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

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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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Typical specifications for the 4M2P used included the following: minimum of 99 wt % 4M2P, specific gravity (20°/20°C): 0.800–0.804, and 0.01 wt % acid (reported as acetic). An equilibrium determination made with a "certified" 4M2P (Fisher Scientific Co.) agreed with the other measurements. Measurements of density were by pycnometer.

Results and Discussion

A total of 139 equilibrium pairs was analyzed for acetic acid by the present authors and their associates. In 114 of these pairs, there was no sodium chloride present in either phase; in 12 pairs the water phase was approximately 0.01*N* with respect to sodium chloride, and in 13 that phase was approximately 0.1*N*. The results of these analyses have been used in preparing the present paper; and, in addition, in certain of the regression analyses described below, 53 equilibrium pairs already reported in the literature (*1, 2, 4, 6, 10–12*) have been included.

In operating such experimental apparatus as spray columns, it is often difficult to maintain any temperature in the equipment other than the ambient. With the possibility of this temperature varying from experiment to experiment, it was important to find out whether or not the equilibrium partition would be noticeably dependent on the temperature. Accordingly, equilibrium partitions of acetic acid were measured at 15.5°, 21.1°, and 26.7°C. The range covered by these temperatures approximates the range of ambient temperatures likely to be encountered in the laboratory. In each of these three runs, the concentration of acetic acid in the equilibrium water phase was close to 3 kg mol/m^3, and there was no sodium chloride present. The measured concentrations in the equilibrium ketone phase were in close agreement with one another. (Later, when a comparison was made between the values of $C_k{}^*$ measured in these three runs and the corresponding values predicted by a regression equation describing all the available data with sodium chloride absent, each measured value lay well within the 95% confidence limits (for observations) associated with the regression equation.)

It seems, then, that over a reasonably small temperature range, it can be assumed that temperature has little or no effect on the equilibrium under consideration here. Of the total of 192 equilibrium pairs considered in this paper, all but four correspond to temperatures between 20° and 28°C. All 192 runs lie in the range from 15.5° to 44.3°C. (In this paper, 95% confidence intervals have been given for both "observations" and "means". An observed value of $C_k{}^*$ should lie within the range defined by the 95% confidence interval for observations in 95% of all experiments. The true polynomial for $C_k{}^*$ will have a 95% probability of lying within the confidence interval for means.)

A polynomial was derived by least-squares regression techniques to relate $C_k{}^*$ to C_w for the 114 data points (without sodium chloride) of the present workers and one for the 53 data points from the literature. Over the range of C_w values from 0.0 to 4.8 kg mol/m^3 involved in the first of these polynomials, the regression curve agrees with that corresponding to the second polynomial, each lying within the other's interval of 95% confidence (for means). It is concluded, therefore, that the results of the present study (without sodium chloride present) agree well with the data reported previously in the literature. On the basis of this conclusion, the 114 data points and the 53 data points were combined, and a polynomial fitted by least-squares regression techniques to relate $C_k{}^*$ to C_w for the total of 167 data points. These data points form Set 1. Table I reports the polynomial coefficients for this set and also similar coefficients for Sets 2 and 3 in which sodium chloride was present.

Comparison of the results corresponding to Sets 2 and 3 in Table I with those for Set 1 indicates that there is no significant effect of 0.01*N* sodium chloride. However, when the water phase was 0.1*N* there was a small effect which may be significant. For example, at a C_w of 1.1 kg mol/m^3, the predicted value of $C_k{}^*$ from the regression equation for Set 3 is 0.02 kg mol/m^3 greater than the value of 0.62 predicted by the curve for Set 1. The regression curve for Set 1 lies outside the 95% confidence limits (for means) for Set 3 at a C_w value of 1.1. On the other hand, the Set 3 data lie either at the edge of or within the 95% confidence limits (for means) for Set 1.

Densities of the equilibrium phases were not measured in the present study above a value of C_w of 4.7 kg mol/m^3, approximately the upper limit for C_w in the equilibrium determinations of the present authors. Literature equilibrium data at higher values of C_w (*6, 10, 12*) were used, however, in deriving the polynomial for Set 1. These data were reported in terms of concentrations in weight percent. The latter were converted into units of kg mol/m^3 by use of density values extrapolated from the present measurements. Therefore, it is believed that the predictions from Set 1 will be less reliable above values of C_w of 4.7 kg mol/m^3 than they will below this value. However, it is believed that any error resulting from this extrapolation will be slight.

