

<i>D</i>	diffusivity of ferricyanide ion, $\text{m}^2 \text{s}^{-1}$
<i>F</i>	Faraday's constant = 96484 A s equiv <sup>-1</sup>
<i>G, G'</i>	constants in current-disk speed regression, various units
<i>I</i>	current density, $\text{A m}^{-2}$
<i>I</i>	current, A
<i>S</i>	standard error of regression, %
<i>T</i>	temperature, °C or K (see text)
<i>z</i>	number of electrons transferred in cathodic reaction, eq 1, $z = 1$
<i>Sc</i>	Schmidt number = $\nu/D$

#### Greek Letters

$\eta$	dynamic viscosity of solution, $\text{kg m}^{-1} \text{s}^{-1}$
$\nu$	kinematic viscosity of solution, $\text{m}^2 \text{s}^{-1}$
$\rho$	density of solution, $\text{kg m}^{-3}$
$\omega$	angular velocity of rotating disk, $\text{s}^{-1}$

Registry No. NaOH, 1310-73-2; potassium ferricyanide, 13943-58-3; potassium ferrocyanide, 13746-66-2.

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## Vapor-Liquid Equilibria of a Slight Amount of Water in Eight Organic Solvents at Atmospheric Pressure

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**Vapor-liquid equilibria of a slight amount of water in methanol, ethanol, 1-propanol, 2-propanol, methyl acetate, ethyl acetate, acetone, and 1,4-dioxane were measured by use of an Othmer-type still in a drybox. As the concentration of water decreases, the equilibrium ratio of water becomes constant in ethanol, 1-propanol, and 2-propanol. In the other solvents it does not become constant within the concentration range studied. It approaches unity in methanol and acetone.**

When organic solvents are purified by distillation, water is a typical impurity which shows up in many processes and sometimes causes trouble. In the design of efficient distillation systems, vapor-liquid equilibrium data of water in the concentration range shown in the actual distillation towers are required. However, accurate data in such a range are scarcely reported up to this time.

In this study, the vapor-liquid equilibria of eight organic solvents containing a slight amount of water were measured at atmospheric pressure and the equilibrium ratios of water are presented.

#### Materials

Relatively mild methods were used for purification of the solvents, to avoid the formation of polar impurities. Guaranteed reagents were purified and dried by the following methods:

Methanol was fractionally distilled after being boiled under reflux with magnesium foil and a small amount of iodine for

about 3 h. Ethanol was distilled after being left for several days with *m*-phenylenediamine hydrochloride. The distillate was dried by the same method as that used for methanol. 2-Propanol was boiled under reflux with calcium oxide for 24 h. The supernatant solution was fractionally distilled. 1-Propanol was left over molecular sieves for more than 2 days. The solution was then boiled under reflux with calcium oxide for 8-12 h. The supernatant solution was fractionally distilled.

Methyl acetate was boiled under reflux with anhydrous potassium carbonate for 3-6 h. The supernatant solution was fractionally distilled. Ethyl acetate was dried over anhydrous potassium carbonate and fractionally distilled.

1,4-Dioxane was distilled after being boiled under reflux with metallic sodium for 6-12 h. Acetone was left over anhydrous magnesium sulfate for more than 2 days. The supernatant solution was boiled under reflux with newly added anhydrous magnesium sulfate for 4-8 h. The supernatant solution was then fractionally distilled.

The purities of the resulting products were checked by gas chromatography using a Shimadzu GC-8A equipped with a flame ionization detector. The impurity contents were less than 0.13% in 1-propanol, 0.06% in methyl acetate, 0.06% in ethyl acetate, 0.25% in 1,4-dioxane, and 0.002% in acetone. No impurities were detected in methanol, ethanol, and 2-propanol.

