data reported by other investigators (*1, 3, 4*) for the $MgCl_2$–KCl and $MgCl_2$–$BaCl_2$ binaries are also included for comparison. Figure 4 is a ternary diagram presenting the density at 800° C. as a function of composition.

DISCUSSION

The density data for pure KCl are in excellent agreement with those of Yaffee and Van Artsdalen but are slightly higher than those of Mashovetz and Lundina and Peake and Bothwell. The density data for $MgCl_2$ are also slightly higher than those of Mashovetz and Lundina. The molal volume plots for the binaries, KCl-$MgCl_2$ and $BaCl_2$-$MgCl_2$, exhibit the same general shape as that reported by other investigators and fall within their range of results.

The molal volume plots of the series of pseudobinary systems presented in Figure 3 indicate that there is a progressive transition from the KCl–$MgCl_2$ type plot to that of the $BaCl_2$–$MgCl_2$ type as the $BaCl_2$ content is increased. Indeed the convex-concave curve of the KCl–$MgCl_2$ system is still evident in the plot for the 65% KCl–35% $BaCl_2$ + $MgCl_2$ system.

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Solubility of Carbon Dioxide in Cyclohexanol, 1,2-Dibromoethane, a Mixture of 1-Chloro-2-bromopropane and 2-Chloro-1-bromopropane, and Mineral Oil

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The solubilities of carbon dioxide in cyclohexanol, 1,2-dibromoethane (ethylene bromide), a mixture of 1-chloro-2-bromopropane and 2-chloro-1-bromopropane (propylene chlorobromide), and mineral oil have been determined at atmospheric pressure in the temperature range of 20° to 50° C. For all four solvents, the solubilities decrease with increasing temperature. For cyclohexanol, the Ostwald absorption coefficient was compared with values for alcohols ranging from C_1 to C_6.

DURING the bubble-cap plate efficiency research program at the University of Michigan (1953–58), the solubilities of carbon dioxide in various solvents were needed to determine the equilibrium conditions for mass transfer experiments.

Solubility measurements were used to determine Henry's law constant. This is possible because at very dilute solutions

$$p = H \cdot c \qquad (1)$$

where p represents the partial pressure of one component in the vapor phase, c represents the concentration of the same component in the liquid phase, and H is Henry's law constant. Equation 1 can be rewritten as,

$$\frac{RT}{v} = \frac{H}{V} \qquad (2)$$

where v represents the volume of gas dissolved in the liquid phase and V the volume of the liquid phase. Equation 2 becomes,

$$\frac{v}{V} = \frac{RT}{H} = \alpha \qquad (3)$$

which is often independent of pressure.

Thus, to calculate the constant, H, it was only necessary to determine the volume of gas absorbed per unit volume of liquid at atmospheric pressure.

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APPARATUS

The equipment used to study the absorption of carbon dioxide is basically identical to other equipment already described in the literature (*7, 9*). The absorption of carbon dioxide is measured by determination of a volume change of carbon dioxide (gas) after being in contact with the solvent (liquid) at constant temperature until equilibrium is reached.

Figure 1 is a sketch of the apparatus. The main component parts are a gas buret, *G*, and an absorption flask, *C*, both located in a water jacket and connected by the stopcocks *A* and *B*. All connections between the different parts are made of capillary glass tubing. The heating mantle *M* is used during the degassing of the liquid in flask *F*. The gas buret has a capacity of 100 ml. and has 0.2-ml. subdivisions which can be read with an accuracy of ±0.1 ml. The volume of container *C* was changed according to the solubility of the gas in the solvent. A thermostatic water bath was used to maintain the temperature of the water in jackets *I* and *J* constant with maximum deviations of ±0.1° C. Thermometers T_1 and T_2 measured temperatures of the gas and liquid containers.

The equipment is clamped to a wooden frame (not shown in the figure) which is held in an upright position. The frame is mounted on wheels and can be shaken by means of an arm actuated by an a.c. motor. In this way, the liquid in *C* is forcefully shaken, and thus the liquid surface is constantly renewed. Equilibrium is normally attained after 1 to 1½ hours.

