Densities, Viscosities, and Diffusivities in Aqueous Sodium Hydroxide–Potassium Ferri- and Ferrocyanide Solutions

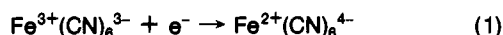**John R. Bourne,* Peter Dell'Ava, Othmar Dossenbach, and Thomas Post**

Technisch-chemisches Laboratorium ETH, CH-8092 Zurich, Switzerland

The physical properties needed to evaluate liquid film mass-transfer coefficients from accurate electrochemical measurements are tabulated as functions of temperature and composition.

Introduction

Local mass-transfer rates can be conveniently and accurately determined from the cathodic reduction of the ferricyanide ion according to the reactions

cathode

$$Fe^{3+}(CN)_6^{3-} + e^- \rightarrow Fe^{2+}(CN)_6^{4-} \qquad (1)$$

anode

$$Fe^{2+}(CN)_6^{4-} \rightarrow Fe^{3+}(CN)_6^{3-} + e^- \qquad (2)$$

operating under limiting conditions (current independent of cathode potential), so that the cathode reaction becomes diffusion controlled (1, 2). When one correlates and generalizes such mass-transfer information, accurate values of the density and viscosity of the solution as well as the diffusivity of the ferricyanide ion are required. Values recently determined in this laboratory are communicated here and refer to the following conditions:

(a) Concentrations of potassium ferri- and ferrocyanides were 10 and 20 mol m^{-3}, respectively. (The higher ferrocyanide concentration gives some protection against its anodic oxidation and, together with a larger anode than cathode area, causes the cathodic processes to become rate determining).

(b) To suppress mass transfer by ionic migration, 500–3000 mol m^{-3} of NaOH was added as indifferent electrolyte.

(c) Temperature was varied in the range 288–308 K. This variation coupled with the wide range of NaOH concentrations permitted a range of Sc from 873 to 6279 to be obtained.

Experimental Section

Temperature was determined with mercury-in-glass thermometers guaranteed to ±0.01 K and supplied by the Swiss Bureau of Standards, Bern. Water was ion exchanged, distilled, and stripped with nitrogen. NaOH–Titrisol standard solutions (Merck, West Germany) ensured accurate sodium hydroxide concentrations. Potassium ferri- and ferrocyanides (pro-analysi, Merck) were weighed to within ±1 mg and made up in 2000 mL of NaOH–Titrisol at 293 K. Concentrations were checked periodically by titration [NaOH with HCl/phenolphthalein (3), ferricyanide iodometrically with starch following neutralization of NaoH (3, 4)]. NaOH concentrations were within ±0.4% of their nominal values (500, 1000, 2000, 2500, and 3000 mol m^{-3} at 293 K), while the average of 90 ferricyanide determinations was 9.923 mol m^{-3} (S = 0.44%).

Densities were determined with pycnometers (10-mL volume calibrated to ±0.0015 mL). The maximum fluctuation in the thermostat temperature was 0.1 K. The differences in repeat runs were smaller than 0.05%.

Viscosities were measured with a KPG-Ubbelohde capillary viscometer. Calibration with water determined the temperature dependence of the capillary "constant". At a given temperature ±0.03 K, the error in the kinematic viscosity in three to five

Table I. Constants of the Density/Temperature Equation (5)

c_{NaOH}, mol m^{-3}	c_1	c_2	S, %
500	1033.87	−0.331 821	0.02
1000	1055.54	−0.378 249	0.03
1500	1074.97	−0.381 381	0.03
2000	1096.53	−0.461 474	0.01
2500	1114.26	−0.442 498	0.01
3000	1131.98	−0.429 847	0.01

repeat runs was smaller than 0.1%. Dynamic viscosities were calculated from the measured kinematic viscosities and densities.

