dn/dc of DNA on wavelength except for the considerably higher value found at 435.8 nm than at the other wavelengths studied.

The value at 632.8 nm is slightly higher than that at 589.3 nm, opposite to the behavior found in solutions of polystyrene in toluene, where the value decreased monotonically with increasing wavelength. Likewise in the case of the other aqueous solutions (BSA, GPDH, amylopectin), the value of the specific refractive increment at 632.8 nm was either the same or slightly higher than that at 589.3 nm. This is contrary to the usual decrease in refractive index with increasing wavelength, described for pure substances empirically by the Cauchy equation (*3*). This effect, which was observed with all the aqueous solutions, may quite possibly be due to the 940.0- and 820.0-nm absorption bands of water (*13*) in the near infrared, which are not far removed from the longest wavelength at which refractive index measurements were made.

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Liquid-Liquid Distribution. Tributyl Phosphate Between Immiscible Solvents

Willis H. Baldwin[1] **and Cecil E. Higgins**
Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830

The extractability of tributyl phosphate from diluents by polar solvents, immiscible with the diluent, was measured at 25°. Distribution coefficients >1 resulted when using dipropylene glycol, methyl carbitol, and 1,2-propanediol with hexane as the diluent for the tributyl phosphate. 1,2-Propanediol extracted more tributyl phosphate from kerosine (Amsco 125–82), tri-*n*-butylamine, and petroleum ether than from hexane. The tributyl phosphate concentration had little effect on the distribution coefficients until enough was present to make the three components miscible.

Tributyl phosphate (TBP), in a hydrocarbon diluent, is an important and useful solvent for the separation and purification of electrolytes in nuclear energy technology. Because the purification or analysis of contaminated solvent mixtures may involve the separation of TBP from its diluent, this work was undertaken to demonstrate TBP's extractability from various diluents. The analysis of solutions was simplified by the use of ^{32}P-labeled TBP (*5*).

The hydrogen bonding ability of TBP (*10*) and related compounds (*13, 16*) suggested the possibility of removing the TBP by using polar solvents (*1*). Significant TBP extraction by polar compounds has been noted by several investigators (*1, 3, 4, 9, 11, 12, 14*). No data, however, other than ours in an institutional document (*1*), apparently have been published except those showing the small amount of TBP extracted by alkaline ethylene glycol (*3*) and by ethanolamine (*3, 4*). Therefore, this summary covering the distribution of P in a wide variety of immiscible solvent mixtures is presented.

Experimental

Phosphorus-32-labeled tributyl phosphate (TBP-^{32}P) was prepared by using the ester interchange method (*5*). The distilled product (118°C at 1 torr) was treated with 1*M* NaOH and several water washes before being dried in vacuo (1 torr at room temperature for several hours). Its specific activity decreased from 5×10^3 d/m/mg TBP-^{32}P to 1.2×10^3 d/m/mg TBP-^{32}P during the course of the study.

The glycol solvents, purified by distillation, were vacuum dried at 1 torr for at least 2 hr at room temperature just prior to their use. The kerosine (Amsco 125-82), hexane, and petroleum ether were used as received since they were mixtures of hydrocarbons. Dibutyl ether was distilled before use; the remaining solvents were used as received.

Distribution measurements were made in 15-ml, glass-stoppered graduated centrifuge cones. Five-ml portions of each solvent were pipeted into the cone, and 0.050 ml of TBP-^{32}P was added. The cones were stoppered and tum-

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[1] To whom correspondence should be addressed.

bled end over end for at least 30 min at 25°C. At the end of this time, the tubes were centrifuged for 30 sec (long enough to produce gross separation but not long enough to cause heating of the mixture) (*6*). Any volume change in each phase was noted. The tubes were then kept in the bath at 25°C for at least 2 hr. Aliquots were removed from each phase and counted as previously described (*7*). The average material balance on the TBP-^{32}P from all tests was 101%; the highest was 106% and the lowest, 97%.

The distribution coefficient (K_d) in each immiscible solvent pair was the ratio of the TBP-^{32}P activity per ml in the polar phase to that in the diluent. K_d was usually obtained from one sample equilibration; replicate counts, however, were made on each phase. Duplicate sample distributions of TBP between 1,2-propanediol and hexane showed that the distribution coefficients were precise within ±3%.

Results and Discussion

Tests of the distribution of TBP between 1,2-propanediol and diluents having low miscibility with propanediol are summarized in Table I. Distribution coefficients greater than one were observed when hydrocarbons and tributyl amine were the diluents. In the aromatic solvents and some others, the K_d's were less than one; i.e., TBP preferred the other phase to the 1,2-propanediol phase.