PROCEDURE

The liquid sample, to be investigated as absorbent, was introduced in flask *F*. A few liquid drops were introduced on the mercury level in the gas buret to saturate the gas with the absorbent. Once the flask was filled, the vacuum was applied through *E* and *H*, *N* being closed. The liquid was heated to ebullition until all the dissolved gases were removed. *H* was then turned in the "off" position and the vacuum pump connected to *E, B,* and *O* (*N* being closed). The pressure in *C* was lower than in *F*, and by opening *N* the liquid rose from the distillation flask and flowed into the container *C*.

After this operation, *O* was closed and the vacuum pump turned off. The gas was then allowed to flow through *D, A, B, E, H, O,* and exit at *N*. After the line was flushed with gas, the buret was connected with the carbon dioxide cylinder and filled with carbon dioxide by lowering *L*. *B* was turned to the closed position, and the gas in the buret was allowed to go through *A* to *B*. When the temperatures indicated by T_1 and T_2 were constant and nearly identical, a first reading of the gas volume was made. Then *B* was opened, and the carbon dioxide in the buret was allowed to make contact with the liquid. Carbon dioxide gas flowed into *C*, and the mercury level difference corresponded to the free space above the liquid level in *C*. Knowing the capacity of *C*, this first measurement gave the volume of the liquid present. At the end of the run, the liquid was withdrawn through *O* and *N* and weighed. The liquid volume was then calculated and checked against the previous measurement. A sampling device, *P*, consisting of a rubber cap introduced on the end of the glass tubing, was used to take samples of the equilibrium liquid by means of a hypodermic syringe. These samples were used to determine the equilibrium concentration by chemical analysis.

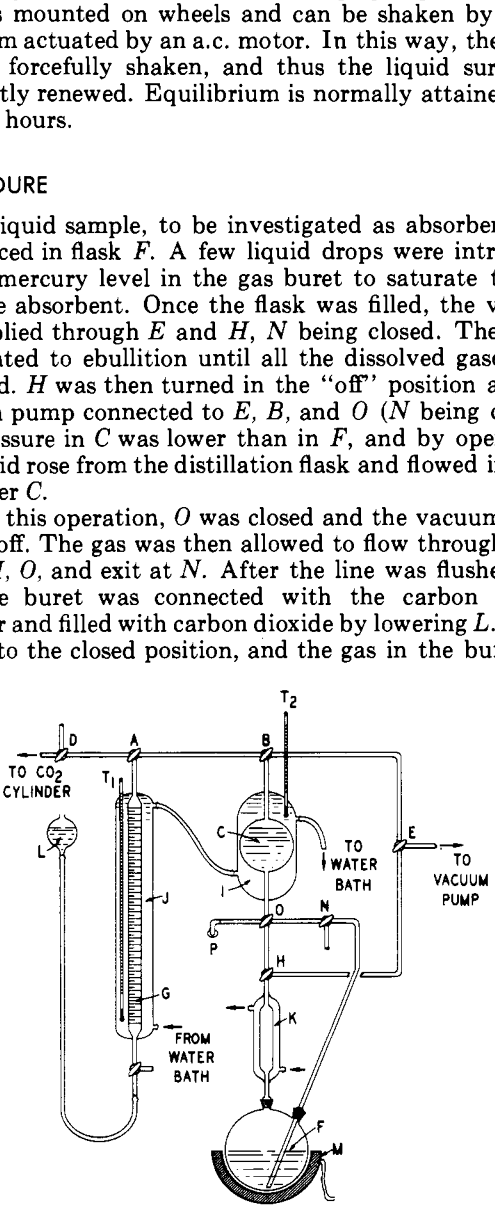

Figure 1. Diagram of the solubility apparatus

Repetitive determinations of the solubility coefficient indicated a reproducibility of about ±0.5% for all solvents except Ramol 350.

PHYSICAL PROPERTIES OF THE MATERIALS USED

Carbon Dioxide. The carbon dioxide was obtained in cylinders from the Mathieson Chemical Company. The purity is normally 99.99%. The density at standard conditions and the coefficients of expansion were taken from the International Critical Tables (*6*, pp. 3, 11).

Cyclohexanol. The cyclohexanol plus the ethylene bromide and propylene chlorobromide were technical grade, obtained from the Dow Chemical Company. Pure grade chemicals were not used because the solubilities were intended for use in mass transfer studies where the various technical grade solvents were to be employed. The Dow Chemical Company reports the physical properties for technical grade solvents in their chemical catalog. The impurities in the cyclohexanol were: phenol, maximum 0.5 wt. %, cyclohexanone, maximum 0.1 wt. %, and water, maximum 0.5 wt. %. The density and vapor pressure from the International Critical Tables (*6*, p. 29) were used in calculating solubilities.

