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LETTER

MAXIMUM MOBILITY OF EXCESS ELECTRONS IN INSULATING MOLECULAR FLUIDS, RELATED TO POLARIZABILITY AND SHAPE

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In liquids of spherical molecules (Ar, Kr, Xe, CH₄) the mobility of thermal electrons passes through a maximum at a density near 1×10^{28} molecule/m³. The ratio $R_{\mu n}^{\max}$ of the maximum mobility to the mobility in the gas phase, normalized for density, correlates strongly with the isotropic molecular polarizability α . The value of $R_{\mu n}^{\max}$ decreases with decreasing sphericity of the molecules.

KEY WORDS: Polarizability, molecular volume, shape.

1. INTRODUCTION

There is a growing body of data on the mobility μ of excess electrons injected into a variety of insulating molecular fluids, and the dependences of the mobilities on the molecular shape and on the density and temperature of the fluids^{1–8}. Figure 1 shows typical changes of the density-normalized mobility μn as the molecular number density n is increased from that of the normal gas to that of the normal liquid; for spherical molecules the relative mobility typically increases on going from the gas to the liquid, and for nonspherical molecules the relative mobility decreases. The spherical-molecule type curve applies, for example, to Xe^{2a} and CH₄³, whereas the nonspherical-molecule type curve applies to *n*-C₅H₁₂⁸; the curve for C₂H₆ is intermediate, with a small hump in the liquid region⁴.

It will be convenient, in what follows, to work with the scaled mobility $(\mu n)/(\mu n)_{\text{gas}} = R_{\mu n}$, where $(\mu n)_{\text{gas}}$ is labelled in Figure 1. This ratio is the focus of the present letter. More specifically, we shall be concerned with its maximum value $R_{\mu n}^{\max}$ and the way this varies as the molecular shape is changed. Table 1 therefore records values of $R_{\mu n}^{\max}$ and the corresponding density n_{max} and temperature T_{max} for spherical molecules.

In Figure 2 we examine the way in which $R_{\mu n}^{\max}$ depends on the isotropic polarizability α ⁹. While the dashed straight line represents an oversimplification, its

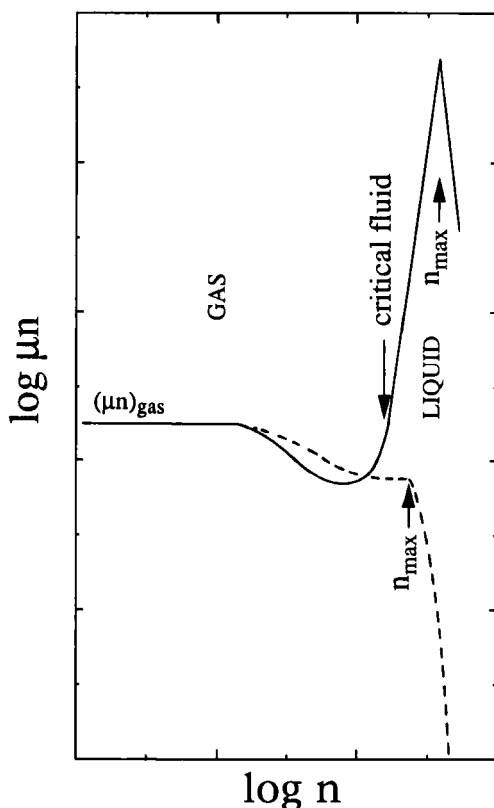


Figure 1 Schematic log-log plots of density-normalized mobility μn of thermal electrons in a fluid against molecular number density n , for sphere-like molecules (—) and chain-like molecules (---).

equation is

$$R_{\mu n}^{\max} \approx e^{2\alpha}, \quad (1)$$

where 2\AA^{-3} is the slope of the line. As a check we have recorded values of $R_{\mu n}^{\max} \exp(-2\alpha)$ in Table 1; the variations in $R_{\mu n}^{\max}$ are in this way reduced by an order of magnitude.

Table 1 Thermal electron mobility maxima in liquids of spherical molecules, relative to mobility in the gas phase.