Densities were measured for each phase of 13 equilibrium pairs with no sodium chloride present. Regression of these data gave the polynomial coefficients shown in Table II.

At zero concentration of acetic acid, the predictions of Table II for the densities of the mutually saturated phases agree quite well with values in the literature (*7, 9, 13*). However, it is believed that the density values of Sherwood et al. (*12*) are in error, increasing too slowly with the concentration of acetic acid. This conclusion is

Table I. Distribution of Acetic Acid Between Mutually Saturated Phases

$C_k{}^* = aC_w + bC_w{}^2 + cC_w{}^3 + dC_w{}^4$

Set	No. of data points[a]	Approx normality of sodium chloride in water phase	Coefficients of equil polynomial				95% Confidence intervals		Applicable range of C_w, kg mol/m^3
			a	*b*	*c*	*d*	Observations	Means	
1	167	0.0	0.4487	0.1162	−0.01861	0.001987	±0.07	±0.03	0.0–5.9
2	12	0.01	0.4843	0.06972	0.0	0.0	±0.02	±0.015	0.0–1.02
3	13	0.1	0.4950	0.07308	0.0	0.0	±0.01	±0.01	0.0–1.10

[a] Data for each experimental point are listed in supplementary material deposited with the ACS Microfilm Depository Service.

Table II. Density of Mutually Saturated Phases as Function of Acetic Acid Concentration at 22 ± 0.5°C[a] (No Sodium ChloridePresent)

ρ, g/ml $= e + f(C \text{ or } W) + g(C \text{ or } W)^2 + h(C \text{ or } W)^3$

		Coefficients of polynomials				95% Confidence intervals		
Phase	Acetic acid concn in	e	f	g	h	Observations	Means	Applicable range of concn
Water	Kg mol/m³ = C	0.9952	7.408×10^{-3}	3.027×10^{-4}	-1.568×10^{-4}	±0.0003	±0.00015	0.0–4.7
Water	Wt % = W	0.9952	1.220×10^{-3}	1.168×10^{-5}	-8.257×10^{-7}	±0.00035	±0.00015	0.0–28.0
Ketone	Kg mol/m³ = C	0.8034	2.020×10^{-2}	8.856×10^{-4}	0.0	±0.003	±0.0015	0.0–3.8
Ketone	Wt % = W	0.8023	3.384×10^{-3}	-4.446×10^{-5}	2.047×10^{-6}	±0.003	±0.0015	0.0–26.0

[a] Number of data points is 13 for each line of the table. Data for each point are listed in supplementary material deposited with the ACS Microfilm Depository Service.

reached because it was necessary to use the density data measured in the present research to get agreement of the weight percent data of other workers with the kg mol/m^3 data of the present work.

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Nomenclature

a, b, c, d = coefficients of polynomials giving the equilibrium concentrations in the ketone phases (Table I)
C = concentration of acetic acid, kg mol/m^3
e, f, g, h = coefficients of polynomials giving the densities of the mutually saturated phases (Table II)
W = concentration of acetic acid, wt %

Greek Letters

ρ = density, g/ml

Subscripts

k = in or of the ketone phase
w = in or of the water phase

Superscripts

$*$ = value at equilibrium

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Supplementary Material Available. Data for the experimental points in Tables I and II will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JCED-74-154.

Correction

It has been brought to our attention that a formula in our paper, "Viscosity Measurements of Water in Region of Its Maximum Density" [*J. Chem. Eng. Data*, **19** (1), 1 (1974)], is incorrect. It is possible if someone were to follow the cleaning directions using $KMnO_4$ and concentrated sulfuric acid that an explosion could result. We, of course, used the usual cleaning solution of $Na_2Cr_2O_7$ in sulfuric acid to clean our viscometers. The $KMnO_4$ was used in a distillation procedure to remove organic impurities from the experimental water for the viscometry experiments.

We are indebted to Oliver Brown, Connecticut College, for pointing out this error in our paper.