1,2-Dibromoethane (Ethylene Bromide). The physical properties for ethylene bromide reported by the Dow Chemical Company are approximately the same values reported in the literature (*3*), indicating the ethylene bromide did not contain significant amounts of impurities. The density and vapor pressure data from the International Critical Tables (*6*, pp. 28, 216) were used in the solubility calculations.

1-Chloro-2-bromopropane and 2-Chloro-1-bromopropane Mixture (Propylene Chlorobromide). Technical propylene chlorobromide is a mixture of $CH_3CHBrCH_2Cl$ and $CH_3CHClCH_2Br$. The density of propylene chlorobromide was measured in the temperature range of 27° to 46° C. Table I summarizes the experimental results.

A boiling point of 118° C. at 756 mm. of Hg has been reported by Dewael (*2*) for 1-chloro-2-bromopropane and 1-bromo-2-chloropropane. No data are available concerning the vapor pressure at different temperatures. Considering that the ratio of the absolute temperatures at which two liquids have the same vapor pressure is constant, then:

$$T_1'/T_1'' = T_2'/T_2'' \tag{4}$$

Table I. Variation of the Density of Propylene Chlorobromide with Temperature

t, ° C.	d. G./Cc.	*t*, ° C.	d, G./Cc.
27	1.503	41.6	1.482
30.6	1.497	46	1.475
39	1.485	20[a]	1.515

[a] This point was obtained by extrapolation. To be compared with 1.531 obtained by Dewael (*2*).

By comparing a liquid of known vapor pressures at different temperatures with propylene chlorobromide, it is possible to calculate approximate vapor pressures with sufficient accuracy to be used in the calculation of Henry's law constant.

Ethylene bromide, similar in chemical structure to propylene chlorobromide, was chosen as reference liquid. At 760 mm. of Hg, we obtain:

$$391/404.4 = T_2'/T_2'' \tag{5}$$

$$T_2' = T_2''\,0.965 \tag{6}$$

For $T_2'' = 293°$ K., the vapor pressure of ethylene bromide is 11.5 mm. of Hg, $T_2' = 282°$ K. Thus, the vapor pressure of propylene chlorobromide at 9° C. is 11.5 mm. of Hg. Table II summarizes some calculated vapor pressures.

Ramol 350. Ramol 350 is a light mineral oil from Sherwood Refining Company, Detroit, Mich. Table III summarizes the density measurements obtained for the mineral oil. To calculate Henry's law constant, it was assumed that the vapor pressure of Ramol 350 is negligible in the temperature range 20° to 45° C. To further characterize Ramol 350, the viscosity of the oil was measured at several temperatures. Measurements were made with an Ostwald viscosimeter, and the results are presented in Table IV.

EXPERIMENTAL RESULTS

The experimental results obtained for the solubility of carbon dioxide in cyclohexanol, ethylene bromide, propylene chlorobromide, and Ramol 350 are presented in Table V. Partial pressures for carbon dioxide were evaluated from the vapor pressure of the pure solvent and the total pressure of 760 mm. of Hg. The Henry's law constants for the various solvents are plotted in Figure 2. In the interval of temperature studied, the Henry's law constant and the absorption coefficient (not shown) are linear functions of temperature.

Cyclohexanol. For cyclohexanol, only one measurement of α is reported in the literature (*1*). At 26° C., the value is reported to be α = 677 cc. per liter. By interpolation of the present data, we obtain α = 1010. Such a discrepancy cannot be explained. In one case, the volumetric measurement was checked by the analytical method involving the use of an aqueous solution of $Ba(OH)_2$. α was determined to be 843 and 830 for repetitive samples. Some carbon dioxide was lost in sampling, as evidenced by bubbles forming in the liquid. In spite of this loss, the solubility coefficient was found to be greater than that reported by Cauquil. The results obtained for ethylene bromide are comparable with the data published in the literature, indicating that the present volumetric measurements are reliable.

