Excess electron mobility in liquid Ar - Kr and Ar - Xe mixtures

Excess electron mobility in liquid Ar–Kr and Ar–Xe mixtures*

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Abstract. The mobility of excess electrons in liquified noble gas mixtures Ar–Kr and Ar–Xe has been measured as a function of the solute concentration and of the applied electric field at the normal boiling point of Ar ($T_b = 87.4$ K). The experimental results are in strong disagreement with the results of a modified *deformation potential* model, while they can be well described within the frame of reference of a *gas-kinetic* model by suitably introducing concentration dependent scattering cross sections.

1. Introduction

In many areas of physics the transport properties of excess electrons in insulating liquids are of great interest. The large number of experimental data for pure non-polar liquids has not received a completely satisfactory theoretical explanation yet. In high-mobility liquids, such as Ar, Kr, or Xe, the excess electrons are assumed to be quasifree because their mean free paths are fairly long although they move in a very dense environment of closely packed atoms which are very effective scattering centres in the gas phase [1].

Two different approaches have been pursued for the description of the observed behaviour of the electron mobility μ as a function of the liquid and thermodynamic parameters. These two models assume that the scattering processes that determine the mobility in the condensed medium are of very different natures.

In the first model, the so called *deformation potential theory*, the excess electrons are assumed to move in an instantaneous lattice made up by the atoms of the host liquid because the electron speed is much larger than that of the atoms. Therefore, the electron motion has to be described in terms of energy bands as in crystalline solids. The thermalized excess electrons occupy the bottom of a conduction band whose minimum (of energy V_0) depends on the local environment and thus on the liquid density N. The intrinsic density fluctuations modulate the electron energy at the bottom of the conduction band and these energy modulations act as a source for electron scattering [2]. According to this model electrons are scattered off long-wavelength collective modes (phonons) of the liquid. This model automatically accounts for the multiple-scattering effects that arise as a consequence

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of the wide extension of the excess electron wavefunction over a region that includes several atoms at once.

Some gross features of the experimental data are correctly described by this theory in the *single-phonon* approximation, such as the maximum of the zero-field mobility μ_0 at a density where the excess electron ground state energy V_0 is minimum. Some improvements have been achieved by including *two-phonon* scattering processes [3]. However, this approach does not consider the effect of the applied electric field that heats up the electrons and is therefore limited to the description of the zero-field mobility only.

The second approach, the so called *gas-kinetic model*, is based on the observation that the mean free paths of the excess electrons are very long and that the electric field dependence of the mobility μ in pure non-polar liquids is very similar to that in hard-sphere gases like He. Therefore, this model is based on the solution of the Boltzmann equation for the momentum distribution function of the excess electrons obtained by expanding it into Legendre polynomials about the direction determined by the electric field. The collision term in the Boltzmann equation is described within a *single-scattering* picture, i.e., a differential scattering cross section is used throughout.

While in the case of dilute gases the scattering cross section is the usual electron–isolated atom cross section that can be determined in swarm experiments, in the case of liquids, in contrast, the cross section to be used includes *many-body* effects as well as multiple-scattering effects and must therefore be determined by a fit to the experimental data. In this way, the electric field dependence of μ in liquid Ar and CH_4 has been reproduced [4] fairly well.

The two approaches cannot be reconciled with each other because the scattering mechanisms are different. In the first one the role of disorder is most important, in the second the transport properties are determined by single scattering off a single-centre effective potential. In order to clarify the actual mechanisms determining the excess electron scattering, measurements in liquid mixtures of non-polar fluids should give valuable information. Within the first model, in fact, the addition of an atomic impurity should increase the disorder inherent to the fluid because of the occurrence of concentration fluctuations in addition to density fluctuations. In the second model, the atomic solute acts as an additional scattering centre that increases the overall scattering rate of excess electrons.

For these reasons we have carried out preliminary electron mobility measurements in dilute solutions of Xe in Ar at the normal boiling point (n.b.p.) of Ar [5] where we observed a reduction of the zero-field mobility μ_0 as a function of the solute concentration x. Here we report extensive mobility measurements in liquid mixtures of Xe and Kr in Ar at the n.b.p. of Ar. We will show that the *gas-kinetic* model gives an excellent fit to the experimental data, while the *deformation potential* model modified so as to handle concentration fluctuations does not.

