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Vapor–Liquid Equilibrium Data for the Propane/-, *n*-Butane/-, Isobutane/-, and Propylene/Isopropyl Fluoride Systems at 30 and 50 °C

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This paper presents vapor–liquid equilibrium data at 30 and 50 °C for the binary systems of isopropyl fluoride + propane, propylene, isobutane, and *n*-butane. The isopropyl fluoride/butane systems exhibit positive azeotropes. The computed, equimolar Gibbs free energy for the propylene system is roughly one-half that of the three aliphatic systems.

Introduction

Hydrofluoric (HF) alkylation units are an important component of many modern refineries in upgrading the octane quality of gasoline. In some cases it is important that the propane stream leaving the HF unit be free of fluoride compounds, of which isopropyl fluoride is the major component. For designing propane–fluoride compound separation systems, we took liquid–vapor equilibrium data for isopropyl fluoride with propane, isobutane, *n*-butane, and propylene at 30 and 50 °C.

Materials Used

The hydrocarbons used were Phillips Petroleum Co. pure grade with a stated purity of 99.35 mol % or greater. The isopropyl fluoride was obtained from Armageddon Chemical, and GC analysis showed it to have a purity of at least 99.5 mol % with the major impurity being propylene. To minimize decomposition, we stored the isopropyl fluoride at 0 °C. All materials were used as received.

Standard safety procedures for handling flammable fluids were followed. However, isopropyl fluoride presented special problems because it can decompose into propylene and HF. Since basic metals catalyze the decomposition, the apparatus contained only 316 stainless-steel or glass components and Teflon gasket materials. Even so, we had slow decomposition when trying to obtain experimental data at 70 °C. Also, gas samples at 1 bar and 80 °C showed increasing propylene content over a period of several hours.

Experimental Section

A schematic diagram of the apparatus used in this work is shown in Figure 1. A 60-cm^3, windowed Jerguson cell is the equilibrium cell, and both liquid and vapor phases are recirculated by using Emco magnetic piston pumps. To ensure representative sampling of the recirculating fluids, the recirculating vapor phase is superheated to 15–20 °C above the bath temperature and the liquid phase is subcooled to ambient temperature. The cell, the magnetic pumps, and the vapor reservoir are immersed in a well-stirred, constant-temperature, silicone oil bath. Temperature stability is better than ±0.05 °C. Cell temperature is read by using a precision bulb thermometer immersed in the bath. The estimated uncertainty in the system temperature is ±0.1 °C. System pressure is measured by reading the pressure required to null a 0–1-bar differential pressure transducer which is connected to the equilibrium cell. A 0–69-bar Texas Instruments pressure gauge is used, and the estimated uncertainty in the pressure reading is ±0.03 bar.

Table I. Equilibrium Phase Compositions for the Isopropyl Fluoride/Propane System

	mole fraction propane in			mole fraction propane in	
press., bar	liquid phase	vapor phase	press., bar	liquid phase	vapor phase
		$T = 30.0$ °C			
4.07	0.0000	0.0000	9.49	0.6768	0.8062
4.49	0.0371	0.1215	9.99	0.7782	0.8595
5.14	0.0940	0.2647	10.35	0.8600	0.9058
5.66	0.1450	0.3583	10.55	0.9090	0.9372
6.33	0.2165	0.4610	10.62	0.9308	0.9507
7.66	0.3791	0.6215	10.79	0.9740	0.9810
8.34	0.4776	0.6905	10.84	1.0000	1.0000
8.75	0.5475	0.7315			
		$T = 50.0$ °C			
7.00	0.0000	0.0000	15.08	0.6850	0.7892
7.67	0.0424	0.1155	15.70	0.7650	0.8379
8.58	0.1001	0.2382	16.42	0.8698	0.9052
9.38	0.1541	0.3300	16.62	0.8986	0.9245
10.13	0.2065	0.4041	16.86	0.9434	0.9566
11.16	0.2861	0.4956	17.05	0.9752	0.9806
12.42	0.3960	0.5947	17.15	1.0000	1.0000
13.85	0.5419	0.7007			