Table II. Variation of the Vapor Pressure of Propylene Chlorobromide with Temperature

t, ° C.	*P*, Mm. Hg
20	18
30	29
40	46
50	70

Table III. Variation of the Density of Ramol 350 with Temperature

t, ° C.	d, G./Cc.
20	0.872
38.6	0.861
45	0.858

Table IV. Variation of Viscosity of Ramol 350 with Temperature

t, ° C.	Viscosity, Cp.	*t*, ° C.	Viscosity, Cp.
19.4	219.5	37.8	67.9
35.8	77.8	40.5	58.9
36.6	71.9	44.4	47.9

Ethylene Bromide. The solubility data for carbon dioxide in ethylene bromide available in the literature are compared with the data from this work in Figure 3. The previous data were obtained by Kunerth (*9*) and Just (*7*). The solubility decreases with increasing temperature, and the slope, $d\alpha/dt$, is nearly the same for the three different sets of data. However, the more recent data are between 1.5 to 5% lower than the data reported by Kunerth and Just. The maximum deviation of the solubility coefficient is of the

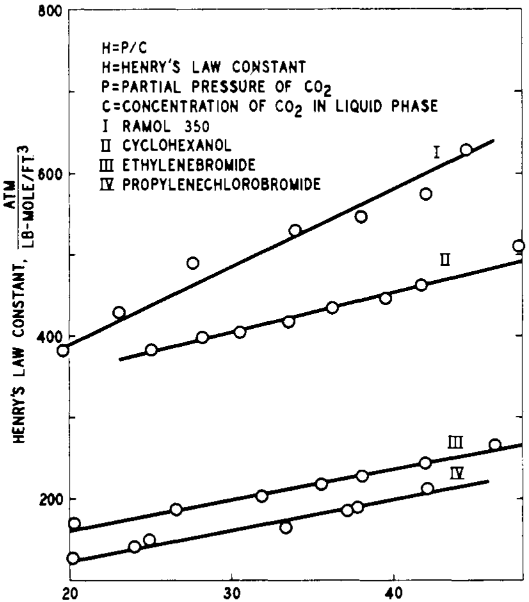

Figure 2. Solubility of CO_2 in organic solvents

Table V. Effect of Temperature on the Absorption of Carbon Dioxide by Various Solvents

Solvent	*t*, ° C.	Coefficient of Absorption, $\alpha = v/V$, Cc. of CO_2/Liter	H, Atm./ Lb.-Mole/Ft.^{3}
Cyclohexanol	25.1	1017	383
	28.3	990	398
	30.6	980	405
	33.6	957	418
	36.3	925	436
	39.6	910	448
	41.8	887	462
	47.8	830	512
Ethylene bromide	20.3	2224	170
	26.6	2067	186
	31.9	1905	204
	35.6	1789	219
	38.1	1728	228
	42.0	1617	245
	46.3	1495	266
Propylene chlorobromide	20.2	2930	128
	24.0	2660	142
	24.9	2525	150
	33.4	2325	165
	37.2	2065	186
	37.8	2025	190
	42.1	1816	212
Ramol 350	19.5	998	383
	23.1	903	429
	27.7	800	492
	34.0	764	526
	38.1	747	546
	42.1	717	576
	44.6	660	630

order of ±0.5% when considering a linear relationship between the coefficient of absorption and temperature, although most of the experimental points fall on the straight line. The reason for the difference in the experimental data when compared to Kunerth's results could be due to the presence of impurities in either solvent.

For this reason, the solubility of carbon dioxide was investigated in a reagent grade ethylene bromide from Eastman and was found to be 2160 and 2170 cc./liter at 20.5° C. The solubilities for technical and Eastman products are compared in the following tabulation with those reported by Kunerth and Just.

2165–this investigation, Eastman product
2225–this investigation, technical product
2260–Kunerth
2280–Just

The data seem to indicate that the solubility of carbon dioxide in ethylene bromide will depend on the purity of the solvent.

Propylene Chlorobromide. The solubility coefficient, α, for propylene chlorobromide decreases with increasing temperature, but the slope, $d\alpha/dt$, is higher than for all the previous solvents.

Solvent	$-d\alpha/dt$
Cyclohexanol	7.5
Ramol 350	11.8
Ethylene bromide	27.8
Propylene chlorobromide	50.8

No data are available in the literature to compare with the present results.