#### Experimental Method

**Apparatus.** Vapor-liquid equilibria were measured by use of an Othmer-type still (1) in a drybox, which was held at low

Table I. Vapor-Liquid Equilibrium Data for Organic Solvent-Water Systems

Methanol											
$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$
0.00240	0.00217	0.904	0.00770	0.00605	0.786	0.0437	0.0304	0.696	0.234	0.122	0.520
0.00270	0.00244	0.904	0.00789	0.00663	0.840	0.0728	0.0471	0.647	0.292	0.146	0.498
0.00300	0.00258	0.860	0.0112	0.00841	0.751	0.127	0.0687	0.539	0.348	0.164	0.470
0.00393	0.00386	0.982	0.0157	0.0108	0.688	0.208	0.113	0.544	0.635	0.257	0.405
0.00531	0.00452	0.851	0.0277	0.0190	0.686						
Ethanol											
$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$
0.00348	0.00406	1.17	0.0154	0.0180	1.17	0.0671	0.0765	1.14	0.193	0.210	1.09
0.00440	0.00509	1.16	0.0185	0.0203	1.10	0.0826	0.0864	1.05	0.272	0.292	1.08
0.00869	0.0101	1.16	0.0190	0.0226	1.19	0.105	0.120	1.15	0.424	0.464	1.10
0.00986	0.0118	1.19	0.0233	0.0274	1.17	0.122	0.134	1.10	0.490	0.541	1.19
0.0137	0.0144	1.05	0.0288	0.0326	1.13	0.134	0.157	1.17	0.494	0.556	1.12
0.0143	0.0166	1.16	0.0565	0.0660	1.17						
2-Propanol											
$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$
0.00620	0.00830	1.33	0.00994	0.0152	1.53	0.0383	0.0590	1.54	0.0846	0.127	1.50
0.00687	0.00904	1.32	0.0157	0.0234	1.50	0.0417	0.0630	1.51	0.112	0.174	1.55
0.00824	0.0111	1.35	0.0185	0.0288	1.56	0.0583	0.0946	1.62	0.239	0.363	1.52
0.00970	0.0135	1.39	0.0197	0.0295	1.50	0.0783	0.117	1.49	0.356	0.535	1.50
1-Propanol											
$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$
0.00880	0.0277	3.15	0.0219	0.0647	2.95	0.0285	0.0750	2.63	0.0540	0.155	2.87
0.00964	0.0268	2.78	0.0222	0.0613	2.76	0.0327	0.0857	2.62	0.0600	0.176	2.93
0.0129	0.0327	2.54	0.0238	0.0730	3.07	0.0397	0.105	2.64	0.163	0.465	2.85
0.0173	0.0493	2.85	0.0268	0.0707	2.63	0.0397	0.116	2.92	0.271	0.806	2.97
0.0219	0.0600	2.74									
Methyl Acetate											
$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$
0.405	0.512	1.26	0.764	1.18	1.54	1.06	1.41	1.33	2.75	2.97	1.08
0.528	0.703	1.33	0.801	1.09	1.36	1.36	2.06	1.41	3.00	3.51	1.17
0.540	0.776	1.44	0.886	1.33	1.54	2.12	2.51	1.18			
Ethyl Acetate											
$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$
0.00723	0.0244	3.37	0.0106	0.0339	3.20	0.0204	0.0659	3.23	0.0313	0.104	3.32
0.00743	0.0239	3.22	0.0126	0.0431	3.42	0.0268	0.0889	3.32	0.0384	0.135	3.52
0.00801	0.0254	3.17	0.0147	0.0503	3.42	0.0297	0.101	3.40	0.0399	0.146	3.66
0.00821	0.0260	3.17	0.0178	0.0572	3.21						
Acetone											
$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$
0.197	0.183	0.929	0.300	0.278	0.927	0.386	0.344	0.891	0.565	0.495	0.876
0.200	0.187	0.935	0.347	0.331	0.953	0.517	0.459	0.888			
1,4-Dioxane											
$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$	$10^2x$	$10^2y$	$K$
0.0112	0.0340	3.04	0.0200	0.0713	3.57	0.0860	0.413	4.80	0.101	0.470	4.65
0.0156	0.0503	3.22	0.0264	0.106	4.02	0.0860	0.419	4.69	0.105	0.497	4.73
0.0181	0.0533	2.94	0.0347	0.134	3.86	0.0894	0.421	4.71	0.179	0.903	5.04
0.0182	0.0645	3.54	0.0713	0.340	4.77	0.0943	0.413	4.38			

humidity with dry air. A schematic diagram of the experimental apparatus is shown in Figure 1.

