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
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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 + $H_2O \rightarrow$ 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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D. R. OLANDER

University of California
Berkeley, California
    Received February 25, 1963

Effect of Temperature Variation on "Intermediate-Resonance" Formulas

The "intermediate-resonance" formulas derived by Goldstein and Cohen (*1*) for effective resonance integrals in homogeneous systems have found wide acceptance as a means of interpolating between the extreme "narrow-resonance" and "infinite-mass" approximations at absolute zero temperature. However, there appears to be no reference in the literature to the validity of applying these formulas to the determination of effective resonance integrals at working temperatures. The effect of temperature variation is considered in this note.

Theoretical Background

Neglecting interference scattering and the variation in the reciprocal of the energy over a resonance, we may write the first and second order approximations to the effective resonance integral at working temperatures in the form

$$I_\lambda^{(1)} = \frac{\Gamma_\gamma \, \sigma_0 \, a_\lambda}{2E_0} \int_{-\infty}^{\infty} \frac{\psi(\theta, x)}{a_\lambda + \psi(\theta, x)} \, dx \qquad (1)$$

and

$$I_\lambda^{(2)} = I_1^{(1)} \left[\frac{1 + \sigma_{pa}(1 - \alpha)}{\alpha \sigma_p} \right] + \frac{\Gamma_\gamma \, \sigma_{pa}(a_\lambda - a_\infty)}{2E_0 \, x_0 \, a_\infty}$$
$$\cdot \int_{-\infty}^{\infty} \frac{\psi(\theta, x)}{a_1 + \psi(\theta, x)} \int_x^{\frac{x+x_0}{\alpha}} \frac{\psi(', x')}{a_\lambda + \psi(\theta, x')} \, dx' \, dx, \qquad (2)$$

where the notation is the same as that used by Dresner (*2*), except that

$$a_\lambda = \Gamma(\sigma_m + \lambda\sigma_{pa})/\sigma_0(\Gamma_\gamma + \lambda\Gamma_n),$$
$$a_1 = \sigma_p/\sigma_0 = \text{Dresner's } \beta,$$
$$a_\infty = \Gamma\sigma_{pa}/\Gamma_n\sigma_0$$

and

$$x_0 = 2E_0(1 - \alpha)/\Gamma.$$

Equations (1) and (2) give, to first and second order respectively, the "infinite-mass" approximation if λ is put equal to zero and the "narrow-resonance" approximation if λ is taken as unity. These extreme approximations may be combined linearly, following Goldstein and Cohen (*1*), to give

$$I_\mu^{(1)} = (I_0^{(1)} + \mu I_1^{(1)})/(1 + \mu) \qquad (3)$$

and

$$I_\mu^{(2)} = (I_0^{(2)} + \mu I_1^{(2)})/(1 + \mu), \qquad (4)$$

where the "best" value of I results from the choice of μ in

such a way that $I_\mu^{(1)} = I_\mu^{(2)}$. Hence

$$\mu = (I_0^{(1)} - I_0^{(2)})/(I_1^{(2)} - I_1^{(1)})$$

$$a_0 \, J(\theta, a_0) - a_1 \, J(\theta, a_1) \left[\frac{1 + \sigma_{pa}(1 - \alpha)}{\alpha \sigma_p} \right]$$

$$= \frac{- \dfrac{a_1 \, \sigma_{pa}(a_0 - a_\infty)}{2a_\infty \, \sigma_p \, x_0} L(\theta, a_1, a_0, x_0)}{a_1 J(\theta, a_1)\sigma_{pa} \dfrac{(1 - \alpha)}{\alpha\sigma_p} + \dfrac{a_1 \sigma_{pa}(a_1 - a_\infty)}{2a_\infty \, \sigma_p \, x_0} L(\theta, a_1, a_1, x_0)}, \qquad (5)$$

where

$$L(\theta, a_1, a_\lambda, x_0) = \int_{-\infty}^{\infty} \frac{\psi(\theta, x)}{a_1 + \psi(\theta, x)}$$
$$\cdot \int_x^{(x+x_0)/\alpha} \frac{\psi(\theta, x')}{a_\lambda + \psi(\theta, x')} \, dx' \, dx$$

and $J(\theta, a_\lambda)$ is the well-known function tabulated by Dresner (*2*) and others.

Equation (5) may be used to give an interpolation parameter, μ, appropriate for use in (3) or (4) at any given temperature.

Numerical Procedure

(i) Generation of $\psi(\theta, x)$

The line shape function was obtained by solving the differential equation

$$\psi''(\theta, x) = \tfrac{1}{4}\theta^4 - \theta^2 x\psi'(\theta, x) - \tfrac{1}{4}\theta^2(2 + \theta^2 + \theta^2 x^2) \psi(\theta, x), \qquad (6)$$

where the primes denote differentiation with respect to the variable x. The infinite range required for the integrals was truncated to the range $x = -d$ to $x = d$, and the range subdivided into $2j$ equal steps in x of width h. It was necessary to choose d so that x_0/h was exactly an even integer n.

Using the notation

$$x_i = -d + (i - 1)h$$

and

$$\psi_i = \psi(\theta, x_i),$$

the line shape function was obtained from the following algorithm.

$i = j + 1$ (center of resonance): $\qquad (7)$

$$\psi_i = \tfrac{1}{2}\sqrt{\pi}\,\theta e^{\theta^2/4} \, \text{erfc} \, \tfrac{1}{2}\theta,$$
$$\psi_i' = 0.$$

$2j + 1 + n \geqq i > j + 1$ and $x_i < 12/\theta$:

$$\psi_i = \psi_{i-1} + h\psi_{i-1}' + \tfrac{1}{2}h^2\psi_{i-1}'' + \tfrac{1}{6}h^3\psi_{i-1}''',$$
$$\psi_i' = \psi_{i-1}' + h\psi_{i-1}'' + \tfrac{1}{2}h^2\psi_{i-1}'''$$
$$\psi_i'' = \tfrac{1}{4}\theta^4 - \theta^2 x_i\psi_i' - \tfrac{1}{4}\theta^2(2 + \theta^2 + \theta^2 x_i^2)\psi_i,$$
$$\psi_i''' = -\theta^2 x_i\psi_i'' - \tfrac{1}{4}\theta^2(6 + \theta^2 + \theta^2 x_i^2)\psi_i' - \tfrac{1}{2}\theta^4 x_i\psi_i.$$

$2j + 1 + n \geqq i > j + 1$ and $x_i \geqq 12/\theta$:

$$\psi_i = \frac{1}{1 + x_i^2}\left\{1 + \frac{2(3x_i^2 - 1)}{\theta^2(1 + x_i^2)^2}\right\}.$$