Phase Diagram of the $CaCl_2$–EtOAc–H_2O System at 20° C.

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A phase diagram of the three-component system $CaCl_2$–EtOAc–H_2O at 20° C. has been made as a fundamental of the salting-out technique. The rate of hydrolysis of EtOAc in the brine phase has been found to be very small. Results concerning the water content of EtOAc coexisting with $CaCl_2$ anhydrous or dihydrate are also given.

THE TECHNIQUE of salting-out is based on the studies of salt-solvent-water systems. Although many diagrams of such systems have been determined, the exact diagram of the system calcium chloride ($CaCl_2$)-ethyl acetate (EtOAc)-water (H_2O) is still unknown. If hydrolysis of the ester proceeds to a noticeable extent, it will make the phase relation too complicated to study closely. According to Poethke (*11*), the rate of hydrolysis of EtOAc is small in pure water, but this is not confirmed in the brine phase.

The following materials are reported as the third component of systems containing $CaCl_2$ and H_2O: acetone (*5*), methyl ethyl ketone (*7*), dioxane (*1*), pyridine (*15*), phenol (*13*), phenylurea (*14*), and sodium benzoate (*2*).

Various investigators (*6*) have reported different mutual solubilities for the binary system EtOAc–H_2O, while the system $CaCl_2$–H_2O has been studied in detail by Roozeboom (*12*).

By neglecting the variation of the pressure of the vapor phase, the phase diagram of the three-component system can be illustrated on a plane at constant temperature. A conventional triangular diagram is used in this report.

MATERIALS AND METHODS

Materials used are analytical reagent grade, whose water contents are shown in Table I. EtOAc can be dehydrated to 0.000% by means of repeated passages through a tower (22ϕ × 1000mm.) filled with Molecular Sieve 4A. In this way, dry or semi-dry material is supplied as required.

The content of $CaCl_2$ in a phase sample was determined by means of a drying method such as gentle evaporation of the volatile components and later ignition of the remainder. For a very small $CaCl_2$ content, Fajans' method (*4*) was used. When no calcium was detected by this method, a particular chelatemetry (*10*) was used, which procedure made it possible to detect even 0.6 p.p.m. as calcium. Water content was determined by Karl-Fisher titration, and the content of EtOAc was obtained as the remainder.

Solubility of EtOAc in the water-rich phase was determined by Othmer's (*9*) method: a solution of $CaCl_2$ of given concentration was titrated with dehydrated EtOAc to the cloudy end point. A trace of oil-soluble dye (Brome Indigo R) was used to sharpen the end point.

For the determination of the tie line, an adequate mixture of the three components was shaken in a 20° C. bath for a week. The two separated layers, water-rich phase and ester-rich phase were analyzed. Only $CaCl_2$ was determined for the water-rich phase since the solubility curve was already known. The rate of hydrolysis of EtOAc was also measured in the water-rich phase with a pH meter.

A procedure similar to the above was used for the determination of the solubility of $CaCl_2$ in an aqueous solution of EtOAc and of the characteristic points in this system.

Table I. Water Content of Reagents

Reagent	Water Content, Wt. %
EtOAc	0.045
$CaCl_2$ anhydrous (powder)	5.197(0.34 mol. water)
$CaCl_2$ anhydrous(granular)	8.041(0.54 mol. water)
$CaCl_2$ dihydrate	28.059(2.41 mol. water)

Table II. Tie Line Data between the Ester-Rich Phase $\overline{FG}$ and the Water-Rich Phase *ED*

Ester-Rich Phase, Wt. %			Water-Rich Phase, Wt. %		
$CaCl_2^a$	EtOAc	H_2O	$CaCl_2$	EtOAc	H_2O
0.00	97.15	2.85	3.05	6.73	90.22
0.00	97.28	2.72	7.95	4.86	87.19
0.00	97.63	2.37	14.73	2.99	82.28
0.00	97.83	2.17	16.69	2.68	80.63
0.00	98.21	1.79	22.21	2.23	75.56
0.00	98.58	1.42	27.20	1.73	71.07
0.00	98.71	1.29	28.84	1.71	69.45
0.00	98.98	1.02	33.51	1.37	65.12
0.00	99.24	0.75	36.73	1.17	62.10
0.00	99.40	0.60	40.13	1.05	58.82
0.00	99.51	0.49	42.99^b	...	...
0.00	99.52	0.48	43.22^b	...	...
0.00	99.53	0.47	43.51^b	...	...

[a] No calcium detected by chelatemetry (*10*). [b] Supersaturated with $CaCl_2$ in the water rich phase.

Table III. Composition of the Characteristic Point

		$CaCl_2$, Wt. %	EtOAc, Wt. %	H_2O, Wt. %
Mutual solubility	*E*	...	8.06	91.94
	F	...	96.99	3.01
Quadruple point	*D*	42.44	1.00	56.56
	G	0.00	99.49	0.51

Table IV. Solubility of $CaCl_2$ in Aqueous Solution of EtOAc ($\overline{DH}$)

Saturated Solution of $CaCl_2$, Wt. %			Solid Phase in Equilibrium
$CaCl_2$	EtOAc	H_2O	
42.68	...	57.32	$CaCl_2 \cdot 6H_2O$ (K)
42.60	0.45	56.95	$CaCl_2 \cdot 6H_2O$ (K)
42.50	0.79	56.71	$CaCl_2 \cdot 6H_2O$ (K)

To investigate the region containing solid phases of $CaCl_2$, either the anhydrous salt or dihydrate was added to the ester-rich phase and was crushed with a glass rod. After several days, a small sample was analyzed.