Table II. Equilibrium Phase Compositions for the Isopropyl Fluoride/*n*-Butane System

	mole fraction *n*-butane in			mole fraction *n*-butane in	
press., bar	liquid phase	vapor phase	press., bar	liquid phase	vapor phase
		$T = 30.0$ °C			
4.02	0.0000	0.0000	3.93	0.5489	0.4698
4.06	0.0325	0.0389	3.85	0.6122	0.5183
4.08	0.0631	0.0753	3.63	0.7444	0.6293
4.11_8	0.1124	0.1246	3.49	0.8048	0.6969
4.12_3	0.1480	0.1595	3.27	0.8893	0.7991
4.13_0	0.1922	0.2002	3.21	0.9047	0.8268
4.13_1	0.2349	0.2353	3.06	0.9494	0.8940
4.12_5	0.2679	0.2613	2.93	0.9790	0.9567
4.10_8	0.3259	0.3057	2.85	1.0000	1.0000
4.03	0.4503	0.3958			
		$T = 50.0$ °C			
7.02	0.0000	0.0000	6.91	0.5337	0.4661
7.13	0.0115	0.0114	6.75	0.6111	0.5265
7.18	0.0464	0.0530	6.41	0.7195	0.6168
7.20_9	0.0916	0.0998	6.09	0.8235	0.7272
7.22_5	0.1339	0.1397	5.73	0.8869	0.8109
7.24_2	0.2177	0.2150	5.44	0.9398	0.8877
7.22_3	0.2615	0.2528	5.18	0.9759	0.9525
7.19_8	0.2997	0.2865	4.98	1.0000	1.0000
7.07	0.4362	0.3912			

Upon leaving the equilibrium cell, the vapor enters a heat-traced line which goes directly into a small valve oven kept at 15–20 °C above bath temperature. The 100-cm^3 reservoir in the valve oven provides additional vapor volume for replicate analyses of the same sample. Vapor-phase samples are taken

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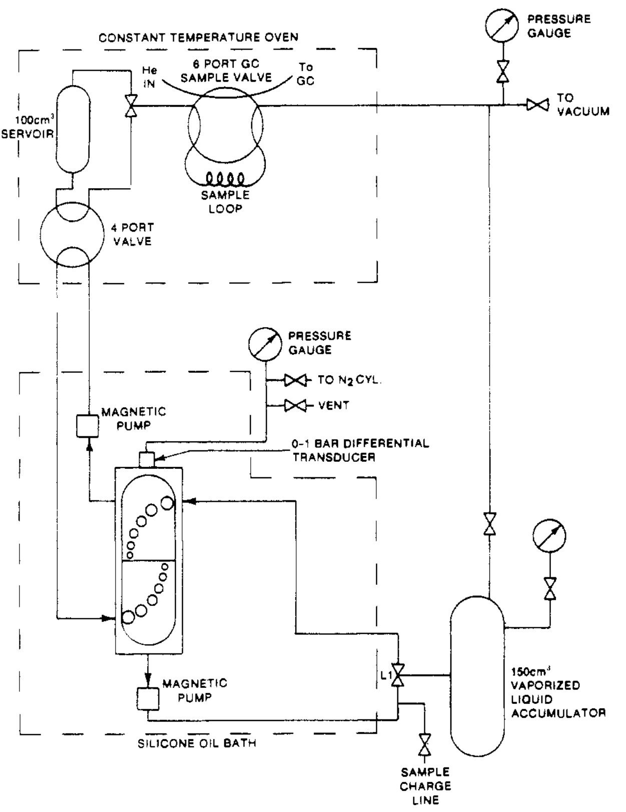

Figure 1. Schematic diagram of apparatus.

Table III. Equilibrium Phase Compositions for the Isopropyl Fluoride/Isobutane System

