Contribution to the Study of the Dielectric Relaxation Process of 1-Iodoalkanes

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A study of the dielectric relaxation process of 1-iodoalkanes (from 1-iodopropane to 1-iodohexadecane) was carried out by measuring their static dielectric constants at 2 MHz and complex dielectric permittivities at 9.23 and 15.05 GHz, in the range of temperature 293.15—343.15 K. The 1-iodoalkanes are classified as belonging to an unsymmetrical distribution of relaxation times of Cole-Davidson type. Activation enthalpies for the relaxation process are obtained by fitting the data of relaxation time as a function of temperature to the Eyring equation. The influence of the aliphatic chain length in the 1-iodoalkane on the characteristic parameters of the relaxation process is discussed.

Systematic studies of the dielectric relaxation parameters for haloalkanes have been reported previously[1-5] for 1-bromoalkanes at several frequencies and as a function of the aliphatic chain length. In the case of other 1-haloalkanes, only a few suitable data are available in the literature.[1-7]

We report measurements of the static dielectric constants at 2 MHz according to the heterodyne beat method, and complex dielectric permittivities at 9.23 and 15.05 GHz, using rectangular waveguides, for eight 1-iodoalkanes (1-iodopropane, 1-iodobutane, 1-iodopentane, 1-iodohexane, 1-iodoheptane, 1-iodooctane, 1-iodododecane, and 1-iodohexadecane) in the temperature range 293.15—343.15 K.

The aim of this work is to study the influence of the aliphatic chain length of the iodoalkane molecules on their characteristic relaxation parameters.

Experimental

The liquids used were: 1-iodopropane and 1-iodobutane (Fluka AG, Buchs, better than 99 mol%), 1-iodopentane, 1-iodohexane, 1-iodoheptane, and 1-iodooctane (Fluka AG, Buchs, better than 98 mol%), 1-iodododecane (Ventron GMBH, Karlsruhe, better than 98 mol%), and 1-iodohexadecane (Merck-Schuchardt, better than 90 mol%).

Dielectric permittivity measurements were performed with a WTW Dipolmeter (model DM01), using a DFL 2 cell at a constant frequency of 2 MHz. The frequency of 2 MHz is well below the dielectric absorption frequency range of similar systems. The cells were thermostated through the outer water jacket using a water thermostat providing a temperature control to ±0.05 K.

The complex permittivities have been measured using rectangular waveguides at 9.23 and 15.05 GHz, described fully elsewhere.[8] The limits of accuracy achieved were 2% in ε' and 5% in ε''.

Refractive index measurements were carried out (at several temperatures) by means of a thermostated Abbé refractometer. Values were obtained for Na-D light. The reproducibility was as good as ±0.00002. Thermoregulation for the complex permittivity and refractive index measurements was the same as that for dielectric constant measurements.

Results

The experimental values of the complex permittivities ε' and ε'' at 9.23 and 15.05 GHz in temperature range 293.15—343.15 K are given in Table 1 along with the static dielectric constants at 2 MHz, ε_s, and ε_∞ assumed to be equal to n^2 (Figs. 1 and 2).

These results let us classify the 1-iodoalkanes as belonging to an unsymmetrical distribution of relaxation times of Cole-Davidson type[9] in which the com-

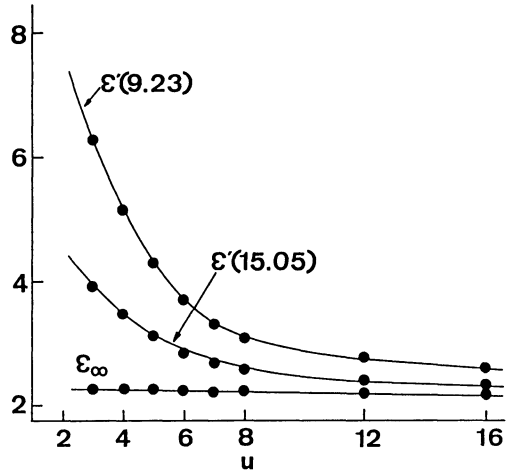

Fig. 1. Plot of ε' (9.23 GHz), ε' (15.05 GHz), and ε_∞ against the number of carbon atoms, u, at 303.15 K in 1-iodoalkanes.

