1000	3.42
		0.1	%w/w	1000	
DBP	25	13	ppm	13	
	25	0.9	mM	25	
		0.013	%	130	5.38
		0.45	%w/w	4500	
DIBP		< 0.025	%	< 250	5.32
		0.01	%w/w	100	
DAP		0.01	%	100	2.72
		< 0.01	%w/w	< 100	
BBP		insoluble			
		insoluble			5.63
DEHP		0.01	%	100	
	20	< 0.01	%w/w	< 100	9.64

107 : partition coefficient (n-octanol/water). All experiments were conducted at 20 ± 1°C.

UV measurements were made either on aqueous solutions (diluted when necessary) or on octanolic solutions diluted with dichloromethane.

For GC determinations, samples were fortified with an internal standard, extracted as described by EPA Method 606 (PHILLIPS 1969), section 9, and concentrated to 1 mL of hexane solution. "Solvent flush" and "hot needle" injection techniques were used; the syringe was cleaned and dried after every injection. All separations were done isothermally. Peak heights were measured throughout.

Chromic acid was used for glassware cleaning.

Table 2 : Literature data on UV absorption of phthalates.

	Solvents.	Ref.	λ max nm (log ε)					
DMP	Isooctane	5	223.5	(3.93)				
	Ethanol	7	225	(3.87)				
	(a)	2	228	(4.0)	276	(3.2)	283	(3.1)
DEP	Ethanol	5			275	(3.08)		
	Ethanol	5	225	(3.9)	227	(3.7)s	275	(3.1)
	Ethanol	6	227	(3.9)			275	(3.1
	(a)	2	228	(3.9)	276	(3.1)	283	(3.1)
DBP	Ethanol	5			275	(3.09)		
	Ethanol	5	228	(3.9)	276	(3.1)	283	(3.1)s
	Ethanol	6	226	(3.98)	272	(3.18)		
	(a)	2	228	(4.0)	276	(3.2)	283	(3.1)

(a) : 50:50 ethanol-water

Table 3 : Aqueous solubility and octanol-water partition of phthalates at 20°C (Alkyl groupes are n-alkyl unless specified).

	1,2-Benzenedicarboxylic acid-ester	Aqueous solubility mol/L	µg/mL	log p
DMP	Dimethyl	$2.21.10^{-2}$	4290	1.53
DEP	Diethyl	$4.18.10^{-3}$	928	2.35
DI3P	Diisopropyl(a)	$1.33.10^{-3}$	332	2.83
D3P	Dipropyl	$4.32.10^{-4}$	108	3.27
DIBP	Diisobutyl(a)	$7.30.10^{-5}$	20.3	4.11
DBP	Dibutyl	$3.63.10^{-5}$	10.1	4.57
D5P	Dipentyl	$0.3\text{-}2.6.10^{-6}$	0.1-0.8(b)	4.85
DAP	Diallyl(a)	$7.39.10^{-4}$	182	3.23
BBP	Butyl benzyl(a)	$9.02.10^{-6}$	2.82	4.91
DEHP	Diethylhexyl(a)	$1.05.10^{-7}$	0.041	

a : Chemical Abstract Service index names are : bis(1-methylethyl), bis(2-methylpropyl), di-2-propenyl, butylphenylmethyl and bis(2-ethylhexyl).

b : The lowest value was determined by GC and the highest using UV spectrophotometry.

RESULTS AND DISCUSSION

UV absorption spectra of aqueous solutions of all phthalates studied coincided within experimental errors (Fig.1). The absorption coefficients (Table 4) somewhat differ from those previously reported in ethanol or ethanol-water mixtures; we indeed observed that adding as little as 5 volume % ethanol to aqueous