The drybox was made of acrylic board, 5 mm in thickness. On the front, four rubber gauntlets for handling were mounted, the positions of which are represented by dashed circles in Figure 1. The front plate as a whole was tightly attached to the box-body by clamps. The dimensions of the drybox were 104 cm in height, 93 cm in width, and 46 cm in depth.

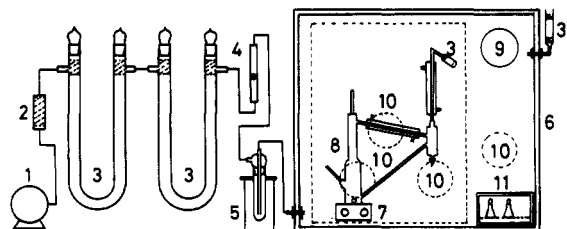
**Procedure.** Dry air flows into the drybox at the rate of 8 L/min for about 3 h. After the humidity in the drybox falls to about 20%, the feed solution is charged into the Othmer-type still, which is operated for about 8 h. During the operating period dry air flows at the rate of about 3 L/min. The samples taken from the vapor-phase reservoir and the bottom of the still are housed in the sample box. After the sample box is sealed,

the front plate of the drybox is taken off.

**Analysis.** The concentration of water was determined with a Karl Fischer water analyzer (CA-02, Mitsubishi Chemical Industry Co., Tokyo).

**Accuracy.** The sensitivity of the water analyzer was  $\pm 1 \mu\text{g}$ . As the sample injected into the cell was taken so as to contain at least 20  $\mu\text{g}$  of water, the error in water concentration measurements is believed to be not more than 5%.

The Othmer-type still had been checked by operating the still with aqueous ethanol solutions and comparing the data with the literature. The agreement between the concentrations in the vapor phase was within 1.5%. As the error from the operation of the still was far less than that from the water determinations, the uncertainties in the data reported in this paper are estimated to be about 5%.



1: Air compressor 5: Trap (methanol-dry ice) 8: Othmer-type still  
2: Oil separator 9: Hygrometer  
3: Silica gel tube 6: Dry box 10: Rubber gauntlet  
4: Rotameter 7: Magnetic mixer 11: Sample box

Figure 1. Schematic diagram of experimental apparatus.

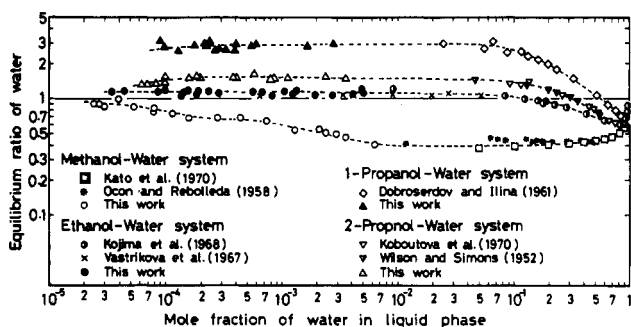


Figure 2. Equilibrium ratio of water in alcohols.

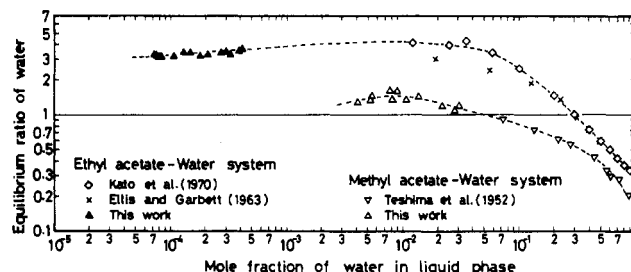


Figure 3. Equilibrium ratio of water in esters.