	Ar^a	Kr^b	Xe^c	CH_4^d
$\alpha(\text{\AA}^{-3})^e$	1.64	2.49	4.01	2.60
$(\mu n)_{\text{gas}}(10^{24} \text{ molec/V.s.m})$	60	11	3.0	22
$T_{\text{gas}}(K)$	120	160	200	160
$(\mu n)_{\text{max}}(10^{24} \text{ molec/V.s.m})$	1900	6500	7300	1100
$T_{\text{max}}(K)$	147	170	223	178
$n_{\text{max}}(10^{27} \text{ molec/m}^3)$	12	14	12	11
$R_{\mu n}^{\max f}$	32	590	2430	50
$R_{\mu n}^{\max} \exp(-2\alpha)^g$	1.2	4.0	0.8	0.3

a: Ref. 5. b: Refs. 6 and 7. c: Ref. 2a. d: Ref. 3. e: Ref. 9.

f: $R_{\mu n}^{\max} = (\mu n)_{\text{max}} / (\mu n)_{\text{gas}}$. g: α in units of \AA^{-3} .

Figure 2 indicates that for these spherical molecules the dominant variable in determining $R_{\mu n}^{\max}$ is the isotropic molecular polarizability. Since α is known to correlate with molecular volume, another way of describing Figure 2 is to say that the maximum mobility $(\mu n)_{\max}$, scaled by the dilute gas value $(\mu n)_{\text{gas}}$, correlates strongly with molecular size for spherical systems.

However, when we turn to non-spherical molecules, such as ethane, C_2H_6 , or to *n*- and *neo*-pentane, not only is molecular size important, but also molecular shape. Thus, we have collected in Table 2 similar data to that recorded in Table 1, but for molecules with more complex molecular shapes. If we take the mean polarizability $\bar{\alpha}$ for the example of ethane, the product $R_{\mu n}^{\max} \exp(-2\bar{\alpha}) = 2 \times 10^{-4}$: quite different

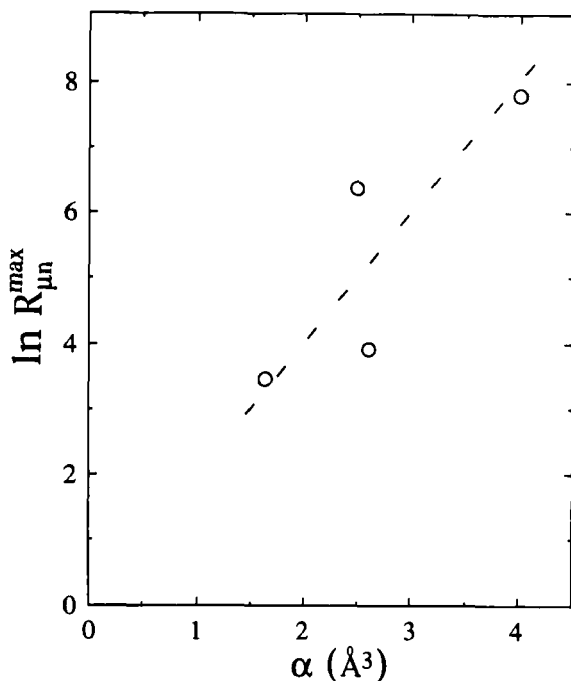


Figure 2 Variation of $\ln R_{\mu n}^{\max}$ with polarizability α for spherical molecules. Data from Table 1.

Table 2 Thermal electron mobility maxima in liquids of less spherelike molecules, relative to mobility in the gas phase.

	$C_2H_6^a$	$C(CH_3)_4^b$	$n-C_5H_{12}^c$
$\bar{\alpha}(\text{\AA}^3)^d$	4.4	9.8	9.8
$(\mu n)_{\text{gas}}(10^{24} \text{ molec/V.s.m})$	31.0	3.3	10.0
$T_{\text{gas}}(K)$	285	~350	~350
$(\mu n)_{\max}(10^{24} \text{ molec/V.s.m})$	31.0	70	4.0
$T_{\max}(K)$	302	~400	~450
$n_{\max}(10^{27} \text{ molec/m}^3)$	5.7	3.5	2.7
$R_{\mu n}^{\max e}$	1.0	21.0	0.4
$R_{\mu n}^{\max} \exp(-2\alpha)^f$	2×10^{-4}	6×10^{-8}	1×10^{-9}

a: Ref. 4. b: Refs. 2b and 8. c: Ref. 8. d: Mean polarizability, Ref. 9.
e: $R_{\mu n}^{\max} = (\mu n)_{\max} / (\mu n)_{\text{gas}}$. f: α in units of \AA^3 .

from the values of this same product in Table 1 for spherical molecules. This immediately highlights the importance of molecular shape in determining the maximum mobility $(\mu n)_{\max}$ in systems composed of non-spherical molecules (see Fig. 1).

