TABLE I

LINEAR EXTRAPOLATION DISTANCE, d, AS A FUNCTION OF THE MEAN NUMBER OF SECONDARIES PER COLLISION, c, FOR THE SEMI-INFINITE HALFSPACE

c	d/λ_{tr}-Milne source	d/λ_{tr}-Constant source
0	1.000	∞
$\vdots$	$\vdots$	$\vdots$
0.5	0.920	3.602
0.6	0.875	2.272
0.7	0.830	1.610
0.8	0.787	1.219
0.9	0.747	0.959
1.0	0.710	0.710

TABLE II

LINEAR EXTRAPOLATION DISTANCE, d, REQUIRED TO GIVE EXACT TRANSPORT LEAKAGE FROM A SEMI-INFINITE HALFSPACE WITH A SPATIALLY CONSTANT SOURCE

c	d/λ_{tr}; $D = 1/3\Sigma$	d/λ_{tr}; $D = (1 - c)/\nu^2\Sigma$
0.0	0.756	3.000
0.1	0.755	2.676
0.2	0.753	2.361
0.3	0.751	2.012
0.4	0.749	1.747
0.5	0.746	1.517
0.6	0.743	1.312
0.7	0.739	1.141
0.8	0.735	1.001
0.9	0.729	0.874
1.0	0.710	0.710

analysis to the diffusion theory result in terms of an unknown linear extrapolation distance, d. This equality can then be solved for d. Using this value of d to compute the thermal absorption of a control slab by diffusion theory will then give an exact transport result if the assembly is large and the slowing down source to the thermal group is spatially constant in the vicinity of the control element. If these two conditions are only approximately satisfied, as is the actual situation, one would still expect the result to be more accurate than that obtained using the Milne value for d.

The diffusion theory result for the leakage, L, from a semi-infinite halfspace with a spatially constant source of magnitude S and isotropic scattering is

$$L = \frac{S/\Sigma}{\sqrt{(1 - c)/D\Sigma} \, [1 + \sqrt{(1 - c)/D\Sigma} \, (\Sigma d)]}. \quad (6)$$

whereas the transport result for this problem is easily found from the analysis of Davison (3) to be

$$L = \frac{S}{\Sigma c}\left[\frac{1}{\nu} - I(c)\right], \quad (7)$$

where D is the diffusion coefficient and $I(c)$ is tabulated by Case et al. (1). Equating Eqs. (6) and (7) and solving for d gives[1]

$$\frac{d}{\lambda_{tr}} = \frac{c}{[(1/\nu) - I(c)][(1 - c)/D\Sigma]} - \frac{1}{\sqrt{(1 - c)/D\Sigma}}. \quad (8)$$

To use Eq. (8) to compute d, one must know D as a function of c. The two most widely used diffusion theories are classical (P-1) diffusion theory with $D = 1/3\Sigma$ and asymptotic (transport) diffusion theory with $D = (1 - c)/\nu^2\Sigma$. Table II gives numerical values of d as a function of c according to Eq. (8) for these two choices of D.

For $(1 - c) \ll 1$ and $D = 1/3\Sigma$, Eq. (8) can be expanded as

$$d/\lambda_{tr} = 0.7104[1 + 0.0926(1 - c)^{1/2} - 1.5573(1 - c) + 0(1 - c)^{3/2}]. \quad (9)$$

A similar expansion for $D = (1 - c)/\nu^2\Sigma$ yields

$$d/\lambda_{tr} = 0.7104[1 + 0.4178(1 - c)^{1/2} - 0.7573(1 - c) + 0(1 - c)^{3/2}]. \quad (10)$$

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G. C. POMRANING

General Electric Company
Atomic Power Equipment Department
Vallecitos Atomic Laboratory
Pleasanton, California

On the Existence of Tributyl Phosphate Monohydrate

Tributyl phosphate (TBP) has found wide utility in the processing of heavy metal ores and spent fuel elements by solvent extraction. Wallace Davis has reported a study of the nitric acid–TBP system in which equilibrium distribution data are used to obtain a quantitative description of the extraction process (1). In common with earlier work (cited in ref. 1), Davis' description assumes the existence of the complex TBP·H₂O. A second article by Davis (2a) expresses some doubt as to whether the complex is actually formed; a third article (2b) implies that free TBP and TBP·H₂O are simply not distinguishable thermodynamically (Equation 7).

Olander and Benedict have recently reported the use of mass transfer data on the TBP—H₂O system to indicate the nonexistence of TBP·H₂O (3). The latter authors compare the mass transfer rates of water entering the organic phase with "ordinary" systems in which they claim no complexing between water and solvent takes place. The "ordinary"

solvents are ethylacetate, furfural, chloroform, and isobutanol. Olander and Benedict conclude that no appreciable complexing takes place between TBP and H_2O but qualify their conclusion by stating that it is based on the assumption that water does not complex with the "ordinary" solvents.