Ramol 350. The data for Ramol 350 can also be represented by a straight line when plotting α as a function of temperature. The deviations are of the order of ±4%, and are larger than in previous cases. This could be explained by the fact that during the operation of removal of the gas dissolved in the oil, the lighter fraction of the oil could also be removed, and since these light hydrocarbons are better solvents of carbon dioxide than the heavier parts, a decrease in dissolving power of the mineral oil could result.

The few data available in the literature include the solubility of carbon dioxide in Russian petroleum (*4*). The coefficient of solubility is reported to be 1360 and 1250 cc./liter at 10° and 20° C., respectively. The slope, $-d\alpha/dt = 11.0$, is close to the value of 11.8 obtained for Ramol 350. Kubic (*8*) measured the solubility of carbon dioxide in mineral oil and reported a value of 841 cc./liter for room temperature. The latter value is within the range of solubility (800 to 903.5) reported in Table V for temperatures of 23.1° and 27.7° C.

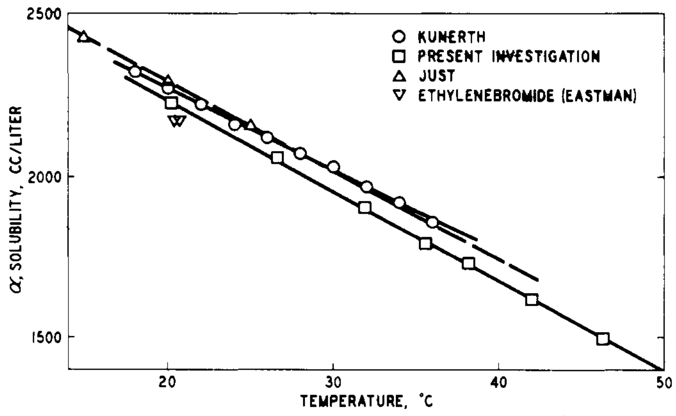

Figure 3. Solubility of CO_2 in ethylene bromide

INTERPRETATION AND DISCUSSION OF THE RESULTS

Prausnitz and Shair (*10*) have demonstrated the use of the regular solution theory from Hildebrand to predict the solubilities of a number of gases in several nonpolar solvents. Yen and McKetta (*13*) extended the regular solution theory to binary systems consisting of a nonpolar and a polar, nonassociated liquid. The data of Just (*7*) for the solubility of carbon dioxide in ethylene bromide were used in the study. Cyclohexanol is an associated polar solvent, and there is no sound basis for predicting the solubilities of gases in this type of solvent. Therefore, correlation of the solubility for carbon dioxide in various alcohols, including cyclohexanol, was attempted. In Table VI, a few physical properties are summarized for the homologs of the alcohol series, including cyclohexanol.

$$P = \frac{\epsilon - 1}{\epsilon + 2}\frac{MW}{d} \qquad (7)$$

Table IV shows that the solubility of carbon dioxide in alcohols decreases with increasing molecular weight, density, and molecular polarization. In Figure 4, α is plotted as a function of MW/d, molar volume, and P. Hildebrand (*5*) and Sander (*11*) suggest that solubility should be a direct function of the molar volume. However, the results in Figure 4 and Table VI indicate that the polarization or molecular weight give a slightly better representation of

Table VI. Solubility of Carbon Dioxide in Different Alcohols and Physical Properties of the Solvents at 25° C.

Alcohol	ϵ	α	d	MW	P	MW/d
CH_3OH	32.6	3837[a]	0.790	32	37.0	40.50
C_2H_5OH	24.3	2706[a]	0.780	46	52.2	58.97
C_3H_7OH	20.1	2498[a]	0.800	60.1	64.5	75.13
$IsoC_4H_9OH$	17.7	1849[a]	0.799	74.1	78.5	92.74
$C_5H_{11}OH$	13.9	1831[a]	0.813	88.15	88.0	108.43
$C_6H_{11}OH$	15.0	1017	0.944	100.2	99.4	100.80

ϵ = dielectric constant
α = coefficient of solubility, cc./liter
d = density, gm./cc.
MW = molecular weight
P = molecular polarization after Clausius-Mosotti

[a] Data from (*12*).

