is the difference between the literature values and the experimental correlations greater than 1%.

The mixture vapor pressure data of this study are approximately 1% greater than those reported by Manley and Swift at the 100°F isotherm. This difference is attributed to the difference in the method of pressure measurement employed with the modified equipment.

The computed relative volatilities are compared with the literature data in Figures 9–13. The data of the previous investigators were acquired by sampling liquid and vapor at equilibrium in all but Figure 13. The data of Mann et al. in Figure 13 were taken in an equilibrium still and exhibit less scatter than other data previously reported and show excellent agreement with the computed values of this study.

CONCLUSIONS

The relative volatilities reported in this article extend the range of information on the propane–propene system to the temperatures of greatest industrial interest. Since most industrial separations of propane and propene are carried out at temperatures in excess of 100°F, the data of this study should provide a useful extension of the data reported by Manley and Swift (*8*). The combined data provide relative volatilities for the propane–propene system from −20° to +160°F.

NOMENCLATURE

ABCD = vapor pressure correlation constants
P = pressure, psia
T = temperature, °F
T_a = temperature, °R
V = specific volume, ft^3/lb-mol
Z = compressibility factor, PV/RT_a
x = mole fraction propene in liquid
y = mole fraction propene in vapor

Greek Letters

α = relative volatility $[y(1 - x)]/[x(1 - y)]$
Δ = difference

Superscripts

L = liquid phase
V = vapor phase

Subscripts

1 = propane
2 = propene
i = component i
r = pressure subscript, P computed using Raoult's law

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Temperature Dependence in Determination of Solubilities in System Methylvinylketone in Water

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The dependence of solubility in the system methylvinylketone–water on temperature was measured using two mutually independent methods. These two substances form a partially miscible system. The immiscibility range is limited by the lower (27.9°C) and upper (83.0°C) critical temperatures of solubility and by the concentrations 34.7 and 73.7 wt % of methylvinylketone in water.

Methylvinylketone (MVK), a technologically important intermediate, may be prepared by various methods. The most usual methods of preparation are based on the hydrolysis of *cis*- or *trans*-1,3-dichloro-2-butene with Na_2CO_3 and H_2SO_4 (*4*), or catalytically with $CuCl_2$ (*3*) or with HCl (*8*). It is also possible to prepare it by condensation from acetone and formaldehyde (*1, 5, 6, 10*), by dehydrogenation of methylethylketone (*7*), or from vinyl magnesium chloride and acetylchloride (*9*).

One of the oldest methods is its preparation by hydration of vinylacetylene (*2*). It is necessary to know the mutual solubility of methylvinylketone and water for this procedure. This paper presents data as to this solubility.

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EXPERIMENTAL

Reagents. Methylvinylketone (National Enterprise Duslo, Sal'a), prepared by the hydration of vinylacetylene, had the following constants:

$bp_{746} = 81.3°C$ $bp_{760} = 81.4°C$ (*10*)

$n^{20}{}_D = 1.4114$ $n^{20}{}_D = 1.4110$ (*4*)

$d_4{}^{20} = 0.8494$ $d_4{}^{20} = 0.8501$ (*4*)

The water was redistilled.

APPARATUS AND PROCEDURE

The solubility determination in the system methylvinylketone–water is difficult because methylvinylketone polymerizes very easily just as do other α,β-unsaturated ketones. Since polymers, even in minute amounts, have a substantial effect on the mutual solubility of the two components of the system, we selected two independent methods for the solubility measurement to increase the accuracy of determination and objectivity of the measurement.

The system was investigated by both cloud point measurement and by refractometry. In the first case, we observed the onset of turbidity in sealed ampuls containing mixtures with known concentrations; in the second case, the phases were equilibrated at a given temperature and both phases then analyzed refractometrically. The composition was then read from a calibration plot prepared by determining the refractive indices of known solutions. In the cloud point determinations, an optical glass vessel was used as the thermostat. It was equipped with a stirrer, temperature was controlled to 0.05°C by Anschutz thermometers (0.1°C calibrations), and a stand was provided for holding the sealed ampuls. For the refractometric method, we used test tubes having a 15-ml volume and equipped with a stopcock. The samples were taken using a syringe with a long needle. The analysis was made refractometrically on an Abbe refractometer with thermally controlled prisms.