	mole fraction isobutane in			mole fraction isobutane in	
press., bar	liquid phase	vapor phase	press., bar	liquid phase	vapor phase
		$T = 30.0$ °C			
4.04	0.0000	0.0000	4.60	0.7003	0.6679
4.18	0.0593	0.0925	4.58	0.7420	0.7029
4.47	0.2092	0.2661	4.54	0.7731	0.7291
4.60	0.3250	0.3708	4.49	0.8097	0.7617
4.66_7	0.4530	0.4744	4.42	0.8543	0.8121
4.67_8	0.5042	0.5089	4.33	0.8969	0.8633
4.68_0	0.5447	0.5411	4.30	0.9145	0.8812
4.67_3	0.5476	0.5442	4.20	0.9526	0.9362
4.65_9	0.6152	0.5990	4.13	0.9834	0.9733
4.63	0.6631	0.6432	4.08	1.0000	1.0000
		$T = 50.0$ °C			
7.07	0.0000	0.0000	7.92_3	0.6059	0.5863
7.38	0.0813	0.1085	7.89	0.6328	0.6066
7.61	0.1600	0.2024	7.75	0.7333	0.6920
7.75	0.2305	0.2736	7.55	0.8152	0.7707
7.93_2	0.3764	0.4027	7.33	0.8803	0.8415
7.95_3	0.4343	0.4476	7.15	0.9319	0.9033
7.95_4	0.4922	0.4960	7.02	0.9602	0.9407
7.95_1	0.5250	0.5221	6.83	1.0000	1.0000
7.95_3	0.5537	0.5447			

Table IV. Equilibrium Phase Compositions for the Isopropyl Fluoride/Propylene System

	mole fraction propylene in			mole fraction propylene in	
press., bar	liquid phase	vapor phase	press., bar	liquid phase	vapor phase
		$T = 30.0$ °C			
4.08	0.0000	0.0000	9.10	0.5169	0.7402
4.36	0.0296	0.0918	9.97	0.6281	0.8032
4.51	0.0476	0.1403	11.28	0.7780	0.8881
4.91	0.0860	0.2329	11.98	0.8631	0.9289
5.65	0.1575	0.3687	12.35	0.9085	0.9519
6.27	0.2258	0.4617	12.68	0.9486	0.9733
7.27	0.3223	0.5792	12.93	0.9802	0.9895
8.16	0.4207	0.6658	13.08	1.0000	1.0000
		$T = 50.0$ °C			
7.02	0.0000	0.0000	15.16	0.5840	0.7467
8.41	0.0958	0.2196	16.41	0.6699	0.8073
9.06	0.1360	0.2968	18.07	0.7984	0.8826
9.81	0.1880	0.3766	19.44	0.9081	0.9464
11.17	0.2786	0.4952	20.04	0.9560	0.9738
12.33	0.3665	0.5792	20.27	0.9721	0.9839
13.21	0.4333	0.6359	20.60	1.0000	1.0000
14.41	0.5201	0.7053			

Table V. Temperature Dependence of Azeotropes

	isobutane/isopropyl fluoride azeotrope	
T, °C	mol % isobutane	press., bar
30	54	4.67
50	51	7.97
	n-butane/isopropyl fluoride azeotrope	
T, °C	mol % *n*-butane	press., bar
30	23	4.14
50	19	7.26

by switching the four-port valve to isolate the six-port GC sampling valve.

Liquid-phase samples are collected by cracking the three-way valve, L1, which flashes sample into a previously evacuated 150-cm^3 accumulator. Accumulator pressure is brought to roughly 1.5 bar, which provides adequate gas for purging the 0.5-cm^3 gas-chromatograph sample loops at least 20 times.

All sample analyses were made by using a Perkin-Elmer Model 3920 gas chromatograph containing a hot wire detector. The isopropyl fluoride/propane and isopropyl fluoride/propylene separations were made on a 10-m long column consisting of 19% BMEE and 1% squalane on 60/80 mesh Chromosorb P support at 35 °C. The isopropyl fluoride/*n*-butane and isopropyl fluoride/isobutane separations were made on a 15-m long column of the same material at 40 °C. Sample compositions were based on peak areas measured by a Perkin-Elmer Sigma 10 digital integrator. The GC was calibrated against approximately 50-50 mol % gas mixtures prepared by weight. The maximum uncertainty in the reported compositions is estimated to be ±0.2 mol %.

Before each isotherm was started, the equilibrium cell was evacuated and flushed 3-4 times with vapors of the hydrocarbon of interest. The vapors were then analyzed by GC; if any impurities were still present, the flushing process was repeated until all traces of impurities were gone. The cell then was filled about three-quarters full with the hydrocarbon, and the system was allowed to equilibrate thermally until the pressure did not change over a 15-min interval. The vapor phase was again analyzed to ensure that the impurity content was less than 0.01 mol % before vapor pressure readings were made.