Table V. pH-Value vs. Time Interval in Three Points (Doubled Respectively) on the Solubility Curve

Composition of Water-Rich Phase, %			pH-Value in Water-Rich Phase after t Minutes						k (Mean), per Second
$CaCl_2$	EtOAc	H_2O	0	10	120	1440	5760	20160	
0.0	8.1	91.9	7.40	7.50	7.51	7.10	5.61	4.40	6.0×10^{-12}
0.0	8.1	91.9	8.10	7.81	7.53	6.73	5.91	4.53	7.0×10^{-12}
13.7	3.2	83.1	7.86	7.32	6.81	6.38	5.53	4.22	6.0×10^{-11}
13.7	3.2	83.1	7.84	7.31	6.80	6.40	5.60	4.22	3.6×10^{-11}
33.4	1.3	65.3	7.98	7.49	5.80	5.42	5.06	4.78	4.1×10^{-10}
33.6	1.2	65.2	8.01	7.49	5.81	5.40	5.13	4.80	5.0×10^{-10}

Table VI. Variation of Water Content of EtOAc Coexisting with $CaCl_2$ or $CaCl_2 \cdot 2H_2O$ with Time

$CaCl_2$ Added, Grams	State[b]	EtOAc,[a] Grams	H_2O in EtOAc, % After 48 hours	After 96 hours
		Mixture I[c]		
1.5	AP	30	0.076	0.076
4	AP	30	0.064	0.076
1.5	AG	30	0.069	0.071
4	AG	30	0.057	0.061
1.5	Di	30	0.262	0.235
4	Di	30	0.184	0.141
1		Mixture II[d]		
5	AP	20	0.082	0.078
1.5	AG	20	. . .	0.065
1	Di	20	0.147	0.148
1	Di	20	0.151	0.151
	Di	20	0.151	0.145

Limiting value with anhydrous—0.07% (mean)
Limiting value with dihydrate—0.17% (mean)

[a] Water in EtOAc: Mixture I, 0.45%; Mixture II, 0.004%. [b] AP = anhydrous powder, AG = anhydrous granular, Di = dihydrate. [c] Start from higher water content near G. [d] Start from lower water content near B.

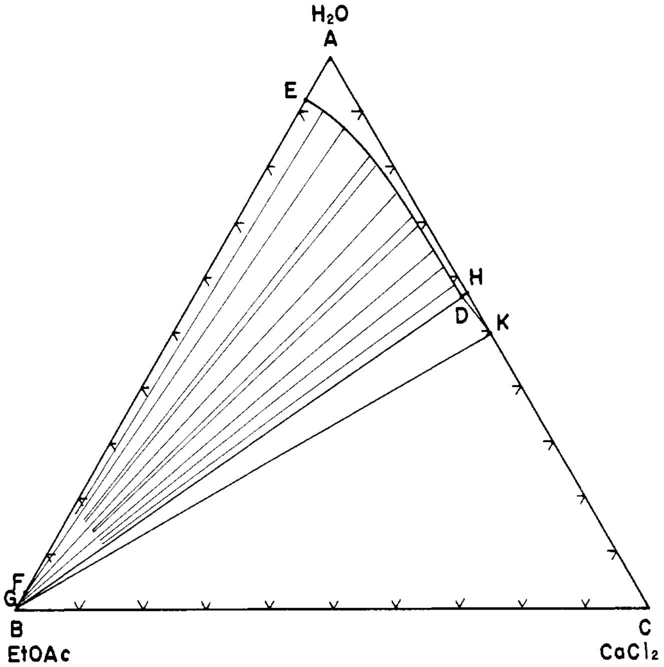

Figure 1. Phase diagram of $CaCl_2$–EtOAc–H_2O at 20° C.

RESULTS AND DISCUSSION

The solubility curve of EtOAc in the water-rich phase is drawn as a smooth line among the five series of measurements, overlapping each other. The tie line data are shown in Table II. Calcium chloride is insoluble in the whole range of the ester-rich phase. This fact was previously reported by Naumann (*8*), only in absolute EtOAc.

The compositions of the characteristic points are shown in Table III. The solubility of $CaCl_2$ in the water-rich phase is shown in Table IV. The bottom solid contains about 49.6% water which corresponds to $CaCl_2 \cdot 6H_2O$.

These results are illustrated in Figure 1. This diagram infers that EtOAc will be dehydrated up to about 99.5% without serious loss, when the saturated solution of $CaCl_2$ is recycled for extraction of the water in EtOAc.

The rate of hydrolysis of EtOAc in aqueous solution of $CaCl_2$ (in the brine phase) was very small—i.e., the rate constant k is calculated to be of the order 10^{-10} to 10^{-11} per second as shown in Table V, when it is assumed the following first-order equation is applicable

$$-d[A]/dt = k[A]$$

where $[A]$ is the concentration of EtOAc (mole per liter) and t is the time interval in seconds. Although the equilibrium constant (*3*) itself is very large, the dissociated products of EtOAc after 1 week are negligible.

The variation with time of the water content of EtOAc, coexisting with the solid phase of $CaCl_2$ anhydrous or dihydrate, is shown in Table VI. The water content approaches a limiting value. This probably suggests the presence of a subequilibrium in the water-containing EtOAc–$CaCl_2 \cdot 6H_2O$–$CaCl_2$ (or $CaCl_2 \cdot 2H_2O$) system. In this case, $CaCl_2 \cdot 6H_2O$ is considered to result from the hydration of a part of the anhydrous or dihydrate salt.

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