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Solvent Extraction of Picric Acid from Aqueous Solutions

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4-Methyl-2-pentanone, 2-methylpropyl ethanoate, and diisopropyl ether have been evaluated as solvents for extraction of picric acid from water or solutions containing $(NH_4)_2SO_4$, Na_2SO_4 and NH_4NO_3. Equilibrium distribution coefficients (K_d) have been measured at 303.15 K and pH = 3. The highest values of K_d were obtained with 4-methyl-2-pentanone; with 2-methylpropyl ethanoate the values of K_d were slightly lower, and with diisopropyl ether the values of K_d were extremely small. It was also verified that the ammonium nitrate increases the extraction yield (salting out effect) while the sulfates have an irregular behavior and may hinder the extraction.

Introduction

Picric acid (2,4,6-trinitrophenol) is usually a byproduct of the nitration of benzene (mononitrobenzene production). The caustic wash of the crude mononitrobenzene to remove traces of sulfuric and nitric acids produces an aqueous stream which contains sodium (or ammonium) nitrates and sulfates, sodium (or ammonium) trinitrophenolate, and traces of dinitrophenolates and mononitrobenzene.

In the past, picric acid was frequently used as a military explosive. Today, this acid is only employed in the production of fungicides and its demand is small. Because picric acid is a hazardous species, it must be removed from streams and incinerated or buried.

Treatment of effluents containing picric acid is carried out in two stages. First, nitric or sulfuric acids are added to transform the trinitrophenolates into trinitrophenol (picric acid). The low solubility of the acid form allows the separation of almost all the picric acid as a solid phase, thus reducing the concentration of this pollutant in the aqueous solution. After separation of the solid phase, the remaining picric acid is extracted with an appropriate solvent.

References in the literature concerning picric acid extraction are scarce. Therefore, in this work we investigated the potential use of several solvents usually employed in the extraction of phenol and its derivatives from aqueous solutions: 4-methyl-2-pentanone (methyl isobutyl ketone), 2-methylpropyl ethanoate (isobutyl acetate), and diisopropyl ether (Gravalle and Panaylotou, 1980; Greminger *et* ., 1982; Bízek *et al*., 1992, 1993; Korenman *et al*., 1991a, 1991b). The influence of some inorganic salts (ammonium nitrate, ammonium sulfate, and sodium sulfate) upon this extraction was also studied.

Experimental Section

Organic chemicals were purchased from Fluka: picric acid (purum 98%, with 40% water), 4-methyl-2-pentanone (puriss 99%), 2-methylpropyl ethanoate (puriss 99%), and diisopropyl ether (purum 99%) and the inorganic p.a. salts ($(NH_4)_2SO_4$, Na_2SO_4, and NH_4NO_3) were used as supplied by the manufacturers. Twice-distilled deionized water was used in all the experiments.

The aqueous phase (water, picric acid, and salts), previously saturated with solvent, and the solvent, already saturated with water, were weighed and equilibrated in a sealed cell of 100 mL capacity, equipped with a water-jacket and a lateral port, held in a constant-temperature bath within ±0.2 K of the selected temperature of 303.15 K. The systems were brought to equilibrium by gentle agitation with Teflon-coated magnetic stirrers. After 2 h of agitation, the mixture was allowed a period of 4 h for phase separation. Known volumes of samples from the aqueous phase were then withdrawn through the lateral port and analyzed.

The picric acid content in the initial aqueous phase and in the samples was obtained by HPLC using a Varian Series 1400 chromatograph, equipped with a UV detector. A mixture of water and methanol (50 mass %) was used as the mobile phase at 1 cm^3/min with a pressure of 78 bar. The accuracy of this analysis was ±2 ppm of picric acid, which corresponds to an error of 0.02−0.6%. The salt content was confirmed by ionic chromatography using Dionex DX-100 equipment. Sodium carbonate and bicarbonate solutions were used as the mobile phase at 2 cm^3/min with a pressure of 137.9 bar and a nitrogen pressure of 34.5 kPa.

Due to its explosive properties, the picric acid is supplied as an aqueous suspension. This fact hinders the preparation of organic standards for calibrations and consequently the direct analysis of the picric acid in the organic phase. Therefore, the concentration of picric acid in this phase was obtained by mass balance by assuming that, in both phases, the mass of water, organic solvent, and salts remained unchanged during the mass transfer of picric acid between phases.

Results and Discussion

The experimental values of the organic and aqueous phases concentrations are summarized in Table 1 and Figure 1, together with the calculated values of K_d (distribution coefficient of the picric acid between organic and aqueous phases, in mass fractions).