2. Experimental technique

We have used the well-known pulsed photoemission technique with a double-gridded drift chamber previously exploited to measure electron mobility in liquid Ar and CH_4 [6]. Technique and apparatus are described elsewhere [7]. Nearly 10^6 electrons at a time are injected into the liquid by irradiating a brass photocathode with short UV light pulse of a Xe flashlamp. The signals induced on the electrodes by the drifting electrons are fed to low-noise charge amplifiers with an integration time constant ≈ 400 μs. The mobility is calculated with an overall accuracy of $\pm 2\%$ by measuring the transit time of the electrons

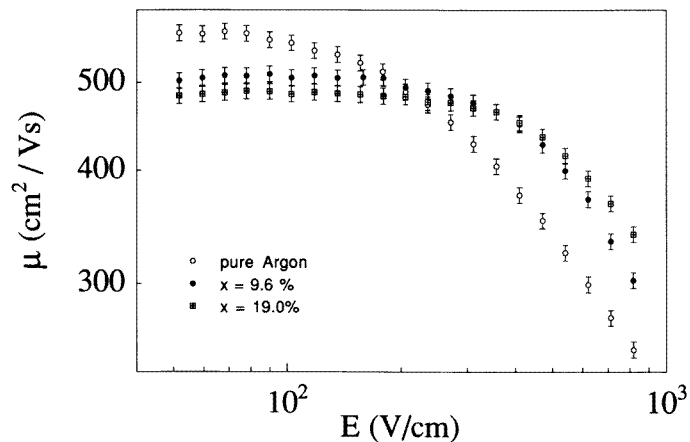**Figure 1.** Log–log plot of the electron mobility for Ar–Kr mixtures as a function of the electric field E. The Kr concentration x of the mixtures is shown.
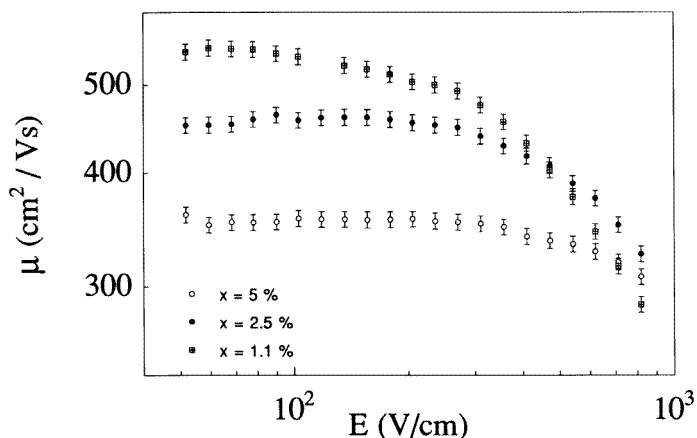

Figure 2. Log–log plot of the electron mobility for Ar–Xe mixtures as a function of the electric field E. The Xe concentration x of the mixtures is shown.

between the two grids. The cell temperature is maintained at $T = 87.4$ K by submerging it in a open liquid Ar bath. The mixtures are obtained by condensing gaseous mixtures of given nominal concentration. The purification of the condensing gases is described elsewhere [8]. The residual O_2 impurity content is estimated to be ≈ 0.5 parts per billion. At the end of the mobility measurements the mixtures were collected and subjected to gas chromatographic analysis.

3. Experimental results and analysis

We have investigated Ar–Kr mixtures up to a concentration $x \approx 30\%$ and Ar–Xe ones up to a concentration $x \approx 5\%$. These values correspond to the solubility limits of Kr and Xe, respectively, for $T = 87.4$ K. In figure 1 we show the mobility of excess electrons as a function of the electric field E for some of the Ar–Kr mixtures. In figure 2 we show the same
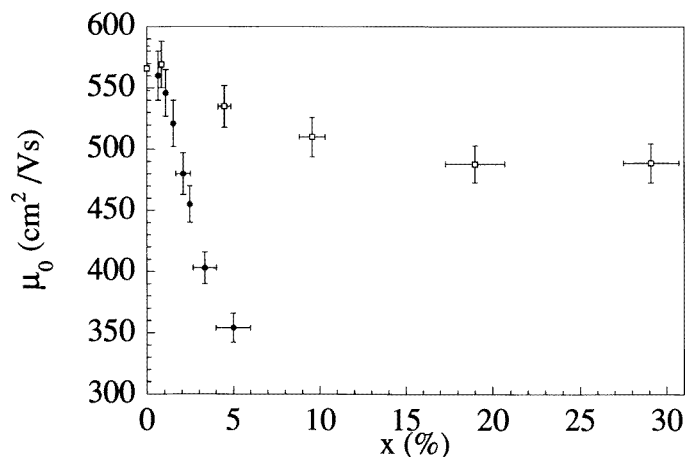
Figure 3. Zero-field mobility μ_0 for the mixtures Ar–Kr (open squares) and Ar–Xe (closed circles) as a function of the solute (Kr or Xe) concentration x.

