sured system forms a closed curve between the upper and lower critical limits of solubility limited by the temperatures 27.9° and 83.0°C and by the concentrations 34.7 and 73.7 wt %, respectively. The determination of solubility using two methods (cloud point and refractometry) has given identical results except for the methylvinylketone phase at higher temperatures (refer to Figure 1, hatched section) where the refractometer (circles) indicated a higher methylvinylketone content and therefore a lower water solubility in the methylvinylketone phase.

Although measurements by the cloud point method are commonly more accurate (it is possible to weigh the samples into the sealed test tubes very precisely by differential weighing, the lower limit of turbidity detection is less than 0.1°), it is less suitable than refractometry for this particular system because of the polymerization activity of the methylvinylketone. Even with 0.05 wt % of diethylhydroxylamine added as stabilizer, a partial polymerization occurs at higher temperatures, as the sample is exposed to the influence of heat and light a rather long time (on the order of several hours).

Since polymers affect the cloud point considerably, even in small amounts, the authors tend to the opinion that the refractometric method of determination gives more truthful results. The same concentration of polymers affects the change of cloud point more than the refractive index of the mixture. Besides, the possibility of an error in the refractometric method was decreased by changing the samples for each temperature measurement, and the calibration measurements were made with mixtures containing only pure methylvinylketone without polymers.

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Viscosity Studies of Certain Alkyl Phosphates and Their Aqueous Mixtures

GABRIELLA THAU-ALEXANDROWICZ and GABRIEL MICHAELI[1]

Polymer Department, The Weizmann Institute of Science, Rehovot, Israel

The temperature- and water-concentration-dependent kinematic viscosity of the phosphate esters, tri-*n*-butylphosphate (TBP), di-*n*-butylcresylphosphate (DBCP), dicresyl-*n*-butylphosphate (DCBP), tetra-butylhydroquinonediphosphate (HQDP), tetra-butylbutylenediphosphate (TBBDP), and their water mixtures, was measured by use of water-calibrated Ubbelhode-Cannon viscometers within the temperature range 0–45°C. The results are well represented by the relationship $\nu(T) = \exp(A + B/T + C/T^2)$ in which the activation energy has the form $E_a(T) = A + R(B + C/T)$. These results are discussed with relation to the solvents' self-association and H-bonding properties.

Solvent membranes made of tri-*n*-butylphosphate (TBP) exhibit highly selective water transport properties (*13*), attributed to the formation of TBP-water complexes in the organic phase (*7*). Similar effects were observed in several other organophosphate solvent membranes examined in our laboratory (*1, 6, 12*).

The viscosity study reported here is part of a project aimed at determining the molecular mechanisms involved in the water transport properties of these solvent membranes.

EXPERIMENTAL SECTION

Materials. Pure tri-*n*-butylphosphate (TBP) was obtained from Fluka A.G., di-*n*-butylcresylphosphate (DBCP) (bp 132–3°C/0.3 mm Hg), dicresyl-*n*-butylphosphate (DCBP) (bp 180°C/2.5 mm Hg), tetrabutylhydroquinone diphosphate (HQDP) (bp > 100°C/10^{-3} mm Hg) and tetrabutylbutylenediphosphate (TBBDP) (bp > 100°C/10^{-3} mm Hg) were synthesized at the Plastics Research Laboratory, Weizmann Institute by Sylveta Marian and David Vofsi. The purity of the phosphate esters was estimated at >97% by comparing their empirical phosphorus content to the calculated one. All solvents were dried in a vacuum desiccator heated to 60°C and containing solid NaOH for at least 24 hr before use.

Methods. Densities were measured with an A. P. Gratz digital densitometer. Water concentrations were determined by the Karl Fischer method. The kinematic viscosity of the organophosphates and their water mixtures was measured with water-calibrated Ubbelhode-Cannon viscometers, within the temperature range 0–45°C. The temperatures were kept constant within ±0.05°C during each measurement. The precision of the viscosity measurements was estimated at $< \pm 0.2\%$. For checking the viscosity water-concentration dependence, a measured volume of distilled water from an Agla microsyringe was added after each viscosity run, into the weighted solvent sample being measured. Complete mixing of the organophosphates' water mixtures was

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[1] Present address, Department of Atmospheric Sciences, The Hebrew University of Jerusalem, Israel. To whom correspondence should be addressed.

ensured by bubbling air through the liquids for several minutes before each measurement.

RESULTS

The viscosity of the pure solvents (Table I) is strongly dependent on the alkyl groups of the phosphoric esters which influence both the dipole moment of the —P=O groups and the geometry of the molecules.