Diffusivities were deduced from limiting current measurements on a rotating disk (5). For Sc > 100, but not infinite (as assumed initially by Levich), the limiting current density is given by (6)

$$i = 0.6205zFc_f(\nu\omega)^{1/2}Sc^{-2/3}/(1 + 0.298Sc^{-1/3} + 0.14514Sc^{-2/3}) \qquad (3)$$

The rotating disk electrode type B of Riddiford (7) (central disk radius 3 mm of pure electroplated nickel, surrounded by outer Teflon disk of 14.5-mm radius in a baffled glass tank, having a diameter of 0.115 m) maintained laminar flow longer than a cylindrical type. The current vs. speed measurements should follow eq 4, with G' = 0, according to eq 3. If, however, G'

$$I = G\omega^{1/2} + G' \qquad (4)$$

deviated from zero, deactivation of the disk surface was the most likely cause (8, 9). After cleaning, G' was usually zero. The error in repeated runs was 0.1% in I. Light (10) and oxygen (11) were excluded during diffusion measurements. Figures 1 and 2 show how limiting current conditions could be well-defined: the plateau extended from some 0.2 to 1.2 V potential difference, above which hydrogen evolution occurred. The higher NaOH concentration in Figure 2 caused a higher viscosity and therefore lower currents than in Figure 1. Limiting currents as functions of $\omega^{1/2}$ at the same two NaOH concentrations are shown in Figures 3 and 4, where $G' \simeq 0$ as required. The slopes of such curves were used to evaluate from eq 3 D, which is then the integral diffusivity of ferricyanide ions at concentrations between 0 and 10 mol m^{-3} in the given medium. It was reproducible to within 0.2%. Further experimental details are available (12, 13).

Results

Density. Measured densities (kg m^{-3}) were expressed as functions of temperature (T, °C) according to

$$\rho = c_1 + c_2 T \qquad (5)$$

giving the values of c_1 and c_2 as functions of NaOH concentration, as shown in Table I. The standard error of fit (S) is also given there. The densities given in Table II were calculated from the fitted c_1 and c_2 values: comparisons with the literature are given. The addition of potassium ferri- and ferrocyanides at the low concentrations considered here resulted in an increase of around 0.6–0.7% compared to NaOH solu-
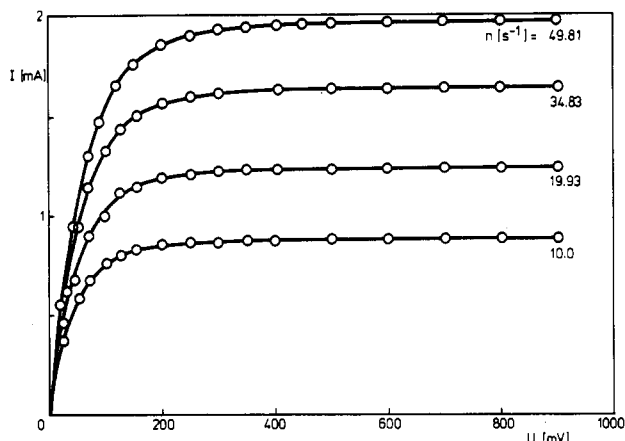
Figure 1. Current from rotating disk electrode as function of applied potential at four rotational speeds. $T = 289.1$ K, [NaOH] = 500 mol m^{-3}.
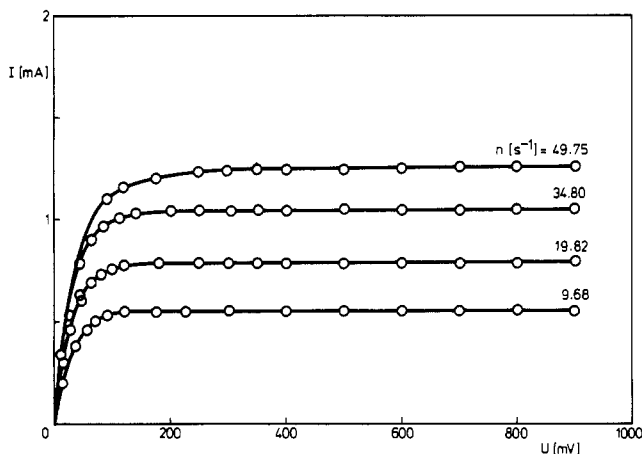

Figure 2. Current from rotating disk electrode as function of applied potential at four rotational speeds. $T = 288.9$ K, [NaOH] = 3000 mol m^{-3}.