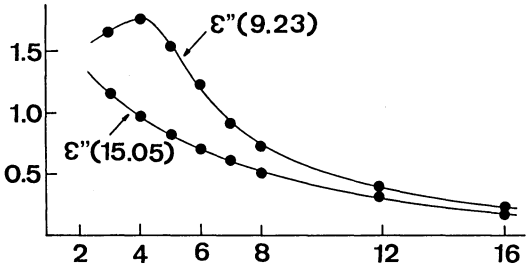

Fig. 2. Variation of ε'' (9.23 GHz) and ε'' (15.05 GHz) with the number of carbon atoms, u, at 303.15 K in 1-iodoalkanes.

Table 1. Measured Values of ε_s, ε', ε'', and ε_∞ for 1-Iodoalkanes

T/K	ε_s	9.23 GHz ε'	9.23 GHz ε''	15.05 GHz ε'	15.05 GHz ε''	ε_∞	ε_s	9.23 GHz ε'	9.23 GHz ε''	15.05 GHz ε'	15.05 GHz ε''	ε_∞
	1-Iodopropane						1-Iodobutane					
293.15	7.08	6.23	1.98	3.84	1.19	2.26	6.27	4.99	1.86	3.38	0.97	2.25
298.15	6.96	6.26	1.89	3.89	1.18	2.26	6.17	5.08	1.82	3.43	0.98	2.24
303.15	6.84	6.27	1.80	3.93	1.17	2.25	6.08	5.14	1.77	3.47	0.98	2.23
308.15	6.73	6.26	1.73	3.95	1.15	2.24	5.99	5.18	1.72	3.50	0.97	2.22
313.15	6.62	6.25	1.65	3.97	1.12	2.23	5.90	5.20	1.66	3.53	0.96	2.21
318.15	6.51	6.23	1.58	3.98	1.09	2.22	5.82	5.21	1.60	3.54	0.95	2.21
323.15	6.40	6.21	1.52	3.98	1.06	2.21	5.73	5.20	1.55	3.55	0.93	2.20
328.15	6.30	6.19	1.46	3.96	1.04	2.21	5.65	5.20	1.50	3.56	0.92	2.19
333.15	6.20	6.19	1.40	3.93	1.02	2.20	5.58	5.20	1.46	3.56	0.91	2.18
	1-Iodopentane						1-Iodohexane					
293.15	5.78	4.14	1.53	3.06	0.81	2.24	5.35	3.60	1.17	2.85	0.69	2.23
298.15	5.70	4.23	1.54	3.09	0.81	2.23	5.27	3.66	1.20	2.86	0.69	2.22
303.15	5.62	4.30	1.53	3.12	0.82	2.22	5.20	3.70	1.22	2.87	0.70	2.21
308.15	5.54	4.35	1.52	3.15	0.82	2.21	5.13	3.75	1.23	2.89	0.70	2.21
313.15	5.46	4.39	1.49	3.18	0.82	2.21	5.07	3.78	1.22	2.92	0.71	2.20
318.15	5.38	4.42	1.45	3.20	0.82	2.20	5.00	3.82	1.21	2.94	0.71	2.19
323.15	5.31	4.43	1.41	3.22	0.82	2.19	4.94	3.84	1.18	2.97	0.72	2.19
328.15	5.24	4.43	1.37	3.24	0.81	2.18	4.88	3.86	1.15	2.99	0.72	2.18
333.15	5.17	4.43	1.33	3.24	0.80	2.18	4.82	3.87	1.11	3.02	0.72	2.17
338.15	5.10	4.42	1.29	3.23	0.78	2.17	4.76	3.88	1.07	3.04	0.72	2.16
343.15							4.70	3.87	1.03	3.06	0.72	2.16
	1-Iodoheptane						1-Iodooctane					
293.15	4.99	3.29	0.89	2.73	0.59	2.22	4.72	3.15	0.75	2.66	0.52	2.22
298.15	4.92	3.30	0.91	2.71	0.59	2.21	4.66	3.11	0.72	2.62	0.52	2.21
303.15	4.86	3.32	0.92	2.71	0.59	2.21	4.61	3.08	0.69	2.60	0.51	2.20
308.15	4.80	3.33	0.93	2.71	0.60	2.20	4.55	3.07	0.68	2.60	0.52	2.19
313.15	4.74	3.35	0.93	2.73	0.61	2.19	4.50	3.07	0.67	2.60	0.53	2.19
318.15	4.68	3.38	0.93	2.75	0.62	2.19	4.44	3.09	0.67	2.62	0.54	2.18
323.15	4.62	3.41	0.92	2.78	0.63	2.18	4.39	3.12	0.67	2.65	0.55	2.18
328.15	4.57	3.44	0.90	2.81	0.64	2.17	4.34	3.17	0.68	2.69	0.56	2.17
333.15	4.52	3.49	0.89	2.85	0.64	2.17	4.30	3.22	0.68	2.72	0.57	2.16
338.15	4.46	3.54	0.86	2.89	0.65	2.16	4.25	3.29	0.69	2.77	0.58	2.16
343.15	4.41	3.60	0.84	2.93	0.65	2.15	4.20	3.37	0.70	2.81	0.58	2.15
	1-Iodododecane						1-Iodohexadecane					
293.15	3.96	2.66	0.36	2.30	0.24	2.20						
298.15	3.92	2.74	0.39	2.36	0.27	2.20						
303.15	3.88	2.80	0.41	2.41	0.30	2.19	3.50	2.57	0.23	2.29	0.19	2.18
308.15	3.84	2.85	0.42	2.45	0.32	2.18	3.47	2.59	0.24	2.27	0.19	2.18
313.15	3.80	2.88	0.43	2.47	0.33	2.18	3.44	2.61	0.25	2.27	0.21	2.17
318.15	3.77	2.91	0.44	2.49	0.34	2.17	3.41	2.63	0.26	2.28	0.21	2.17
323.15	3.74	2.92	0.44	2.40	0.34	2.17	3.38	2.64	0.26	2.27	0.22	2.16
328.15	3.70	2.92	0.44	2.49	0.34	2.16	3.35	2.65	0.27	2.28	0.23	2.15
333.15	3.67	2.91	0.44	2.48	0.35	2.16	3.32	2.66	0.28	2.28	0.23	2.15
338.15	3.64	2.90	0.44	2.47	0.35	2.15	3.29	2.69	0.28	2.30	0.25	2.14
343.15	3.61	2.88	0.43	2.45	0.35	2.14	3.27	2.71	0.29	2.31	0.25	2.14

