

FIG. 2. Complex permittivity loci of argon hydrate. Numbers on loci are frequencies in kHz.

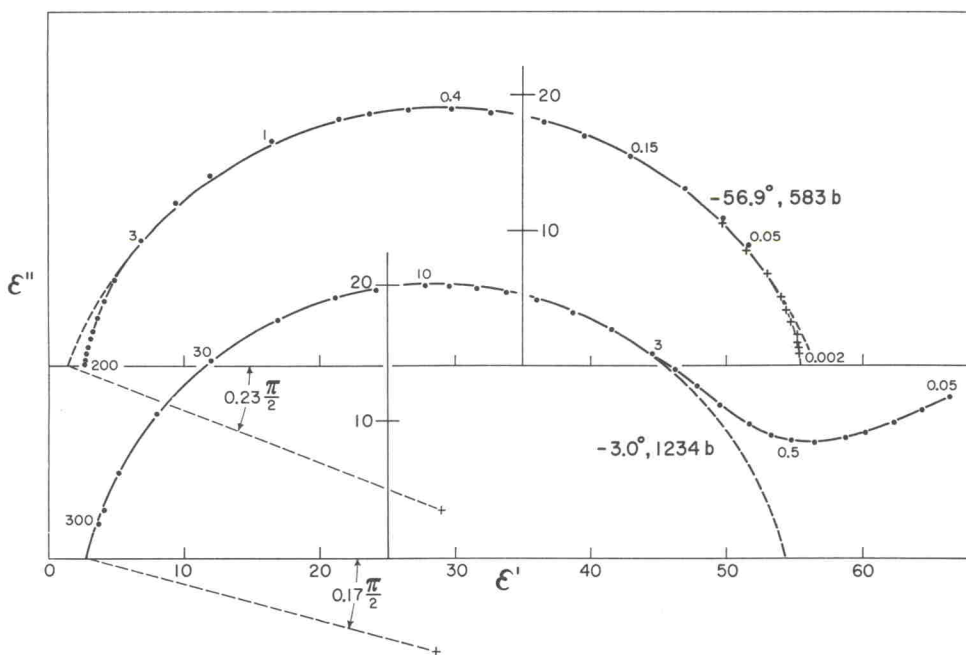


FIG. 3. Complex permittivity loci of nitrogen hydrate. Crosses refer to low-frequency bridge measurements.

TABLE I
 Representative dielectric parameters

Sample	t (°C)	P /bar	$\epsilon_0(\text{exp})$	$\tau(\text{exp})/\mu\text{s}$	α	ϵ_0 (eq. [9])	$\tau/\mu\text{s}$ (eq. [8])	$10^3 \delta$
Argon hydrate								
1	18.5	2000	54.3	8.0	.08	53.7	8.0	0
1	18.8	2985	48.3	7.3	.08	54.2	8.3	3
1	9.2	2080	41.6	9.5	.09	55.4	13.0	9
2	3.9	2010	48.7	11.4	.12	56.4	13.5	4
1	-4.5	1990	33.9	11.8	.09	58.0	21.2	18
2	-13.3	2028	45.8	20.4	.12	59.8	27.6	8
2	-22.8	2013	43.4	27.0	.13	61.9	40.6	10
2	-28.1	2000	41.4	31.8	.14	63.2	52.0	13
Nitrogen hydrate								
3	10.5	1795	~60	8.2	.11	55.0	8.2	0
2	3.0	1233	58	12.6	.14	56.1	12.6	0
1	-9.3	592	55.4	21.7	.17	58.2	23.0	1
1	-21.8	620	52.4	39.8	.20	60.9	48.1	3
2	-35.4	1235	64.6	161	.21	64.5	161	0
1	-45.6	1255	53.7	242	.20	67.2	319	5
3	-50.3	3	57.4	215	.22	67.7	317	3
3	-69.8	1	43.2	730	.26	73.8	1520	10
2	-70.8	808	67.6	1150	.23	74.8	1320	2

Some representative experimental values of static dielectric constant $\epsilon_0(\text{exp})$, α , and relaxation time $\tau(\text{exp})$ are given in Table I. Values of ϵ_∞ lay in the range 2.70 to 2.85.

At relatively high temperatures the measured static dielectric constants (e.g. 54 ± 2 for argon hydrate at 20 °C, 56 ± 2 for nitrogen hydrate at 0 °C) were quite reproducible and, despite the difference of lattice structure, similar to values (e.g. 57 ± 2 at 20 °C) estimated from earlier measurements of structure II hydrates of polar molecules (9, 10) with the dipolar contribution of the guest molecules subtracted. At lower temperatures, however, the apparent values of the static dielectric constant varied considerably from sample to sample and with sample history. They sometimes showed a decrease with decrease of temperature, especially marked for argon hydrate, rather than the increase expected. These effects undoubtedly arose from cracking or shrinkage of the samples away from the electrode surfaces. Such sample contraction affects not only the amplitude of the measured dispersion locus, but also its dependence on frequency. An analysis of contraction effects follows.

The Uniform Gap Model for Cole-Cole Behavior

The complex dielectric constant of the Cole-Cole locus is (17)

$$[1] \quad \epsilon^* = \epsilon_\infty + \Delta\epsilon [1 + (ix)^\beta]^{-1},$$

where $\Delta\epsilon$ is $(\epsilon_0 - \epsilon_\infty)$, $x = \omega\tau$, τ is the relaxa-

tion time corresponding to $1/\omega$ at the frequency of maximum dielectric absorption, and $\beta = 1 - \alpha$.

If the effect of sample shrinkage may be represented by a gap of uniform thickness a fraction δ of the interelectrode distance, in series with the sample, the measured complex dielectric constant is

$$[2] \quad \epsilon^*(\text{exp}) = k\epsilon^*[\delta\epsilon^* + (1 - \delta)k]^{-1},$$

where ϵ^* is the sample complex dielectric constant and k is the dielectric constant (assumed to have only a real component) of the medium which fills the gap. Substitution of [1] in [2] leads to

$$[3] \quad \epsilon^*(\text{exp}) = [k\epsilon_0 + k\epsilon_\infty(ix)^\beta] \times [b + a(ix)^\beta]^{-1},$$

in which $a = \delta\epsilon_\infty + (1 - \delta)k$ and $b = \delta\epsilon_0 + (1 - \delta)k$. At the low- and high-frequency limits eq. [3] reduces to

$$[4] \quad \epsilon_0(\text{exp}) = k\epsilon_0/b \quad \text{and} \quad \epsilon_\infty(\text{exp}) = k\epsilon_\infty/a.$$

Substitution for ϵ_0 and ϵ_∞ in eq. [3] gives

$$[5] \quad \epsilon^*(\text{exp}) = \epsilon_\infty(\text{exp}) + \Delta\epsilon(\text{exp})[1 + (a/b)(ix)^\beta]^{-1}$$

in which $\Delta\epsilon(\text{exp}) = \epsilon_0(\text{exp}) - \epsilon_\infty(\text{exp})$. Equation [5] has the same form as the Cole-Cole eq. [1] and describes a locus of the same shape. However, $x^\beta = \omega^\beta\tau^\beta$ has been replaced by