Table II. Densities from Eq 5[a]

c_{NaOH}, mol m^{-3}	ρ, kg m^{-3}				
	15 °C	20 °C	25 °C	30 °C	35 °C
500	1028.89	1027.23	1025.57[b]	1023.91	1022.26
1000	1049.86	1047.94[c]	1046.08[d]	1044.19[e]	1042.39
1500	1069.25	1067.35	1065.44[f]	1063.53	1061.63
2000	1089.61	1087.30[g]	1084.99[h]	1082.68[i]	1080.38[j]
2500	1107.62	1105.41	1103.19[k]	1100.98	1098.77
3000	1125.33	1123.38[l]	1121.23[m]	1119.08[n]	1116.93

[a] Footnotes b-n give a comparison with the literature: Values in {} denote equimolar ferri- and ferrocyanide concentrations (mol m^{-3}). Deviation is comparison of present value to literature (). [b]+0.13% {15} (*14*). [c]+0.66% {0} (*15*). [d]−0.04% {10} (*16*); +0.13% {15} (*14*). [e]+0.65% {0} (*15*). [f]+0.06% {15} (*14*). [g]+0.68% {0} (*15*). [h]+0.08% {15} (*14*); 0.0% {10} (*16*); −0.40% {20} (*16*); +0.16% {12} (*10*); +0.28% {10} (*17*). [i]+0.70% {0} (*14*); +0.24% {10} (*17*). [j]+0.20% {10} (*17*). [k]+0.01% {15} (*14*). [l]+0.59% {0} (*15*). [m]−0.01% {15} (*14*). [n]+0.63% {0} (*15*).

tions. The literature values with equimolar ferri- and ferrocyanide concentrations of 15 mol m^{-3} are most nearly comparable with our measurements (10 and 20 mol m^{-3} of ferri- and ferrocyanides, respectively). The difference is 0.07% on average.

Kinematic Viscosity. Measured kinematic viscosities (m^2 s^{-1}) were expressed as functions of temperature (T, °C), according to

$$\nu = c_3 + c_4 T + c_5 T^2 \qquad (6)$$

giving the c values in Table III, together with the standard error

Table III. Constants for Kinematic Viscosity/Temperature Equation (6)

c_{NaOH}, mol m^{-3}	$10^6 c_3$	$10^8 c_4$	$10^{10} c_5$	S, %
500	1.7728	−4.1820	3.9022	0.14
1000	1.9361	−4.5947	4.2905	0.18
1500	2.1239	−5.0700	4.7334	0.25
2000	2.3862	−5.8440	5.5937	0.08
2500	2.6776	−6.6663	6.3109	0.14
3000	3.0521	−7.9737	7.9597	0.38

Table IV. Kinematic Viscosities from Eq 6

c_{NaOH}, mol m^{-3}	$10^8 \nu$, m^2 s^{-1}				
	15 °C	20 °C	25 °C	30 °C	35 °C
500	1.2333	1.0925	0.9712	0.8694	0.8047
1000	1.3434	1.1888	1.0556	0.9438	0.8535
1500	1.4699	1.2992	1.1522	1.0289	0.9292
2000	1.6355	1.4412	1.2748	1.1364	1.0260
2500	1.8197	1.5968	1.4055	1.2457	1.1175
3000	2.0352	1.7758	1.5562	1.3764	1.2364