Table 2. Relaxation Times, τ_0/ps, Calculated from Present Data

1-Iodoalkane	$\tau_0(T/\mathrm{K})$/ps										
	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15
1-Iodopropane	32	31	29	29	28	28	28	27	27		
1-Iodobutane	34	31	29	28	27	26	26	25	24		
1-Iodopentane	44	40	37	34	32	31	29	29	28	28	
1-Iodohexane	60	53	48	44	41	38	36	34	33	32	32
1-Iodoheptane	78	71	66	60	56	52	48	45	42	39	36
1-Iodooctane	90	93	94	91	85	79	72	65	57	51	44
1-Iodododecane	326	243	191	157	134	118	108	99	93	88	82
1-Iodohexadecane			610	538	456	381	312	259	215	180	149

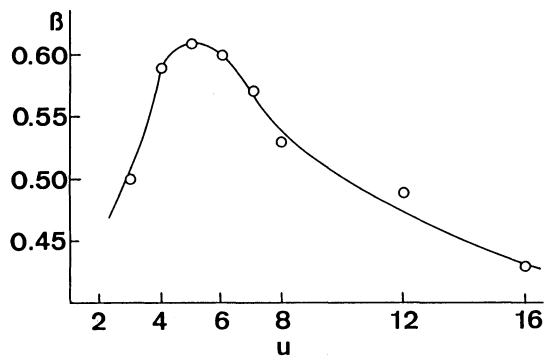

Fig. 3. Variation of β parameter with the number of carbon atoms, u, at 303.15 K in 1-iodoalkanes.