These data show that 4-methyl-2-pentanone and 2-methylpropyl ethanoate are adequate solvents for picric acid extraction, although 4-methyl-2-pentanone appears to be slightly better than 2-methylpropyl ethanoate. The experimental results obtained with diisopropyl ether preclude the use of this solvent for the picric acid extraction.

The large increase of the distribution coefficient, K_d, when the picric acid concentrations in the aqueous and organic phases increase agrees with previous results on the picric acid extraction with benzene, chlorobenzene, toluene, and diethyl ether (Urbánski, 1964). Except for diisopropyl ether, the experimental results can be correlated by the

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Table 1. Picric Acid Extraction with 4-Methyl-2-pentanone, 2-Methylpropyl Ethanoate, and Diisopropyl Ether at 303.15 K[a]

solvent	*R* (g/g)	$100w_1$ (aq)	$100w_1$ (org)	K_d
4-methyl-2-pentanone	19.885	0.0348	0.0523	1.503
(methyl isobutyl ketone)	10.620	0.0374	0.0915	2.447
	5.037	0.0577	0.1887	3.270
	2.026	0.1014	0.4779	4.713
	1.011	0.1377	0.8493	6.168
	0.505	0.1934	1.5913	8.228
	0.201	0.3262	3.5931	11.015
	0.101	0.4704	6.6181	14.069
	0.051	0.5476	9.3909	17.149
diisopropyl ether	9.703	0.2766	0.0821	0.297
	4.988	0.3460	0.1456	0.421
	1.990	0.5194	0.2767	0.533
	1.004	0.6493	0.4174	0.643
	0.505	0.7212	0.6839	0.948
	0.203	0.8942	0.8413	0.941
	0.206	0.8942	0.827	0.925
	0.104	0.9284	1.0994	1.184
2-methylpropyl ethanoate	20.215	0.0484	0.0507	1.048
(isobutyl acetate)	10.030	0.0636	0.0932	1.465
	5.013	0.0874	0.1837	2.102
	2.031	0.1285	0.4636	3.608
	1.011	0.1958	0.8612	4.398
	0.505	0.2446	1.4821	6.059
	0.205	0.3718	2.9837	8.025
	0.102	0.4988	5.3042	10.634
	0.0498	0.6462	7.8457	12.141

R is the final mass proportion between organic and aqueous phases. w_1 is the mass fraction of picric acid.

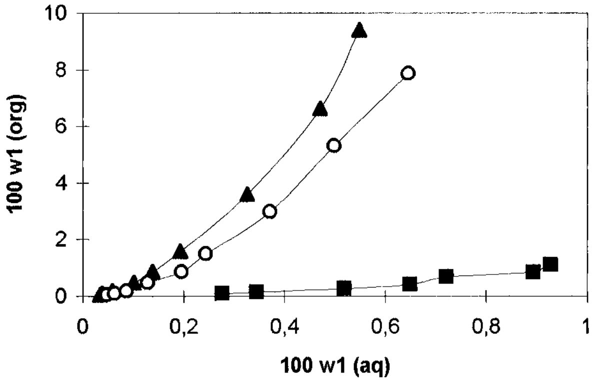

Figure 1. Picric acid extraction with 4-methyl-2-pentanone, 2-methylpropyl ethanoate, and diisopropyl ether at 303.15 K: (▲) 4-methyl-2-pentanone; (○) 2-methylpropyl ethanoate; (■) diisopropyl ether. w_1 is the mass fraction of picric acid.

equation

$$k = \frac{(100w_{\mathrm{aq}})^n}{(100w_{\mathrm{org}})^n} \tag{1}$$

where w_{org} and w_{aq} are the mass fraction of picric acid in the organic and aqueous phase, respectively, *k* is a pseudodistribution coefficient, and *n* is a constant independent of temperature. The values of *k* and *n* are summarized in Table 2.

However, for industrial purposes, solvents must have not only good extraction properties (high K_d values) but also a very low solubility in water. In this case, 2-methylpropyl ethanoate, with a solubility of 0.6 g/100 g in water (Perry and Green, 1984), is a better choice as solvent for picric acid extraction than 4-methyl-2-pentanone, with a solubility in water of 1.7 mass % (Weissberger and Proskauer, 1955). Therefore, 2-methylpropyl ethanoate was selected for further experiments in the presence of inorganic salts.

