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THE SEPARATION OF MIXTURES OF MONO AND DI SUBSTITUTED ALKYL PHOSPHORIC ACIDS

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A number of alkyl phosphoric acids are available commercially, but only as mixtures of the mono- (H_2RPO_4) and di- (HR_2PO_4) substituted forms. For many purposes, it is desirable to use one or the other of these acids in a separated state. It has been found that this may be readily accomplished by taking advantage of the differences in the distribution of the two forms between two immiscible phases, generally water and some organic solvent. In this latter case, the di-substituted acid favors the organic phase, whereas the mono substituted compound shows more affinity for the aqueous layer. By choosing the appropriate solvent, it is then possible to water wash all of the H_2RPO_4 out of the organic layer by a series of batch extractions, leaving only the HR_2PO_4; and, conversely, similarly to solvent-wash all the di- form away from the mono- form, leaving the latter in a water solution. In the case of the octyl phosphoric acids it was found that the substitution of diethylene glycol for the water phase eliminated difficulty with emulsions and gave distribution coefficients of the right order of magnitude to give satisfactory separation of the two forms.

The distribution of the acids was followed by titrating aliquots of the phases potentiometrically with standardized base, using a Beckman Type G glass electrode pH Meter. It was assumed throughout that no free phosphoric acid was present, so that the difference in titre between the two breaks of the curve could be taken to represent the amount of H_2RPO_4 present, and the difference between this quantity and the titre to the first break to represent the HR_2PO_4. Using this method, the values

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shown in Table I were obtained for the acid strengths of the commercial mixtures as purchased. The distribution coefficients of the acids between the various pairs of immiscible phases were then similarly obtained, and these are summarized in Table II. For batch type washing, the most satisfactory separation is obtained when the HR_2PO_4 distribution coefficient is greater than 5, coupled with a corresponding E value of less than 1 for the H_2RPO_4 form. The use of counter current column extraction techniques, however, should make separations feasible as long as the two E values differ by a factor of three or more.

Table I

Composition of Commercial Alkyl Phosphoric Acids

Acid	Source	Concentrations H_2RPO_4	Concentrations HR_2PO_4
Ethyl Phosphoric	Eastman	4.66M	4.36M
n-propyl Phosphoric	"	4.36	3.15
n-butyl Phosphoric	"	3.82	2.48
Isobutyl Phosphoric	Monsanto	3.57	2.56
n-amyl Phosphoric	"	3.48	1.81
n-octyl Phosphric	"	2.01	1.75

Table II

Distribution of Acids Between Immiscible Phases

Phosphoric Acid	Distribution Coefficient (E) into Solvents from Water: Solvent	$E_{H_2RPO_4}$	$E_{HR_2PO_4}$
Ethyl	n-primary amyl alcohol	0.69	1.7
	Dibutyl carbitol	0.14	0.51
n-propyl	n-primary amyl alcohol	0.86	5.4
	Dibutyl carbitol	1.4	1.2
n-butyl	n-primary amyl alcohol	2.9	>1000?
	Dibutyl carbitol	2.1	39
	Dibutyl ether	0.66	15
Isobutyl	Dibutyl ether	0.54	11

Table II - continued

n-amyl	Dibutyl ether	0.72	6.2
n-octyl	Diethyl ether	42	~760
	Methyl isobutyl ketone	28	~106
n-octyl	Dibutyl ether	0.44*	7.0*

*Out of diethylene glycol rather than water

Using this technique, completely separated solutions of di-ethyl phosphoric acid in n-amyl alcohol, di-propyl phosphoric acid in isopropyl and dibutyl ethers, di-butyl phosphoric acid in n-amyl alcohol and in dibutyl ether, di-isobutyl phosphoric acid in dibutyl ether, di-amyl phosphoric acid in dibutyl ether, di-octyl phosphoric acid in dibutyl ether and mono-butyl phosphoric acid in water have all been prepared.