## Results and Discussion

Equilibrium data are listed in Table I. In the table, the equilibrium ratio ( $K$ ) is the ratio of the mole fraction of water in the vapor phase ( $y$ ) to that in the liquid phase ( $x$ ), i.e.,  $K = y/x$ . The  $K$  values are plotted in Figure 2-4 with those obtained from binary data in the literature (2-13).

According to Henry's law the equilibrium ratio of a component becomes a constant value as the concentration of the component decreases. However, as shown in Figure 2-4, the equilibrium ratio of water does not always obey the general rule. In ethanol, 1-propanol, and 2-propanol the equilibrium ratio of water becomes constant as the concentration of water decreases. In the other solvents, constant values cannot be observed within the concentration range studied. The  $K$  values approach unity in methanol and acetone.

These exceptional features of the equilibrium ratio of water in slight concentrations are noteworthy in the purification of organic solvents by distillation.

At atmospheric pressure or below, the activity coefficient of a component is represented as follows (14):

$$\gamma = y\pi/xP$$

where  $P$  is the vapor pressure of the pure component and the total pressure ( $\pi$ ) is  $101.3 \times 10^3$  Pa at atmospheric pressure. The activity coefficient of water can be calculated by the following equation:

$$\gamma = 101.3 \times 10^3 K/P$$

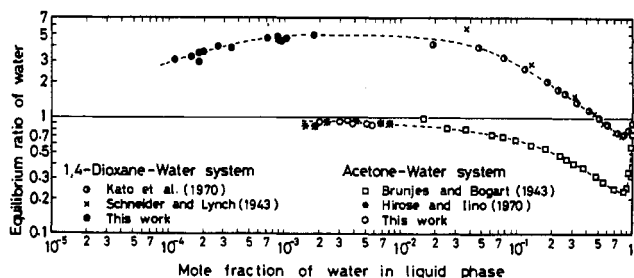


Figure 4. Equilibrium ratio of water in acetone and 1,4-dioxane.

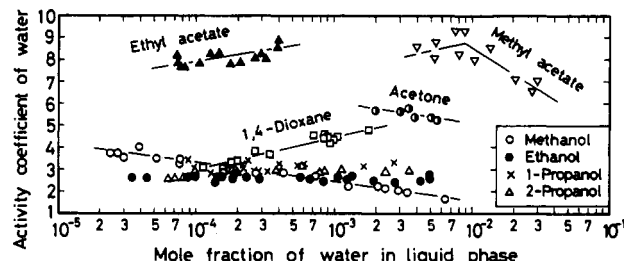


Figure 5. Activity coefficient of water.

Throughout the water concentration range investigated in this study, the boiling point of the solution is approximately equal to that of the pure solvent.  $P$  (in pascals) is the vapor pressure of water at the boiling point of the pure solvent.

The calculated activity coefficients are plotted in Figure 5. For four alcohols the activity coefficients of water are found to have similar values. The activity coefficient of water in ethyl acetate is nearly equal to that in methyl acetate.

## Acknowledgment

We thank Prof. Takesige Takahashi for his excellent suggestions concerning this experiment.

## Glossary

$K$	equilibrium ratio of water
$x$	mole fraction of water in liquid
$y$	mole fraction of water in vapor
$P$	vapor pressure of water, Pa
$\gamma$	activity coefficient of water
$\pi$	total pressure, Pa

Registry No. Methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; 2-propanol, 67-63-0; methyl acetate, 79-20-9; ethyl acetate, 141-76-6; acetone, 67-64-1; 1,4-dioxane, 123-91-1; water, 7732-18-5.

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