The $X_w^{25°C}$ values of the solvents' water mixtures, determined by the Karl Fischer method, were: 0.175 ± 0.005, 0.30 ± 0.01, 0.51 ± 0.01, 0.53 ± 0.01, 0.85 ± 0.03 for DCBP, DBCP, TBP, HQDP, and TBBDP, respectively. The increasing order of water concentrations in the solvents at 25°C is DCBP < DBCP < TBP < HQDP < TBBDP.

The above suggests that water concentration decreases with the introduction of aromatic groups into the phosphate ester and increases considerably with the addition of a second ester group and a decrease in the alkyl groups' dimension.

Since the customary Arrhenius temperature dependence of the kinematic viscosity

$$\nu(T) = \exp\,(A' + B'/T) \qquad (1)$$

did not hold for our solvents and their water mixtures, we employed the relationship of

$$\nu(T) = \exp\,(A + B/T + C/T^2) \qquad (2)$$

This equation, introduced by Girifalco (*4*) for associated liquids, proved to be a useful general empirical relationship for many organosolvent water mixtures (*8, 11*).

The coefficients presented in Table II were calculated from the corresponding experimental kinematic viscosity values, using a nonlinear least-squares fitting computer program. In each case we employed 10–12 $\nu(T)$ values measured between 0° and 45°C at intervals of approximately 5°C. The numerical fitting used in computing Table II was better than ±0.2%, corresponding to the average experimental error of the kinematic viscosity measurements.

Table I. Certain Physical Constants of Pure Measured Solvents Determined at 25°C

Solvent	M	$d^{25°C}$, g/cm^{-3}	$\nu_0^{25°C}$, cSt	$\eta_0^{25°C}$, cP
TBP	266	0.9725	3.42	3.32
DBCP	300	1.049	7.05	7.40
DCBP	334	1.112	17.42	19.34
TBBDP	474	0.962	19.30	18.57
HQDP	494	1.097	28.85	31.65

Table II. Computed Coefficients *A, B,* and *C* of Viscosity-Temperature-Dependence Relation

(For measured solvents and their water mixtures at several water concentrations in the range of 0–45°C, together with the corresponding $E_a^{25°C}$ values)

Solvent	X_w	A	$-B \times 10^{-3}$	$C \times 10^{-6}$	$E_a^{25°C}$, kcal mol^{-1}
DBCP	0	4.5750	4.4278	1.0865	−1.57
	0.12	5.6863	5.0320	1.1664	−2.20
	0.17	5.9938	5.2437	1.2025	−2.40
	0.29	2.5112	3.2919	0.92983	−0.34
DCBP	0	16.377	12.051	2.3911	−8.00
	0.036	14.826	11.147	2.2584	−7.18
	0.10	14.551	10.973	2.2296	−6.98
	0.13	16.508	12.128	2.3980	−8.16
TBP	0	2.0795	1.7459	0.56624	0.30
	0.24	−2.0113	0.23271	0.36380	2.00
	0.32	0.43803	1.7455	0.59712	0.40
	0.49	0.04068	1.6536	0.61279	0.81
HQDP	0	3.2491	3.5940	1.0811	0.08
	0.185	3.2266	3.6751	1.1036	0.05
	0.36	2.6326	3.3759	1.0644	0.38
	0.53	8.2972	6.8063	1.5759	−3.02

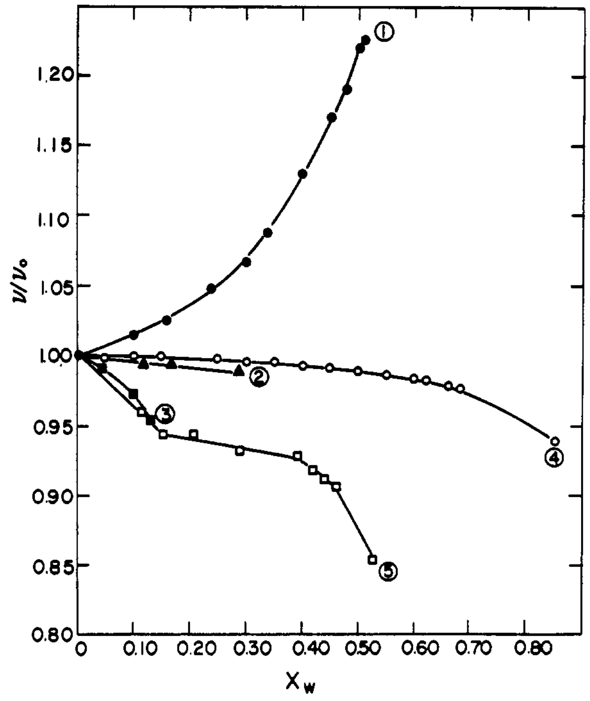

Figure 1. Water-concentration dependence of the reduced kinematic viscosity at 25°C for the mixtures: 1, TBP + H_2O; 2, DBCP + H_2O; 3, DCBP + H_2O; 4, TBBDP + H_2O; and 5, HQDP + H_2O

By use of the computed values of B and C, the activation energies of the form

$$E_a(T) = R(C/T + B) \qquad (3)$$

were calculated at T = 298°K and are presented in Table II.