The purpose of this note is to point out that (1) there is a fair amount of evidence that supports the existence of a $TBP \cdot H_2O$ complex and (2) each of Olander and Benedict's "ordinary" solvents may indeed complex with water.

If a $TBP \cdot H_2O$ complex does occur, the most reasonable configuration would be one in which a water proton is hydrogen bonded to the double-bonded oxygen atom of TBP, i.e.,

$$(C_4H_9O)_3P{=}O \cdots H{-}O{-}H$$
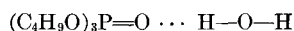
The ester oxygen atoms of TBP should also exhibit some basicity, but they are less accessible. The additional resonance structure for TBP,

$$(C_4H_9O)_3P^+{-}O^-$$
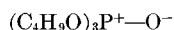
reinforces the selection of the site for proton attachment.

In addition to the work of Glueckauf (3), the evidence in favor of a $TBP \cdot H_2O$ complex is the following:

(a) Alcock et al. report that as water is added to TBP, the infrared peak due to the P=O group at 1283 cm^{-1} decreases and a new peak at 1267 cm^{-1} rises in its place (4). This shift is analogous to the shift in the carbonyl group frequency that is used to substantiate the presence of hydrogen bonded complexes (5).

(b) Geddes found the same shift in the isoamyl alcohol–TBP system and, in addition, a shift to higher energy for a band at 990 cm^{-1} which he assigned to the P—O—bond (6). Again, such a shift is consistent with the formation of a hydrogen bonded complex and is analogous to the increase in frequency observed in the C—C bond stretching frequency when acetone is complexed by water (5). Although isoamyl alcohol is not water, both are known to form hydrogen bonded complexes.

(c) The water proton resonance signal, extrapolated to an infinitely dilute solution of H_2O in TBP, is displaced to high field by 2 ppm relative to the proton signal from pure water (7). Cleavage of all the water-to-water bonds, as occurs at infinite dilution in a noncomplexing solvent or in water vapor, is accompanied by a high field shift of about 4.5 ppm. A shift less than the latter amount indicates the formation of new bonds, i.e., water to solvent bonds (7-9). That the extent of the "H-bond Shift" of the proton signal is related to the strength of the hydrogen bond has been shown qualitatively by Korinek and Schneider (8). According to a calculation (10), the strength of the $TBP \cdot H_2O$ bond indicated by the data of ref. 7 is approximately 5 kcal-mole^{-1}, or about the same as the strength of a single water-to-water bond.

(d) The viscosity of solutions of TBP and chloroform show a pronounced maximum at a molar ratio of 1:1, thus indicating a fairly strong, hydrogen bonded complex (11). While this observation does not prove a $TBP \cdot H_2O$ complex, water is probably a better proton donor in hydrogen bond formation than is chloroform. Viscosity studies of TBP and H_2O solutions could not be expected to yield similar information since the solubility of water in TBP is limited to a 1:1 molar ratio.

(e) The heat of solution of H_2O in TBP has been reported as -1.05 kcal-mole^{-1} (12). That the heat of solution is exothermic at all suggests a fairly stable complex since the heat of solution in this case is the sum of the enthalpy changes for making the TBP to H_2O bonds and breaking the H_2O to H_2O bonds. Pimentel and McClellan cite a number of parallel cases of hydrogen bond formation in which the heat of solution is actually endothermic (13). Although it is unquestionably true that the $TBP \cdot HNO_3$ complex is stronger than the $TBP \cdot H_2O$ complex, such a deduction on the basis of comparative heats of solution (12) in the absence of information on the entropy changes would appear somewhat dubious.

(f) The solubilities of water in most trialkyl phosphates of molecular weights between tripropyl phosphate and triheptyl phosphate correspond to a water-to-solvent molar ratio of approximately 1:1 (14). By itself, this is at best only circumstantial evidence. In systems where a hydrocarbon diluent is present, the solubility of water in TBP may be substantially less than that corresponding to a 1:1 molar ratio (11, 12). This is not surprising since the diluent would solvate the TBP and inevitably affect the equilibrium $TBP + H_2O \rightleftharpoons TBP \cdot H_2O$. As the molecular weight of the diluent hydrocarbon is increased, however, the water solubility also increases (11). This latter behavior is to be expected since the heavier hydrocarbons should be less successful in a competition with H_2O for the polar TBP molecule.

With the exception of chloroform, Olander and Benedict's "ordinary" solvents (3) all contain one or more oxygen atoms that are of a type known to act as acceptor atoms in hydrogen bond formation. The association of water and ethyl acetate was studied as early as 1925 (15). Complex formation with the carbonyl group of aldehydes is reasonably well established (5) and the aldehydic proton may occasionally act as a proton donor (16). The hydrogen bonding in alcohols and isobutanol in particular has been studied extensively. Chloroform, as a proton donor, has also been well studied (5, 9, 11). Water, of course, may act as either a proton acceptor or donor.