Table V. Dynamic Viscosities Derived from Density and Kinematic Viscosity Equations (5) and (6)[a]

c_{NaOH}, mol m^{-3}	$10^3 \eta$, kg m^{-1} s^{-1}				
	15 °C	20 °C	25 °C	30 °C	35 °C
500	1.2689	1.1223	0.9961[b]	0.8902[c]	0.8226
1000	1.4104	1.2458[d]	1.1042[e]	0.9855[f]	0.8897[m]
1500	1.5717	1.3867	1.2276[g]	1.0943	0.9865
2000	1.7821	1.5670[h]	1.3832[i]	1.2304[j]	1.1085
2500	2.0155	1.7651	1.5505[k]	1.3715	1.2279
3000	2.2907	1.9949[l]	1.7449[m]	1.5403[n]	1.3810

[a] Footnotes b-n give a comparison with the literature: values in {} denote equimolar concentrations (mol m^{-3}). Deviation is comparison of present value to literature (); an asterisk denotes temperature interpolation. [b]+0.18% {15} (*14*); −7.63% {12} (*20*)*; +0.08% {10} (*21*)*. [c]−1.09% {12} (*20*)*. [d]+1.04% {0} (*15*). [e]−0.24% {15} (*14*); −0.43% {10} (*20*); −1.08% {10} (*16*). [f]+0.16% {0} (*15*). [g]−1.16% {15} (*14*). [h]+1.36% {0} (*15*); −0.19% {10} (*17*). [i]−1.17% {15} (*14*); +0.23% {10} (*16*); −0.49% {20} (*16*); +0.08% {12} (*10*); −4.70% {0} (*15*). [j]+1.10% {0} (*15*). [k]−1.84% {15} (*14*). [l]+1.52% {0} (*15*). [m]−2.10% {15} (*14*). [n]+0.02% {0} (*15*).

Table VI. Constants for Diffusion Coefficient/Temperature Equation (7)

c_{NaOH}, mol m^{-3}	$10^{10} c_6$	$10^{12} c_7$	$10^{14} c_8$	S, %
500	3.8180	10.191	14.983	0.20
1000	3.4165	10.013	12.363	0.18
1500	2.9106	10.055	8.188	0.22
2000	2.5448	9.535	9.278	0.16
2500	2.1992	9.193	5.731	0.30
3000	1.9631	7.070	9.676	0.23

of fit (S). Viscosities, calculated from eq 6, are given in Table IV. Measurements using 500, 2500, and 3000 mol m^{-3} of NaOH and temperatures between 286.1 and 303.7 K (*18*) agreed to within 0.43% on average with eq 6. The deviation was 1.17% for higher ferri- and ferrocyanide concentrations (each 25 mol m^{-3}) (*19*).

Dynamic Viscosity. The measurements expressed in eq 5 and 6 were used to calculate the dynamic viscosities given in Table V, according to $\eta = \rho \nu$. The literature values when ferri- and ferrocyanide concentrations were 15 mol m^{-3} come nearest to our concentrations; the average deviation is 1.1% from ref *14*. Viscosities for pure NaOH solutions are some 0.8% smaller than the values in Table V, which is understandable. Agreement with ref *10* and *16* is excellent, but limited to a few values.