The concentration dependence of the reduced kinematic viscosity ν/ν_0 for the measured alkylphosphate–water mixtures, is presented in Figure 1. Similar behavior was recently observed in the concentration and temperature dependence of the water proton chemical shifts of the water signal found in the proton magnetic resonance (pmr) spectra of the same organophosphate–water mixtures (*12*).

DISCUSSION

Because of the rather limited scope of our work, a detailed quantitative analysis of the results presented here seems premature. However, some facts concerning the structure and properties of the measured organophosphates and their water mixtures can be deduced from the concentration and temperature dependence of the viscosity. Following Girifalco (*4*), we assume the constants B and C in expression 2 to be proportional to the liquids' dispersion and the dipole-dipole intermolecular interactions, respectively. Thus, according to Table II, the increasing order of the dipole-dipole interactions in the pure solvents is TBP < HQDB < DBCP < DCBP.

We feel that the kinematic viscosity–water concentration dependence outlined in Figure 1 and Table II may be explained qualitatively. This explanation derives from the known self-association and H-bonding properties of trialkylphosphates attributed mainly to dipole-dipole interactions (*2, 10*).

The measured solvents can be divided into three groups:

TBP–Water. In pure TBP there exists an equilibrium reaction, 2 TBP $\rightleftharpoons$ $(TBP)_2$ (*2, 3, 10*). The addition of water creates a series of new equilibrium reactions (*5, 7, 9, 14*) which can be summarized as follows:

$$TBP + (H_2O)_{org} \rightleftharpoons (TBP)_2 + (TBP)_2H_2O + (TBP\text{–}HOH)_x$$

where $x = 1, 2, 4 \ldots n$, depending on X_w. An increase in X_w causes an equilibrium shift to the right, increasing the polymeric TBP hydrate concentration and thus causing the observed kinematic viscosity increase. The sharp decrease of $E_a^{25°C}$ for $X_w = 0.24$ indicates the formation of an H-bonded TBP hydrate of the form $(TBP)_2H_2O$ (*5*), which forms, on further addition of water, a 1:1 TBP polyhydrate.

DBCP–Water and DCBP–Water. For DBCP and DCBP we assume stronger dimerization because of their stronger dipole-dipole interactions compared to TBP. The addition of water to the dry solvents causes partial hydration of the —P=O groups of their monomers, thus bringing about a small decrease in the dimer concentration and a subsequently slight decrease in their reduced kinematic viscosity, and practically no changes in $E_a^{25°C}$.

HQDP–Water and TBBDP–Water. Both compounds possess two relatively strong polar —*P*=O groups, therefore the —P=O- —P=O association might cause a high degree of polymerization in the pure solvents. The generalized self-association reaction can be written as:

$$m\ (AP) \rightleftharpoons (AP)_m$$

where $m = 2, 3, 4 \ldots n$.

In Figure 1 we note for HQDP a two-step decrease of the reduced kinematic viscosity occurring at $0 < X_w < 0.20$ and $0.35 < X_w < 0.53$, indicating two distinct steps of the HQDP hydration process.

The decrease of $E_a^{25°C}$, from 0.38 to −3.02 kcal mol^{-1} at $X_w = 0.36$ and 0.53, respectively, indicates the stabilization of the HQDP hydrate, detected by its measurable decrease in viscosity.

These processes are, probably, the formation of HQDP chain polyhydrates, which dissociate, by further addition of water, into much stabler 1:1 HQDP–hydrates of shorter unit chain length.

In the case of TBBDP, the decrease of the reduced kinematic viscosity at high X_w is smooth.

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NOMENCLATURE

X_w = water molar fraction
$X_w^{25°C}$ = saturation water molar fraction of solvent–water mixture at 25°C
R = gas constant, cal mol^{-1}
M = molecular weight
$d^{25°C}$ = relative density, g/cm^{-3}
$\nu_0^{25°C}$ = kinematic viscosity of pure solvent at 25°C, cSt
$\eta_0^{25°C}$ = viscosity of pure solvent at 25°C, cP
$\nu(T)$ = temperature-dependent kinematic viscosity, cSt
$E_a^{25°C}$ = activation energy at 25°C, kcal mol^{-1}
A', B' = constants, Equation 1
A, B, C = constants, Equation 2
ν/ν_0 = relative kinematic viscosity compared to $\nu_0^{25°C}$

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