for the Ar–Xe samples. The behaviour of μ as a function of E is similar for each mixture. μ shows a low-field region, the so-called thermal region, where μ is independent of E. At these low field values the electrons do not gain a significant amount of energy from the electric field and their mean energy is nearly thermal. At larger fields the electrons become epithermal by gaining energy from E and scatter more frequently so that μ decreases with increasing E. It can be seen from figures 1 and 2 that the zero-field value of the mobility μ_0 decreases with increasing concentration x of the solute. The decrease is much greater for the Ar–Xe mixtures than for the Ar–Kr ones.

In figure 3 we show the thermal value of the mobility μ_0 as a function of the mixture concentration. The decrease of μ_0 with increasing concentration x means that the addition of an atomic solute increases the overall scattering rate of the excess electrons. This is also evident in the enlargement of the electric field range where electrons are still in thermal equilibrium with the host fluid. Similar observations were carried out in liquid mixtures of non-electronegative molecular impurities in rare gas liquids and TMS [9].

4. Gas-kinetic model

According to this model [4] the density-normalized mobility μN is given by the well known formula [10]

$$\mu N = -\left(\frac{e}{3}\right)\left(\frac{2}{m}\right)^{1/2}\int_0^\infty \frac{\epsilon}{\sigma_m(\epsilon)}\left[\frac{dg(\epsilon)}{d\epsilon}\right]d\epsilon \qquad (1)$$

where m is the electron mass, N is the liquid number density, $\sigma_m(\epsilon)$ is the momentum transfer scattering cross section. $g(\epsilon)$ is the Davydov–Pidduck electron energy distribution function given by

$$g(\epsilon) = A\exp\left\{-\int_0^\epsilon \frac{dz}{k_B T + (M/6m)(eE/N)^2 l/z\sigma_m(z)\sigma_E(z)}\right\} \qquad (2)$$

where M is the atomic mass, σ_E is the energy transfer scattering cross section, and A is determined by the normalization condition $\int_0^\infty dz\,\sqrt{z}g(z) = 1$. It has to be noted that even

though the mobility is determined primarily by the momentum transfer cross section because it is a transport property, nonetheless the distribution function is determined also by the rate of energy exchange [10] through the energy transfer cross section.

According to [4] the long-wavelength limit of the static structure factor is set equal to unity, $S(0) = 1$.

The scattering cross sections are to be considered as adjustable parameters. In order to obtain a good fit to the pure argon data we have to choose a constant momentum transfer scattering cross section $\sigma_m = 0.218$ Å^2, in good agreement with the results of Kaneko *et al* [4]. However, in order to improve the agreement of the model with the high-field data we have to give up their assumption of a constant energy transfer scattering cross section σ_E and we have to assume that σ_E is inversely proportional to the electron energy ϵ

$$\sigma_E(\epsilon) = \sigma_{E_0}\left(\frac{\pi k_B T}{\epsilon}\right). \tag{3}$$

This analytic dependence gives the best fit to the data but it has no theoretical explanation yet. With this choice of the cross sections, equation (1) can be solved analytically to yield

$$\mu = \frac{\mu_0}{[1 + (M/6\pi m)(eE/k_B T N)^2 l/\sigma_m \sigma_{E_0}]^{1/2}} \tag{4}$$

where

$$\mu_0 = \frac{4e}{3N\sigma_m\sqrt{2\pi m k_B T}} \tag{5}$$

is the zero-field mobility. In figure 4 we show the excellent result of this model for pure Ar. Equation 4 shows that for large E, $\mu \propto 1/E$, so that the drift velocity saturates to a constant value as observed experimentally [11].