The observed decrease in the volume of the benzene phase corresponds to 18 wt % of benzene in the glycol. This is in good agreement with the solubility of benzene in propylene glycol reported by Palit and McBain (*15*) (i.e., 17.3% at 20°C and 19.9% at 35.6°C).

A number of other hydroxylated solvents were equilibrated with hexane solutions of tributyl phosphate (Table II). TBP was extracted most by those hydroxylated solvents that dissolved the most hexane.

Hydroxylated solvents were selected to interact as Lewis-type acids with tributyl phosphate, which is a Lewis-type base. A number of interactions of TBP with electrolytes (Lewis-type acids) have been studied by distribution measurements and reported by Baldwin et al. (*2*) and Higgins et al. (*8*).

The structure of the hydroxylated solvent had a great influence on the observed distribution coefficient. For example, with 1,2-propanediol the distribution coefficient was greater than twice that using 1,3-propanediol (trimethylene glycol, Table II). Altogether, a wide range of distribution coefficients is available.

1,2-Propanediol extracted the most TBP from Amsco 125-82 (Tables I and III). The highest K_d observed was 2.7 when the glycol was contacted with 0.7*M* TBP in the kerosine (Table III). By comparison, ethanolamine gave a K_d (ethanolamine/kerosine) of only ~0.1 when contacted with an equal volume of 0.5*M* TBP in Amsco 125-82 (*4*). Ethylene glycol containing sodium hydroxide extracted even less TBP (*3*).

Tributyl phosphate concentration affected the distribution coefficients very little until enough TBP was present in hexane and CCl_4 to homogenize those systems (Table III). The distribution coefficients varied only 20–25% for the three TBP concentrations in hexane and Amsco 125-82 shown in Table III.

The effect of the phosphorus compound itself on the observed distribution coefficient was tested by equilibrating equimolar (0.04*M*) solutions of tributyl phosphine oxide, tributyl phosphate, and tri-*n*-octyl phosphine oxide in hexane with ethylene glycol. The observed distribution coefficients (glycol/hexane) were 8.54, 0.14, and 0.006, respectively. The compounds of higher molecular weight were found in the hexane, preferentially.

Table I. Distribution of Tributyl Phosphate Between 1,2-Propanediol and Diluents at 25°C

	Equil concn TBP in diluent, *M*	Change in vol of diluent phase, %	Distribution coeff, K_d[a]
Kerosine (Amsco 125-82)	0.011	0	2.4
Tri-*n*-butyl amine	0.014	−4	1.7
Petroleum ether	0.015	−8	1.5
Hexane	0.017	−8	1.2
Dibutyl ether	0.024	−8	0.60
Nitrobenzene	0.027	−18	0.47
Di-*n*-butyl carbonate	0.026	−4	0.44
Tetralin	0.027	−6	0.42
Diphenyl ether	0.029	−2	0.35
Carbon tetrachloride	0.031	−20	0.31
Benzene	0.032	−26	0.30

[a] K_d = amount of TBP per ml of 1,2-propanediol phase/amount of TBP per ml in diluent phase.

Table II. Distribution of Tributyl Phosphate Between Hydroxylated Solvents and Hexane at 25°C

Hydroxylated solvent	Equil concn TBP in hexane, *M*	Change in vol of hexane phase, %	Distribution coeff, K_d[a]
Dipropylene glycol	0.012	−26	1.9
Methyl carbitol	0.012	−20	1.9
1,2-Propanediol	0.017	−8	1.2
Carbowax 550	0.019	−14	0.90
β,β'-Dihydroxydiethyl sulfide	0.021	−2	0.77
Carbowax 400	0.023	−8	0.64
Triethylene glycol	0.024	−4	0.52
Trimethylene glycol	0.024	0	0.51
Diethylene glycol	0.025	−2	0.48
Ethylene glycol	0.032	0	0.14
Diethanolamine	0.034	0	0.08
Ethanolamine	0.036	−1	0.06

[a] K_d = concentration of TBP in hydroxylated solvent/concentration of TBP in hexane.

Table III. Distribution of Tributyl Phosphate at Different Concentrations Between 1,2-Propanediol and Diluents at 25°C

Diluent	TBP concn in diluent		K_d, 1,2-propanediol/diluent
	Before equil	After equil	
Amsco 125-82	0.036[a]	0.011	2.4
	0.73[b]	0.22	2.7
	1.8[c]	0.65	2.2
Hexane	0.036[a]	0.017	1.2
	0.73[b]	0.43	1.0
	1.2[d]	0.76	1.0
	1.8[c]		Miscible
CCl_4	0.036[a]	0.031	0.31
	0.73[b]	0.58	0.54
	1.8[c]		Miscible

[a] TBP, 0.050 ml, added to 5.0 ml diluent, contacted with 5.0 ml 1,2-propanediol. [b] TBP, 1.00 ml, added to 4.0 ml diluent, contacted with 4.0 ml 1,2-propanediol. [c] TBP, 5.00 ml, added to 5.0 ml diluent, contacted with 5.0 ml 1,2-propanediol. [d] TBP, 2.00 ml, added to 4.0 ml diluent, contacted with 4.0 ml 1,2-propanediol.