The cell then was evacuated and flushed with isopropyl fluoride vapor, and the process for determining its vapor pressure was carried out as above. The desired amount of the hydrocarbon of interest was added, and the liquid and the vapor were circulated and equilibrated until the pressure remained constant for at least 15 min. The vapor and liquid phases then were analyzed by GC. More hydrocarbon was added and the equilibration/sampling process was repeated until the entire concentration spectrum was spanned.

Discussion of Results

Tables I-IV present the experimental data for the four systems studied. Binary systems containing isopropyl fluoride

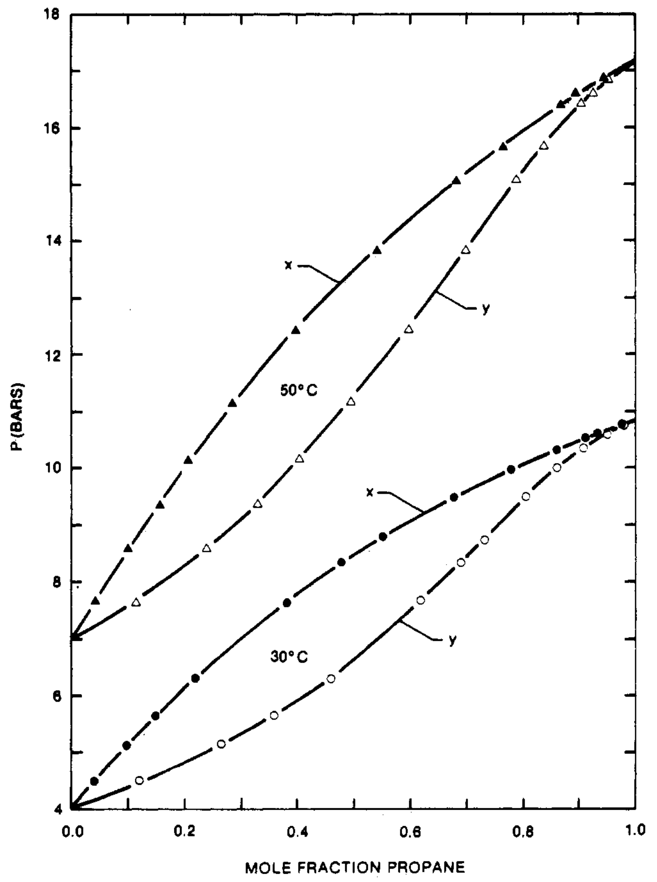

Figure 2. Pressure–composition diagram for propane/isopropyl fluoride system at 30 and 50 °C.

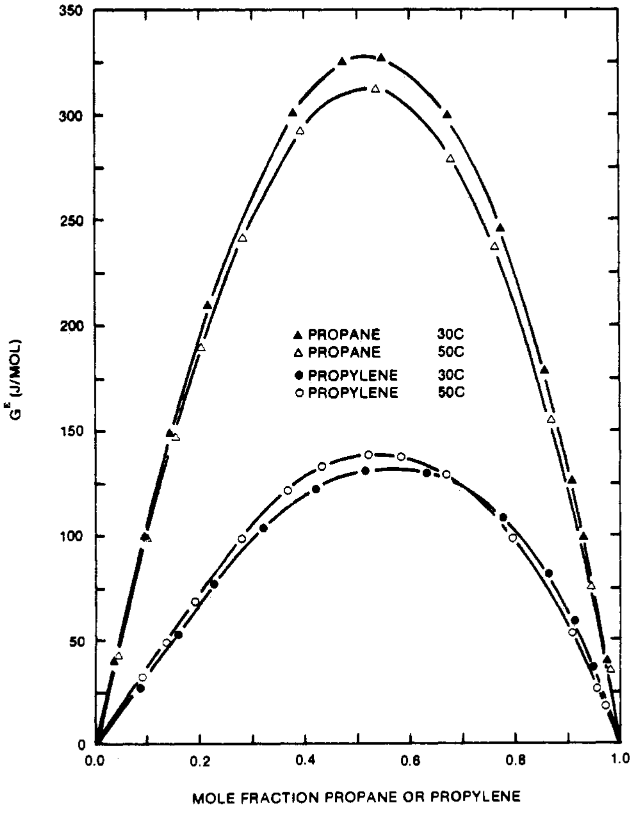

Figure 3. Excess Gibbs free energy as a function of composition for propane/- and propylene/isopropyl fluoride systems at 30 and 50 °C.