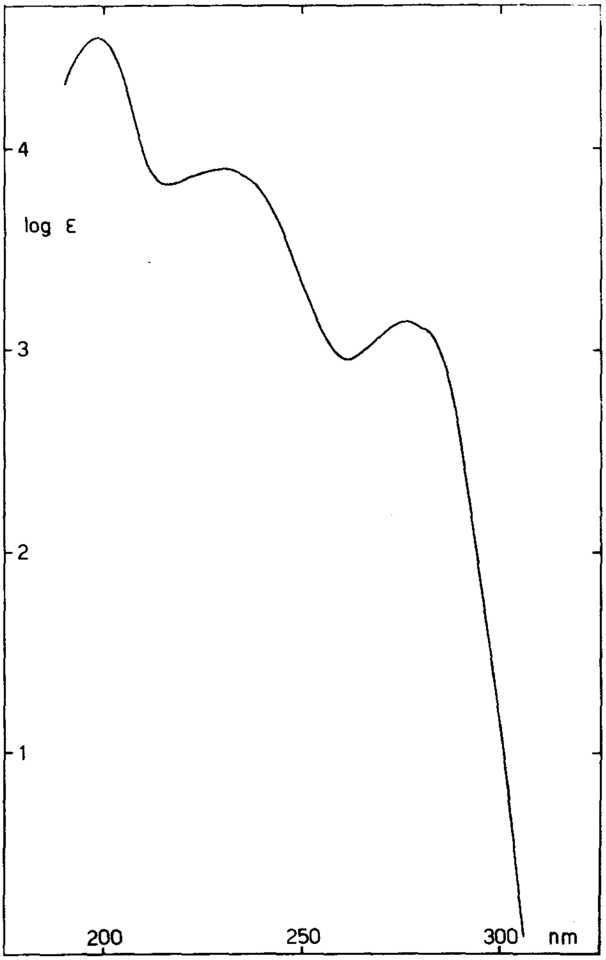

Fig. 1 : UV absorption spectrum of dialkylphthalates.

Table 4 : UV absorption of phthalates.

λ maximum (nm)	log ε
198.5	4.54
229.5	3.90
275.5	3.14
281 s	3.1
± 0.5	± 0.01

phthalate solutions lowered UV absorption at 275.5 and 229.5 nm (log ε for DEP = 3.08 and 3.88, respectively). The absorption maximum at 198.5 nm had not been previously reported. In 1:99 octanol-dichloromethane solutions, log ε was found equal to 3.09 for DMP at 275.5 nm.

Aqueous solubility and octanol-water partition data are listed in Table 3. The values reported for D5P are to be taken with caution; the use of technical grade D5P probably explains why the aqueous solubility seems to depend on the analytical technique used, and why the dispersion of experimental partition coefficients is greater than allowed. The data for all other phthalates studied are linearly related (Fig.2) following the equation

$$\log p = -1.02 \log S - 0.08$$

obtained with a least-squares fit.

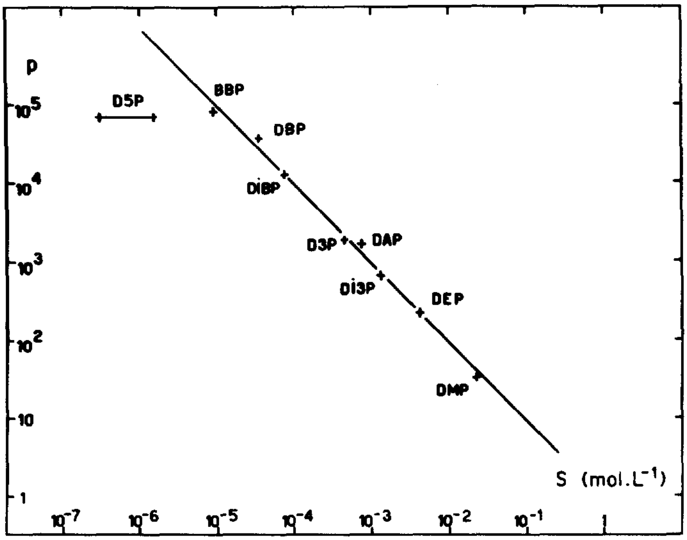

Fig. 2 : Correlation between the logarithm of the aqueous solubility (mol/L and the logarithm of the octanol-water partition coefficient.

LEO et al. defined the substituent constant Π as the influence of a substitution on the value of log p for a substance. Although the average value of Π (CH_2) (Table 5) is in accordance with average values calculated by LEO et al., a significant increase in Π (CH_2) values is observed as one ascends the homologous series of phthalates (Table 5); it is probably due to the shielding of lone-pair electrons by the inert alkyl groups when the aliphatic chain becomes long enough. The influence of branching in the phthalate system ($\Delta \Pi = -0.22$ and -0.23, respectively, for dipropyl and dibutyl esters) is in accordance with the average value of 0-20 proposed by LEO et al.

Table 5 : Evolution of Π for - CH_3

$$\Pi\ (CH_2) = 1/2\ (\log p_{DEP} - \log p_{DMP}) = 0.41$$
$$\Pi\ (CH_2) = 1/2\ (\log p_{D3P} - \log p_{DEP}) = 0.46$$
$$\Pi\ (CH_2) = 1/2\ (\log p_{DEP} - \log p_{D3P}) = 0.65$$

$$\text{average}\ \Pi\ (CH_2) = 1/6\ (\log p_{DBP} - \log p_{DMP}) = 0.51$$

Extrapolation of our measurements to DEHP (*bis*(2-methylhexyl)phthalate), one of the most frequently used plasticizers, is unfortunately not possible without further experiments. We are considering partition coefficients determinations using octanol and a solvent less polar than water.

Environmental studies of phthalates require accurate data concerning their physico-chemical behaviour. It is hoped that the data reported here, although limited to light phthalates, will be of some help.

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