Diffusivity. The temperature dependence (T, °C) of the measured diffusivities (m^2 s^{-1}) was expressed as
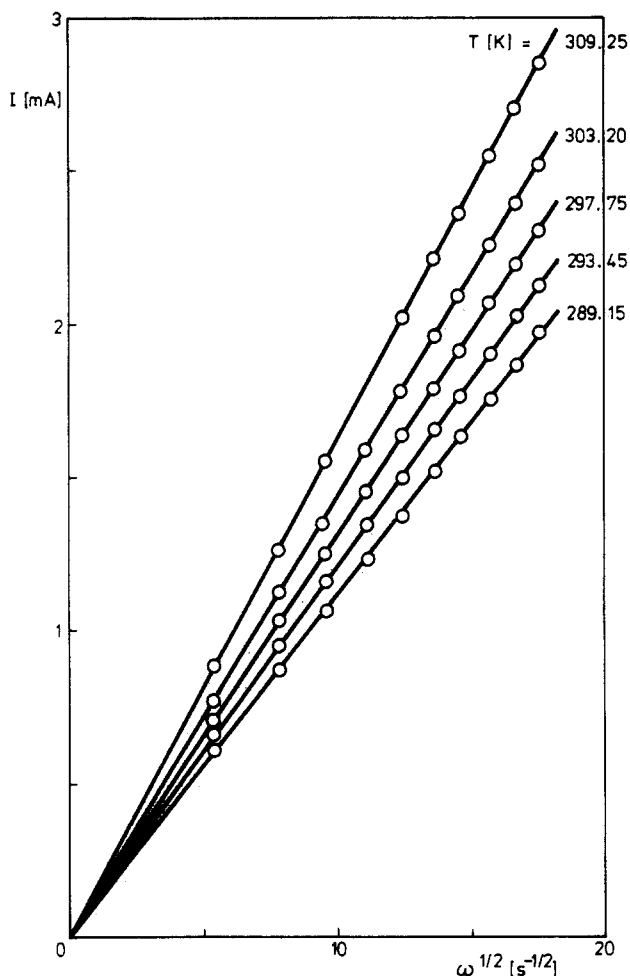
$$D = c_6 + c_7 T + c_8 T^2 \qquad (7)$$

Figure 3. Current from rotating disk electrode as function of square root of rotational speed at five temperatures. U = 600 mV, [NaOH] = 500 mol m^{-3}. Solid line = regression of eq 4.

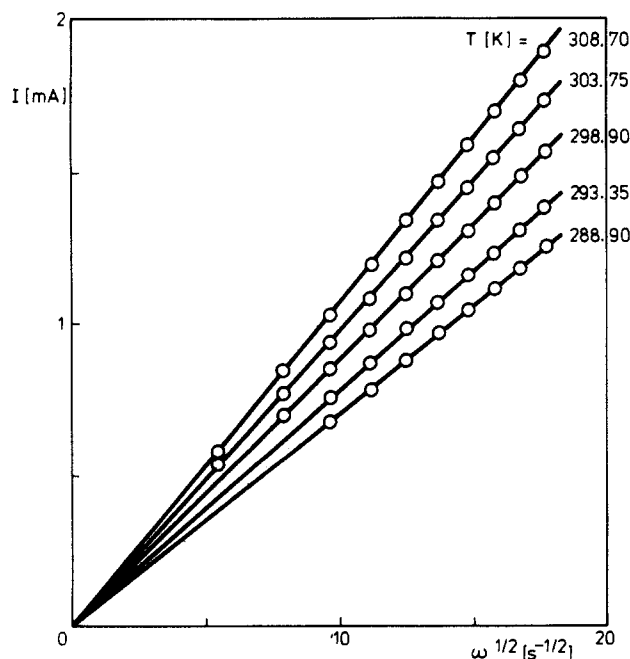**Figure 4.** Current from rotating disk electrode as function of square root of rotational speed at five temperatures. U = 600 mV, [NaOH] = 3000 mol m^{-3}. Solid line = regression of eq 4.

The values of these constants and the standard error of fit (S) are given in Table VI. Diffusivities at regular concentrations

Table VII. Diffusion Coefficients Derived from Eq 7[a]

c_{NaOH}, mol m^{-3}	$10^{10}D$, m^2 s^{-1}				
	15 °C	20 °C	25 °C	30 °C	35 °C
500	5.684[b]	6.455[c]	7.302[d]	8.224[e]	9.220[f]
1000	5.197	5.914	6.693[g]	7.533	8.436
1500	4.678	5.348	6.060	6.813	7.607
2000	4.184	4.823	5.508[h]	6.240	7.019
2500	3.707	4.267	4.856	5.473	6.119
3000	3.241[i]	3.764[j]	4.335[k]	4.955	5.623