RESULTS

The results of the solubility determination obtained by the cloud point method are summarized in Table I. The results obtained using the refractometric method are listed in Table II. The phase diagram of solubility of the system and its dependence on temperature as measured by both methods is shown in Figure 1. The lower and upper critical solubility temperatures, 27.9° and 83.0°C, as well as the concentration ranges limiting the region of heterogeneity, were determined graphically from Figure 1. The limits of this range are at 34.7 and 73.7 wt %, respectively, of methylvinylketone in water.

Table I. Temperature Dependence of Solubilities in System Methylvinylketone–Water as Determined by Cloud Point Measurements

	Cloud point temp	
Concn, wt % MVK	Lower, °C	Upper, °C
32.4	...	...
35.0	50.5	69.5
38.9	36.8	82.5
40.1	35.5	82.9
42.6	33.8	82.8
45.5	30.5	82.5
47.9	29.6	82.2
50.5	28.4	82.0
52.4	28.2	81.7
55.0	28.0	81.1
57.1	28.0	79.5
61.3	28.1	77.3
64.2	28.5	74.0
67.5	30.3	70.5
70.2	33.5	65.1
72.8	41.5	54.0
74.9	...	...

Table II. Temperature Dependence of Solubilities in System Metylvinylketone–Water as Measured Refractometrically

Equilibrium temp	Compn of organic layer, wt % MVK in water	Compn of aqueous layer, wt % MVK in water
27.9	Appearance of the first turbidity	
28.5	63.2	50.0
30.7	67.0	46.9
33.3	69.4	42.6
36.7	71.4	38.8
42.0	72.9	36.5
48.0	73.5	36.1
52.0	73.2	35.7
62.0	71.5	35.0
66.0	70.6	34.8
70.0	68.5	35.2
74.6	67.3	35.6
80.0	60.1	37.7
83.0	Existence of one phase	

DISCUSSION

Figure 1 shows that the solubility dependence of the system methylvinylketone–water on temperature has an unusual shape. The solubility decreases at first with increasing temperatures, but then it increases again. The phase diagram of the mea-

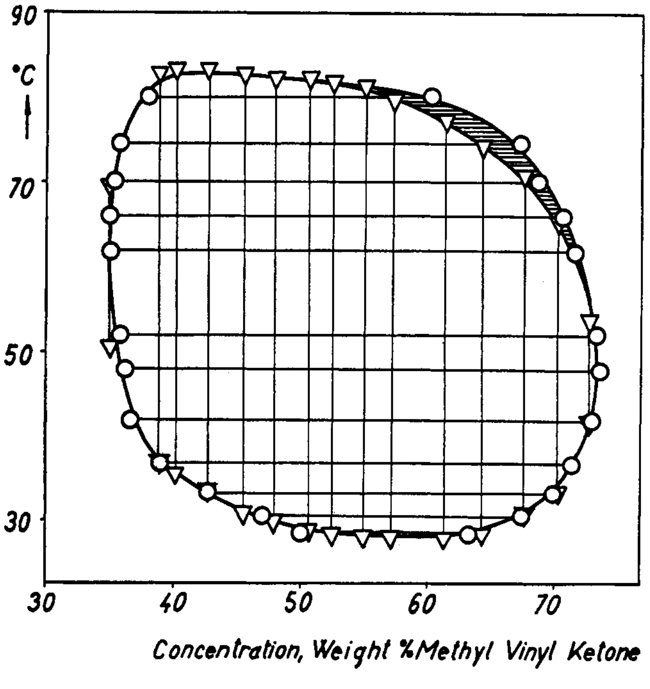

Figure 1. Solubility of methylvinylketone in water

○ = Refractometric data. ∇ = Cloud point data 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

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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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