The mass transfer data on the TBP—H_2O and "ordinary" systems (3) were tested against two hypotheses: (1) the species that diffuses into the organic phase is $(H_2O)_4$ in all of the systems studied (Figure 2 of ref. 3) and (2) the species that diffuses in the TBP system is $TBP \cdot H_2O$ and is $(H_2O)_4$ in the case of the "ordinary" systems (Figure 3 of ref. 3). The data gave best agreement with Hypothesis (1). A third possibility, that the diffusing species is in every case a hydrated solvent molecule, was not tested although it would appear to offer almost as successful a correlation as Hypothesis (1). Alternatively, if the authors had chosen to use experimental values for the diffusivities of the "ordinary" solvents rather than the "more consistent" ones derived from the Wilke-Pin Chang correlation (17), Hypothesis (2) might have given a more successful correlation. In any case, it would be most amusing (in the Wignerian sense (18)) if log-log plots of mass transfer data, computed with the aid of empirical correlations, proved to be a convincing tool for the determination of molecular structure.

In summary, it is my opinion that if the existence of the $TBP \cdot H_2O$ complex is an open question, the weight of evidence is in favor of the species. Undoubtedly the interaction is a weak one. In agreement with the estimate of 5

kcal-mole^{-1} cited above, Davis has estimated from his equilibrium data (1) a strength of 4 kcal-mole^{-1} for the bond between TBP and H_2O (19). Whether the existence of such a weak complex can safely be ignored may depend upon (a) the relative strengths of TBP bonds to other ligands in a given system and (b) the crudity of the data to be explained.

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ROBERT C. AXTMANN

Princeton University
Princeton, New Jersey
Received January 11, 1963

Reply to Preceding Letter "On the Existence of Tributyl Phosphate Monohydrate"

The conclusions based upon the data of ref. 1 (ref. 3 of Letter) were:

(1) Water transfers into TBP-hexane solvents without the restriction of a slow chemical conversion step (such as TBP + H_2O → TBP·H_2O).

(2) Concerning the possible diffusing species, the kinetic data were best correlated by treating TBP-hexane in the same manner as several other organic solvents investigated. It was not necessary to single out TBP from the other solvents by assigning to the diffusing species the specifically

hydrated formula TBP·H_2O. If the diffusivity of water in TBP is estimated by the same methods applied to the reference solvents isobutanol, ethyl acetate, furfural and chloroform (i.e., by assuming the diffusing species to be $(H_2O)_4$ in the Wilke-Pin Chang relation), the resulting correlation is consistent for all solvents to within experimental error. If the diffusivity of water in TBP is estimated by postulating the diffusing species TBP·H_2O, the TBP solvent results are separated from those of the reference solvents by amounts greater than the estimated accuracy of the method.

Assuming the diffusing species in all cases (TBP-hexane and the reference solvents) to be a hydrated solvent molecule does not yield a satisfactory correlation. The choice of $(H_2O)_4$ as the transferring species in water-as-solute diffusion permits the Wilke-Pin Chang correlation to be used for estimating the appropriate diffusivities. From the data given in ref. 2 (ref. 17 of Letter), this assumption reproduces the measured diffusion coefficients to within 2-6% for ethyl acetate, 3-6% for isobutanol, and 7% for furfural (excluding the furfural datum at 30°C, for which the error is 31%). If one attempted to reproduce these same data by assuming the diffusing species to be a hydrated solvent molecule, the diffusivities are underestimated by 23-27% for ethyl acetate, 21-28% for isobutanol, and 20% for furfural (again excluding furfural at 30°C, for which the error is 46%). The hypothesis of diffusing hydrated solvent molecules (in the reference solvents) was rejected because this model does not reproduce the measured diffusivities as well as the estimates based upon $(H_2O)_4$. Even if these incorrect diffusivities were utilized in computing the Schmidt numbers for the reference solvents, the discrepancy between the TBP-hexane and reference solvent results would still be on the order of 25%.

Utilizing the experimental diffusivities for the reference solvents instead of those based upon the empirical estimate would have had little effect. The ordinates of the reference solvent points on Figures 2 and 3 of ref. 1 would have been shifted by factors of approximately the square root error in the diffusivity discrepancies mentioned above, or ∼1-3%. The reference solvent points of Figures 2 and 3 cannot be budged by any postulate concerning the structure of the diffusing water; all of the parameters which locate the position of these points have been experimentally determined.

An unambiguous decision as to which diffusion coefficient is appropriate for TBP-hexane solvents must be deferred until the diffusivity of water in these systems is actually measured. Lacking such information, the most satisfactory way of analyzing the water extraction data is to treat TBP-hexane in the same manner as the reference organic solvents.

While there undoubtedly is hydrogen bond interaction between dissolved water and all of the solvents examined, the kinetic data indicate that it is not strong enough to warrant postulating that each diffusing water molecule carries along its own associated solvent molecule.

The effect of whatever complexing occurs on the extraction kinetics is approximately the same for the TBP-hexane and the reference solvents.

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