[a] Footnotes b–k give a comparison with the literature: values in {} denote equimolar concentrations (mol m^{-3}). Deviation is comparison of present value to literature (). [b] +9.30% {10.20} (18) rde (rotating disk electrode), LV (equation with Levich equation (denominator in eq 3 is unity)). [c] +10.40% {10.20} (18) rde, LV. [d] +11.10% {10.20} (18) rde, LV; +8.39% {12} (20) rde, LV; −9.35% {10} (21) Nernst equation for infinite dilution. [e] +11.20% {10.20} (18) rde, LV; +1.15% {12} (20) rde, LV. [f] +12.90% {10.20} (18) rde, LV. [g] −1.15% {10} (20) rde, LV; +1.63% {10} (16) rde, NM (evaluation with eq 3 following Newman). [h] +3.15% {10} (16) rde, NM; +3.38% {20} (16) rde, NM; −5.02% {25} (19) Stackelberg–Cottrell method; +3.98% {10} (20) rde, LV. [i] +5.24% {10.20} (18) rde, LV. [j] +6.93% {10.20} (18) rde, LV. [k] +7.84% {10.20} (17) rde, LV.

Table VIII. Values of the Stokes–Einstein Product

c_{NaOH}, mol m^{-3}	$10^{15}D\eta/T(K)$, kg m K^{-1} s^{-2}				
	15 °C	20 °C	25 °C	30 °C	35 °C
500	2.504	2.473	2.471	2.416	2.462
1000	2.545	2.515	2.480	2.450	2.437
1500	2.553	2.531	2.496	2.460	2.463
2000	2.589	2.579	2.557	2.534	2.526
2500	2.594	2.571	2.527	2.477	2.439
3000	2.578	2.563	2.538	2.519	2.521

Table IX. Schmidt Numbers Calculated from Eq 6 and 7

c_{NaOH}, mol m^{-3}	Sc				
	15 °C	20 °C	25 °C	30 °C	35 °C
500	2170	1692	1330	1057	873
1000	2585	2010	1577	1253	1012
1500	3143	2429	1901	1510	1222
2000	3909	2988	2314	1821	1462
2500	4909	3742	2895	2276	1826
3000	6279	4718	3590	2778	2199

and temperatures, as well as comparisons with the literature, are in Table VII. In most cases the new measurements are a few percent higher. With the exception of ref *16*, previous authors evaluated D from the Levich equation (i.e., eq 3 with denominator equal to unity), thus causing their values to fall some 3–5% below those using eq 3. Such deviations might also be due to contamination or deactivation of nickel electrodes in earlier measurements. The same is true for too small a cell and for the presence of light and oxygen.

Stokes–Einstein Product. This product is defined as $D\eta/T(K)$. Table VIII contains values, determined from eq 5–7. The average value was 2.511 × 10^{-15} (±1.7%) kg m K^{-1} s^{-2}, although weak trends are evident in Table VIII.

Schmidt Number. Sc, which is defined as ν/D, is a useful quantity in mass-transfer studies and values calculated from Tables IV and VI are given in Table IX.

The densities, viscosities, diffusivities, and Schmidt numbers, presented in regression equations and tables as functions of temperature and NaOH concentrations, may be used directly to evaluate electrochemical mass-transfer measurements, e.g., to correlate liquid film mass-transfer coefficients with physical properties and operating parameters.

Glossary

c_1–c_8	constants in physical property–temperature regression, various units
c_{fi}	concentration of potassium ferricyanide in solution, mol m^{-3}

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

Greek Letters

η	dynamic viscosity of solution, kg m^{-1} s^{-1}
ν	kinematic viscosity of solution, m^2 s^{-1}
ρ	density of solution, kg m^{-3}
ω	angular velocity of rotating disk, s^{-1}

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

Atsushi Ikari, * **Yasuo Hatate, Masato Futai, and Yohichi Kurokawa**

Department of Chemical Engineering, Kagoshima University, Kagoshima 890, Japan

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 Shimazu 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