Table 2. Pseudodistribution Coefficient, *k*, Constant, *n*, Temperature, *T* (K), and Correlation Coefficient, CC, for Picric Acid Extraction with Several Organic Solvents

solvent	10^2k	*n*	*T* (K)	CC
4-methyl-2-pentanone	3.599	1.853	303.15	0.9977
diisopropyl ether	87.63	2.156	303.15	0.9598
2-methylpropyl ethanoate without salts	5.989	1.679	303.15	0.9988
in the presence of NH_4NO_3	14.684	1.259	303.15	0.9995
in the presence of Na_2SO_4	23.618	1.460	303.15	>0.9999
in the presence of $(NH_4)_2SO_4$	24.948	1.383	303.15	0.9999
benzene (Urbánski, 1964)	1.892	1.727	303.15	
chlorobenzene (Urbánski, 1964)	2.965	1.674	313.15	
toluene (Urbánski, 1964)	2.323	1.667	313.15	

Table 3. Picric Acid Extraction with 2-Methylpropyl Ethanoate in the Presence of Salts at 303.15 K[a]

without salts				with Na_2SO_4			
R (g/g)	$100w_1$ (aq)	$100w_1$ (org)	K_d	*R* (g/g)	$100w_1$ (aq)	$100w_1$ (org)	K_d
20.215	0.0484	0.0507	1.048	10.038	0.0666	0.1	1.502
10.030	0.0636	0.0932	1.465	4.925	0.1136	0.195	1.717
5.013	0.0874	0.1837	2.102	1.975	0.2027	0.431	2.126
2.031	0.1285	0.4636	3.608	1.005	0.3023	0.757	2.504
1.011	0.1958	0.8612	4.398				

with $(NH_4)_2SO_4$				with NH_4NO_3			
R (g/g)	$100w_1$ (aq)	$100w_1$ (org)	K_d	*R* (g/g)	$100w_1$ (aq)	$100w_1$ (org)	K_d
10.038	0.057	0.1013	1.777	10.038	0.0383	0.1031	2.692
4.925	0.105	0.1964	1.870	5.000	0.0667	0.2012	3.016
2.012	0.1948	0.4432	2.275	2.022	0.121	0.4693	3.879
1.011	0.2963	0.7677	2.591	1.005	0.197	0.8653	4.392

[a] *R* is the final mass proportion between organic and aqueous phases. w_1 is the mass fraction of picric acid.

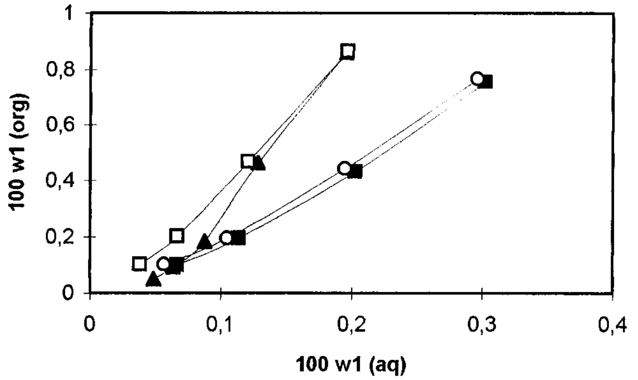

Figure 2. Picric acid extraction with 2-methylpropyl ethanoate in the presence of salts at 303.15 K: (▲) without salts; (□) with NH_4NO_3; (■) with Na_2SO_4; (○) with $(NH_4)_2SO_4$. w_1 is the mass fraction of picric acid.

The salts tested were ammonium nitrate and ammonium and sodium sulfates which are the most common inorganic in the effluents containing picric acid or trinitrophenolates. The salt concentrations in the aqueous phase were kept constant at 1 mass %. The results are summarized in Table 3 and Figure 2.

The results obtained with ammonium nitrate were expected. Even for low concentrations of picric acid in the organic phase, the presence of the ammonium nitrate increases the extraction yield due to the salting out effect. High concentrations of ammonium nitrate do not affect the extraction because the salting out effect is not important due to a high level of water free molecules.

In the presence of sulfates, it was observed that for low concentrations of picric acid in the organic phase, these salts provide an extraction yield slightly lower than obtained with ammonium nitrate, although higher than when the sulfates are not present. The efficiency enhancement due to the presence of nitrates when compared with sulfates agrees with Koremann *et al.* (1991a, 1991b). On the other hand, the efficiency increase observed when sulfates are added to pure water, is mainly due to salting out.

For high concentrations of picric acid in the organic phase (low values of the organic phase/aqueous phase) the sulfates produce anomalous and unexpected results, as the extraction efficiency is always reduced (lower K_d values). A possible explanation for this behavior relates the acid–base interaction between the ion sulfate (electron donor, Lewis base) and the molecule of picric acid by means of the OH group (electron acceptor, Lewis acid). This interaction allows us to stabilize the picric acid in the aqueous phase, thus increasing the difficulty of the extraction.

Almost identical curves were obtained in the presence of sodium and ammonium sulfates, the cations nature having a small effect in the extraction. However, the ammonium ion provides a slightly superior extraction than the one obtained with the sodium ion.

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