Table 3. Eyring Enthalpy of Activation Associated to the Dielectric Process of 1-Iodoalkanes

1-Iodoalkane	ΔH_E/kJ mol^{-1}
1-Iodopropane	0.8
1-Iodobutane	3.5
1-Iodopentane	5.7
1-Iodohexane	7.8
1-Iodoheptane	10.1
1-Iodooctane	9.8
1-Iodododecane	19.3
1-Iodohexadecane	28.4

plex dielectric permittivity is given by

$$\varepsilon^*=\varepsilon_\infty+\frac{\varepsilon_s-\varepsilon_\infty}{(1+j\omega\tau_0)^\beta} \quad (1)$$

where τ_0 is the value of the most probable macroscopic relaxation time and β the characteristic parameter of the distribution. In Fig. 3 the values of β are plotted against the number of carbon atoms, u, in the molecule of iodoalkane. The obtained results for τ_0 are given in Table 2.

Eyring rate equation was used to study the variation of relaxation times with the temperature

$$\ln(\tau_0 T)=\ln\frac{h}{k}-\frac{\Delta S_E}{R}+\frac{\Delta H_E}{RT} \quad (2)$$

were ΔH_E and ΔS_E are the most probable enthalpy and entropy of activation associated to the dielectric process. The values of ΔH_E are listed in Table 3.

Discussion

Figures 1 and 2 show a plot of the complex permittivities ε' and ε'', respectively, at 9.23 and 15.05 GHz, as a function of the chain length of 1-iodoalkane. As it happens with ε_s, the slopes are higher for 1-iodoalkanes of short chain and, from 1-iodooctane up, they tend to the value of ε_∞. On the other hand, a noticeable influence of the length of chain on the dielectric behavior of a molecule in the region of low frequency is observed, although that influence decreases more and more with increasing frequency and it finally becomes hardly significant.

The influence of number, u, of carbon atoms in 1-iodoalkane on the parameter of distribution, β, is illustrated in Fig. 3. As can be seen, β increases at first with u, shows a maximum value between 1-iodobutane and 1-iodohexane, and then diminishes for larger 1-iodoalkanes. This characteristic behavior of β might be put down to an effect of the high mass of I atom. For 1-iodoalkanes with short aliphatic chain the heteroatom represents a high proportion of the molecular mass, but for progressively longer chains, the center of mass moves increasingly away from I atom. This means that the dielectric behavior of short-chain 1-iodoalkanes is basically determined by both volume and mass of I atom, while for longer molecules the hydrocarbon chain exerts a more significant influence.

As Table 2 shows, relaxation time, τ_0, becomes greater as the chain-length increases, which can be imputed to a parallel increase of both viscosity, and molecular mass and volume. Molecules will move slower with increasing length of their aliphatic chains, leading to increasing values of τ_0. 1-Iodododecane and 1-iodohexadecane show a rather extreme behavior as their freezing points lie very close to our experimental temperature and therefore their molecules will move very slowly; with increasing temperature, rapidly decreasing values of τ_0 are expected, as it, in fact, happens.

A similar explanation emerges from observation of the values of ΔH_E. Attributing the unusual behavior of 1-iodododecane and 1-iodohexadecane to a "quasi-crystalline" structure, ΔH_E changes almost lineary with the length of a 1-iodoalkane between $3 \leqq u \leqq 7$, as if the contribution to ΔH_E by each carbon atom (or each $-CH_2-$ group) were constant. The value for 1-iodooctane seems to be the beginning of a constancy of ΔH_E; however, in the absence of any experimental results concerning molecules between $8<u<12$, no definitive conclusion about that is permitted.

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