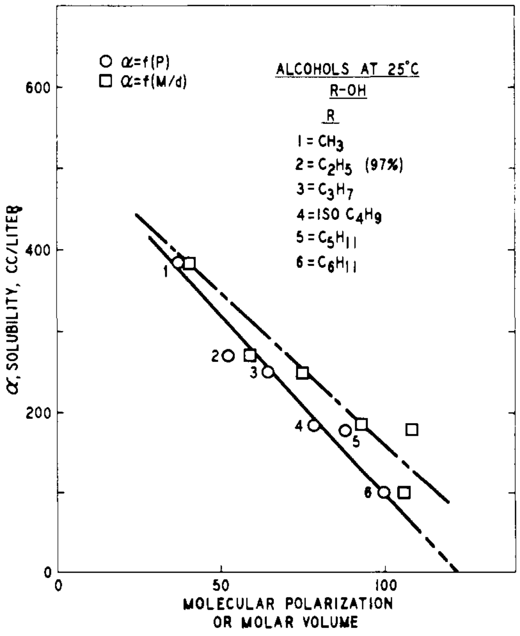

Figure 4. Solubility as a function of molecular polarization and molecular volume

Table VII. Activity Coefficients for Carbon Dioxide in Alcohols at 25° C.

Solvent	α	X_2, Mole Fraction $\times 10^3$	$f_2^L X_2$	γ_2
Methanol	3837	6.36	0.311	3.22
Ethanol	2706	6.52	0.319	3.14
Propanol	2498	7.66	0.375	2.67
Isobutanol	1849	7.01	0.343	2.92
Pentanol	1831	8.10	0.396	2.52
Cyclohexanol	1017	4.42	0.216	4.62

the data. If either of these physical properties correctly represents the behavior of the solvent, it is possible to predict the solubility for an organic solvent, provided the solubilities in other homologs of similar chemical structure are known. In fact, the solubility of carbon dioxide in cyclohexanol corresponds to its extrapolated value in Figure 4. The solubility in ethanol is lower than expected and is attributed to the fact that the purity of this alcohol was only 97%. The solubility of carbon dioxide in water is much lower ($\alpha = 826$) than in alcohol, and it is very probable that the solubility in the pure alcohol would be greater than 2706 cc./liter.

The activity coefficient is the fundamental quantity of interest in studies of behavior of liquid mixtures. In Table VII, the activity coefficients are listed for carbon dioxide in the various alcohols. The activity coefficients at 25° C. were calculated by use of the following equation from Prausnitz and Shair.

$$\frac{1}{X_2} = \frac{f_2^L}{f_2^o}\gamma_2 \qquad (8)$$

Where

X_2 = mole fraction of solute

f_2^L = fugacity of the hypothetical liquid carbon dioxide at 1 atm. = 48.9 atm. at 25° C.

f_2^o = fugacity of the pure gas at 1 atm.

γ_2 = activity coefficient for the gas in solution

Although the activity coefficients for carbon dioxide in the straight chain alcohols appear to be a smooth function of molar volume, the values for isobutanol and cyclohexanol fall above the curve for the linear molecules. Therefore, it appears that the correlation of the solubility coefficient in this case would be preferred in an attempt to predict values for other solvents in a series of alcohols of straight chain, branched, or cylic structure.

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Physical Properties of Saturated Solutions of Magnesium Chloride in *n*-Propanol–Water

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DETERMINATIONS reported in this communication were conducted as part of a program of investigation of the effect of salt addition on vapor-liquid equilibrium data of binary systems.

Binary solutions of *n*-propanol–water of known concentrations were prepared. These solutions were introduced into flasks (capacity of about 17 ml.) containing sufficient weights of magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) to assure saturation. All reagents used in this investigation were analytical grade ones. The *n*-propanol was the analytical grade manufactured by J.T. Baker Chemical Co. (boiling point: 97.2° C., boiling range: 0.8° C.). It was further purified by fractionation in a multiple plate still, the first 10% distilled and a 10% residue being discarded. The physical constants (density, refractive index, and boiling point) of the purified *n*-propanol agreed with data in the literature. The distilled water was obtained from a Barnstead laboratory distillation apparatus, and its specific conductivity was between 200,000 and 600,000 ohm-cm. The magnesium chloride was Fisher Chemical Co., Certified A.C.S. F.W. 203, actual lot analysis reported on label.