EXCESS ELECTRON TRANSPORT AND ELECTRON-ION RECOMBINATION IN NONPOLAR CONDENSED MEDIA

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We have been studying the behavior of excess electrons in nonpolar condensed media, especially their transport mechanism and reactivity, by using an X-ray pulse radiolysis method[1-4] In our previous work, following information has been obtained: (1) on the phase transition from liquid to solid, electron mobility (μ_e) increases in neopentane[1] and tetramethylsilane[2] with larger μ_e than about 10 cm^2/V·sec in liquid states, and decreases in cyclohexane[3] with smaller μ_e than about 1 cm^2/V·sec in liquid state; (2) electron-ion recombination reaction may be diffusion controlled in the range of μ_e from about 0.09 to 160 cm^2/V·sec, because the observed rate constant (k_r) was found almost to agree with the values (k_D) estimated by the reduced Debye equation[1,2,4]

$$k_D = \frac{4\pi e}{\varepsilon} \mu_e \ ,$$

where e is the electron charge and ε is the dielectric constant. We report here the effect of phase change from liquid to solid on μ_e values in isooctane[5] and in methane, and k_r values in gaseous, liquid, and solid methane.

Isooctane shows intermediate values of μ_e (1-10 cm^2/V·sec) and methane gives the highest μ_e among hydrocarbons in their liquid states. It is, therefore, of interest to compare the effect of liquid-solid phase change on μ_e of these media with those of media mentioned above, and to investigate whether or not electron-ion recombination is diffusion controlled even in methane with much higher μ_e value than 160 cm^2/V·sec.

Electron current signal was obtained on irradiation of the samples by a few nsec pulsed X-ray from Febetron 706 under dc electric field. The signal was analyzed by the decay curve analysis method[1,2,4] in methane and partly in liquid isooctane, and the peak current method[3] in solid and partly in liquid isooctane.

On the phase transition from liquid to solid, μ_e increases in methane (fig. 1), which is the similar feature to those for neopentane and tetramethylsilane. In the case of isooctane, on the other hand, μ_e dose not show the significant change on phase transition (fig. 2).

Fig. 3 shows the density dependence of k_r in methane. The value of k_r obeys the reduced Debye equation in solid methane, but not in liquid and gaseous methane (fig. 4). The deviation from the reduced Debye equation is larger in gas phase than in liquid phase, which is probably related to the efficiency of excess-energy loss of electrons within the reaction radius of electron-ion recombination.
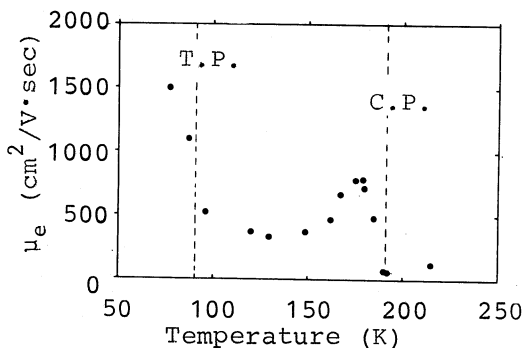
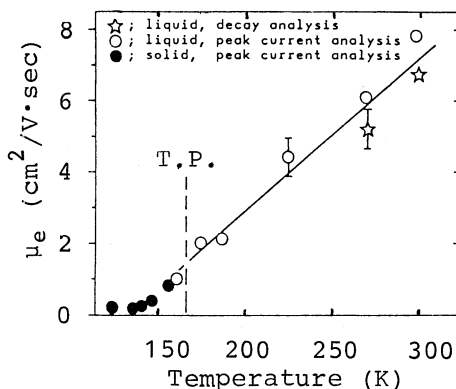Fig. 1 Temperature dependence of μ_e in methane. T.P.;triple point, C.P.;critical point.

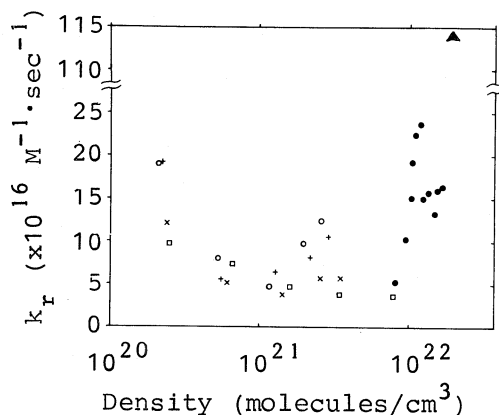Fig. 2 Temperature dependence of μ_e in isooctane.

Fig. 3 Density dependence of k_r in methane. Solid ▲ ; liquid ● ; gas ○ (285 K), + (254 K), × (222 K), □ (193 K).
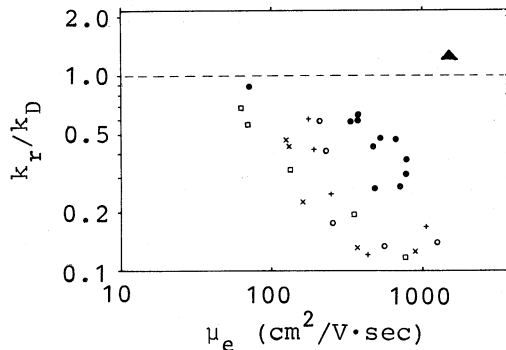

Fig. 4 Plots of k_r/k_D vs μ_e in methane. Symbols are the same as in fig. 3.

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