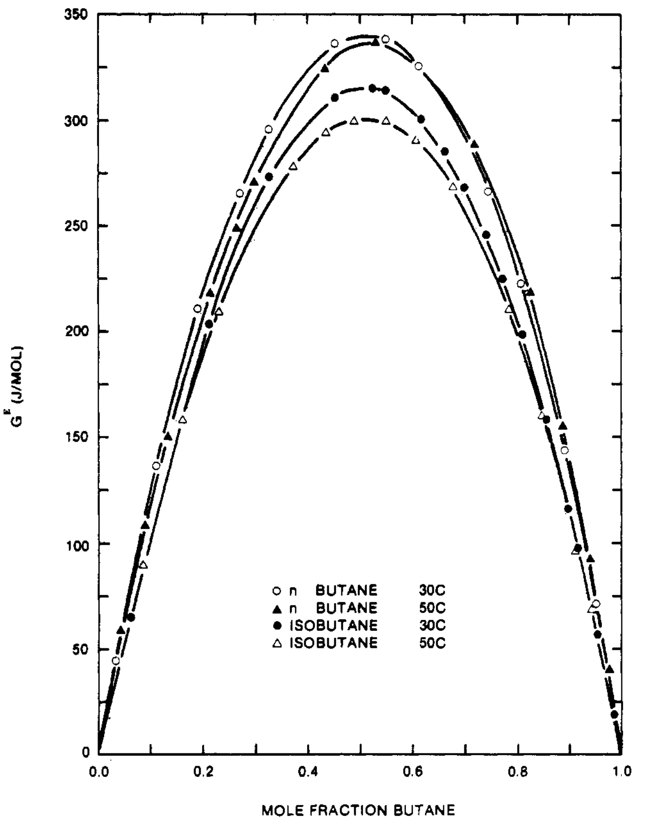

Figure 4. Excess Gibbs free energy as a function of composition for isobutane/- and *n*-butane/isopropyl fluoride systems at 30 and 50 °C.

Table VI. Parameters Used in Redlich-Kwong Equation of State

component	P_c, bar	V_c, cm^3/mol	T_c, K	Z_c	acentric factor
n-butane	37.97	255.00	425.18	0.274	0.1953
isobutane	36.48	263.00	408.14	0.283	0.1825
propane	42.50	200.50	369.82	0.277	0.1538
propylene	46.20	181.60	365.00	0.275	0.1480
isopropyl fluoride	41.75	219.00	417.00	0.263	0.1820

component	liquid phase		vapor phase	
	Ω_a	Ω_b	Ω_a	Ω_b
n-butane	0.4000	0.0780	0.445	0.0906
isobutane	0.4100	0.0790	0.442	0.0898
propane	0.4138	0.0802	0.438	0.0889
propylene	0.4130	0.0803	0.437	0.0889
isopropyl fluoride	0.4100	0.0780	0.438	0.0900

Table VII. Absolute Mean Deviation between Experimental and Calculated Vapor-Phase Compositions

system	mean Δy^a	
	$T = 30$ °C	$T = 50$ °C
isopropyl fluoride/isobutane	0.0057	0.0052
isopropyl fluoride/*n*-butane	0.0060	0.0064
isopropyl fluoride/propane	0.0030	0.0021
isopropyl fluoride/propylene	0.0046	0.0030

[a] y = mole fraction.

and either isobutane or *n*-butane form positive (i.e., pressure maximums) azeotropes. Table V lists the azeotropic composition and pressure for these systems at 30 and 50 °C. Although the isopropyl fluoride/propane system does not form an azeotrope, Figure 2 shows that it contains a "pinch point" in the propane-rich region. This makes trace removal of isopropyl fluoride by distillation extremely difficult.

The data were evaluated for thermodynamic consistency by using Christiansen and Fredenslund's method (*1*). Vapor-phase nonidealities were computed by using Chueh's modification of the Redlich–Kwong equation of state (*2*), and Table VI lists the parameters used in the equation. The binary interaction parameter, k_{12}, was set to zero for all mixtures. Table VII gives the average error between the experimental vapor-phase compositions and the thermodynamically consistent compositions. Based on these results, the data look reasonably consistent.