The various degrees of competitive interactions are reflected in the observed distribution coefficients. The wide range covered indicates several possibilities for the purification of tributyl phosphate solvents by solvent extraction of tributyl phosphate itself. From the data in Table III, it is apparent that 1,2-propanediol effectively extracted TBP from kerosine solution. The comparison of dipropylene glycol and methyl carbitol with 1,2-propanediol (Table II) suggests they should extract P from kerosine even more efficiently than does 1,2-propanediol.

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Liquid-Liquid Equilibrium of System Acetic Acid-Water-4-Methyl-2-pentanone

Larry W. Fish, Jeffery E. Errico, C. Jim Lim, and Stuart D. Cavers[1]
Department of Chemical Engineering, The University of British Columbia, Vancouver 8, B.C., Canada

Measurements are made of the equilibrium partition of acetic acid between water and 4-methyl-2-pentanone. The effect of temperature and sodium chloride concentration is determined. Densities are reported for the equilibrium phases without sodium chloride present.

In liquid-liquid extraction research in spray columns (*3*), the authors have been concerned with evaluating the quantity $(C_k^* - C_k)$, the overall driving force for mass transfer at a particular elevation in the column. To evaluate this quantity, it is necessary to calculate what the solute concentration would be in a ketone phase at equilibrium with the water phase. In other words, it is necessary to have, at hand, information as to the equilibrium partition of solute between coexisting phases. For many of the operating conditions studied, the difference $(C_k^* - C_k)$ is fairly small. It is therefore important to know C_k^* quite accurately.

The 4-methyl-2-pentanone–acetic acid–water system was of particular interest to the authors. (4-Methyl-2-pentanone frequently is referred to as methyl isobutyl ketone.) For the sake of brevity, this ketone is designated as 4M2P in the present paper.

Some values of equilibrium concentrations for the system mentioned were reported earlier (*1, 2, 4, 6, 10–12*). However, in no case are there more than a dozen or so paired values available from any one investigation. In the present study, results from a total of 139 additional equilibrium determinations are reported.

Furthermore, to permit conversion between volumetric concentration units and mass fractions, the density of each of the equilibrium phases has been determined as a function of acetic acid concentration. Measurements of the concentration of water dissolved in 4M2P phases and of the concentration of 4M2P dissolved in water phases have not been made in the present work. To convert the present results to a mole fraction basis, such information would be required, and this is available, for example, at 22°C (*10*) and at 25°C (*6*).

Sodium chloride has been used as a tracer in determining axial mixing coefficients in the continuous phase of spray columns (*5*). It is practically insoluble in the 4M2P phase, the partition coefficient, defined as the ratio of μg/ml of sodium chloride in the water phase to the same in the ketone phase, being of the order of 10,000 when the concentration of acetic acid in the water phase is 1.0 kg mol/m^3 (*8*). In carrying out experiments in which acetic acid was transferred and tracer was used simultaneously, it was important to know whether the equilibrium partition of acetic acid was affected by the presence of sodium chloride (*8*). Therefore, the effect of the tracer on the acetic acid equilibrium was studied in the present investigation.

Experimental

A typical procedure used in the partition studies was as follows. Mixtures containing approximately 100 ml of distilled water, 100 ml of 4M2P, and various amounts of acetic acid were immersed in flasks in a constant-temperature water bath for at least 8 hr. The mixtures were shaken by hand from time to time during this period to ensure that equilibrium was attained. Aliquots of each phase were titrated separately with standard carbonate-free sodium hydroxide solution to a phenolphthalein end point. Blank corrections were applied, although these were small.

To ensure the existence of only one phase during titration of the ketone-rich phase, it was convenient to add SDAG-1K beforehand (*1, 3, 14*). (In some of the work, this was added prior to titration of the water phase as well. SDAG-1K is a mixture of 100 parts by volume ethyl alcohol and five parts by volume methyl alcohol.) Reagent grade acetic acid and technical grade 4M2P were used to duplicate as nearly as possible the conditions of the spray column experiments (*3*) referred to earlier.

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[1] To whom correspondence should be addressed.