It will be of interest in the future to assess, from both experiment and theory, the role of the polarizability asymmetry α_a , defined in terms of polarizability components α_1, α_2 and α_3 by

$$\alpha_a = \frac{1}{\sqrt{2}} \sqrt{(\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2}. \quad (2)$$

To date there are too few data to make possible a quantitative assessment of the importance of this shape parameter. However, an excess electron can not sense more than two C-C bonds in series¹⁰, which means that the influence of molecular shape on the maximum mobility involves a more complex molecular shape parameter than α_a .

Finally, we return to Figure 1 and point out that Cao and Berne¹¹ have modelled such a dependence by hard sphere parameters¹². In essence, they argue, starting from the Ioffe-Regel criterion for electron localization, that a more useful independent variable than the number density n in Figure 1, \bar{n} say, introduces lengths λ and d through¹¹

$$\bar{n} = n \lambda^3 d^3 \quad (3)$$

where λ is the root-mean-square de Broglie radianlength of the thermal electrons,

$$\lambda = h / \sqrt{mk_B T} \quad (4)$$

where k_B is Boltzmann's constant and m is the electron mass. The second length d is an 'effective' hard sphere radius for electron scattering.

We prefer to avoid 'hard sphere' modelling in the present context, and to define

$$n_{\text{eff}} = n \lambda^3 \{f(n)\}^2, \quad (5)$$

where the length $f(n)$ in the low density limit we expect to play the role of a scattering length [which can be either positive or negative: the sign is lost in the definition (5)]. Motivated by Eq. (5), Table 3 records $R_{\mu n}^{\max}$ together with the product

Table 3 Role of electron de Broglie radianlength.

	$R_{\mu n}^{\max}$	$\bar{\lambda}^a$ (nm/rad)	$n_{\text{max}} \bar{\lambda}$ (10^{18} molec/m ² .rad)
Ar	32	2.4	29
Kr	590	2.3	32
Xe	2430	2.0	24
CH ₄	50	2.2	24
C ₂ H ₆	1.0	1.7	10
C(CH ₃) ₄	21	1.5	5
n-C ₅ H ₁₂	0.4	1.4	4

a: Root-mean-square de Broglie radianlength (m/rad) of electrons at T_{max} : $\bar{\lambda} = h / \sqrt{mk_B T_{\text{max}}}$. This quantity was referred to in ref. 11 as the electron wavelength λ , which would have units of m/cy and require the use of h rather than \hbar .

$n_{\max} \lambda$ for the fluids listed in Tables 1 and 2. The final column shows that while $n_{\max} \lambda$ has essentially the same values of Ar, Kr, Xe and CH₄, it reduces for the other molecular fluids recorded there. This presumably reflects $\{\ell(n)\}^2$ of Eq. (5), but we shall not press the point further here.

In summary, the main achievement of the present work is to demonstrate the major influence of molecular isotropic polarizability α in determining the magnitude of the maximum mobility $(\mu n)_{\max}$, measured relative to the low density limit $(\mu n)_{\text{gas}}$, in molecular fluids built from spherical molecules. But when the building block of the fluid is a nonspherical molecule, then $R_{\mu n}^{\max}$ has an essential dependence on some shape parameter. One such is α_a in Eq. (2), but a more complex measure of molecular shape is needed. We conclude by conjecturing that, while the region around the maximum in μn against n is dominated by a single mechanism, which we believe to be long-range interaction characterized by the polarizability α for spherical molecules, the existence or otherwise of a minimum such as depicted in Figure 1 depends on a competition between two mechanisms; namely long-range interaction and fluid structure or density fluctuations. In argon⁵ and neopentane^{2b}, for example, these two mechanisms largely annul one another, and no minimum was observed. The present conclusions lead us to believe that further work, both experiment and theory, to elucidate the microscopic mechanisms responsible for the 'canonical' shape of μn against n will be fruitful.

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