Figures 3 and 4 show the excess Gibbs energy calculated from the consistency test as a function of liquid composition for the systems studied. The liquid-phase nonidealities are comparable for the isopropyl fluoride + alkane systems with G^E decreasing slightly with increasing temperature. However, the isopropyl fluoride/propylene system is much more ideal and G^E slightly increases with increasing temperature. The difference in the liquid-phase behavior between the propane and propylene systems is in the affinity of the fluorine atom for the π electrons in the double bond of propylene.

Acknowledgment

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Low-Temperature Solubility of Caprolactam in Water

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The low-temperature (0 to −20 °C) solubility and a phase diagram for caprolactam (CAP) (=nylon 6 monomer) have been determined in pure water. Results show a stable eutectic with ice at −13.7 °C and 52.4 mass % CAP in the aqueous solution. Also they show a metastable eutectic at −19.3 °C with 60.3% CAP in the solution. The solid phase for the metastable eutectic is anhydrous CAP, called phase a, while that for the stable eutectic is of unknown composition, called phase b. There is also an incongruent melting point (a + b + solution) at −7 °C and 67.5 mass % CAP. The low-temperature data presented here line up well with the higher-temperature data of Puffr (*1*), although no data exist in the range 11–20 °C.

Introduction

Caprolactam (CAP) is a monomer which, when polymerized, yields nylon 6, and as such it is an important industrial chemical. The 1980 production of CAP was 9.05 × 10^8 lb (4.1 × 10^5 metric ton) in the USA. Caprolactam is made from cyclohexane and NH_3 or NO_x, but one can also start with benzene or toluene. Waste products are usually aqueous solutions containing 20 ppm to 2% CAP by mass, with several other organic and inorganic substances present in small amounts. The main inorganic salt present in these waste streams is ammonium sulfate.

It would be useful to have a process to clean up these waste streams and also to recover the CAP. Such a process would be eutectic freezing (*2*, *3*), but to design such a process requires low-temperature solubility data and a phase diagram for CAP in water. We have determined these data and report on them here. For process design one really needs the low-temperature solubilities of the complex collection of materials in a specific waste stream, but the data on CAP alone in water make a necessary starting point with which to do further work.

Seidel (*4*) gives data on the binary system $(NH_4)_2SO_4$ + water and on the ternary CAP + $(NH_4)_2SO_4$ + H_2O, but the latter are very few and limited to only two temperatures, 30 and 50 °C.

Table I. Refractive Indices for CAP Solutions in Water at about 25 °C

C, mass % CAP	n_D	$\Delta C/\Delta n$	*C*, mass % CAP	n_D	$\Delta C/\Delta n$
0	1.3327		45.84	1.4095	568
9.86	1.3484	628	85.47	1.4752	603
20.67	1.3652	643			

Experimental Methods

The melting point of pure ϵ-caprolactam is at least 69 °C, so it can be dried at 60 °C. Samples manufactured by Aldrich Chemical Co. were dried for 24 h and assumed to be anhydrous. Aldrich's stated purity is 99+%.

Dried samples were weighed, partially dissolved in distilled water with warming, and placed in a cell of about 1500-cm^3 volume, and the cell was put in a refrigerated bath, the temperature of which could be set between +10 and −30 °C, and regulated to ±0.2 °C. The cell was rocked by a mechanical rocker in the bath, and samples taken at successive intervals indicated that equilibrium was easily reached in 24 h since the liquid composition remained fixed.

Analysis for CAP was made by refractive index measurements with frequent recalibration of the curves of refractive index vs. mass % CAP in solution, particularly in the composition range to be used immediately. Checks on different samples showed the repeatability to be ±0.2% CAP.

The refractometer was an Abbé type made by Bausch and Lomb. The temperature for this determination was usually about 26 °C, and the refractive indices are temperature sensitive. To determine whether this method was suitable, we first made a curve of mass % CAP vs. n_D at about 25 °C with the results as shown in Table I.

The precision was not great, but the results above plus many others showed that this method was adequate to analyze CAP in water to ±0.19% CAP (with 90% confidence) and to ±0.26% CAP (with 95% confidence).

Each time a sample of solution from the equilibrium cell was to be analyzed, a short new calibration curve spanning the expected composition range was made with three to five standard solutions at the same temperature in the refractometer

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