This model can be extended to a binary fluid by introducing an equivalent one-component fluid with density N and mass M of the pure solvent (Ar) but described by effective scattering cross sections $\sigma_m(x)$ and $\sigma_E(x)$ which depend now on the concentration of the mixture.

On the basis of the results obtained for pure Ar, we assume now that the momentum transfer scattering cross section does not depend on the electron energy ϵ

$$\sigma_m(x, \epsilon) = \sigma_m(x). \tag{6}$$

Moreover, we assume that the energy transfer scattering cross section is inversely proportional to ϵ and that its concentration dependence is contained in the proportionality constant σ_{E_0}

$$\sigma_E(x, \epsilon) = \sigma_{E_0}(x)\left(\frac{\pi k_B T}{\epsilon}\right). \tag{7}$$

We point out once more that this particular choice of the energy dependence of the scattering cross sections is determined only by the results of the fitting procedure. No other choice gives better agreement than this one.

By inserting these relations (6) and (7) in equation (4) we obtain

$$\mu = \frac{\mu_0(x)}{[1 + (M/6\pi m)(eE/k_B T N)^2 l/\sigma_{E_0}(x)\sigma_m(x)]^{1/2}} \tag{8}$$

where the zero-field mobility is given by

$$\mu_0(x) = \frac{4e}{3N\sigma_m(x)\sqrt{2\pi m k_B T}}. \tag{9}$$
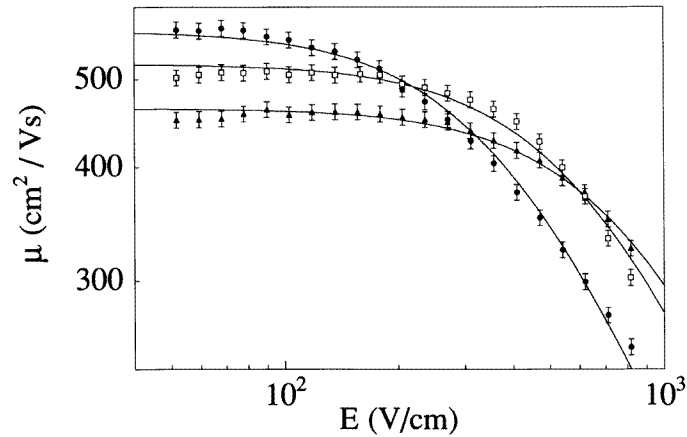
Figure 4. Log–log plot of the electron mobility in pure Ar (closed circles), in the mixture Ar–2.46% Xe (closed triangles), and in the mixture Ar–9.6% Kr (open squares). The solid lines are the results of the gas-kinetic model.
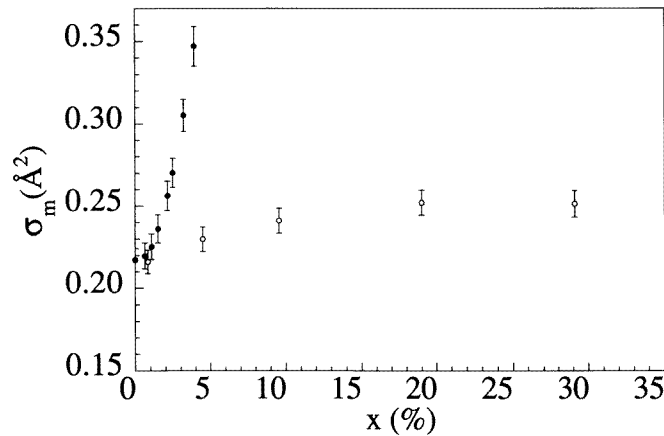

Figure 5. Momentum transfer scattering cross section for the mixture Ar–Kr (open circles) and for Ar–Xe (solid circles) as a function of the solute (Kr or Xe) concentration.

The parameters $\sigma_{E_0}(x)$ and $\sigma_m(x)$ have to be adjusted so as to fit the experimental data. In figures 5 and 6 we show the values of the resulting effective cross sections.

The results of this model for all mixtures are of the same quality as for pure Ar. In figure 4 we show, as an example, the results for two of the mixtures. The values for the momentum transfer scattering cross sections are in the range $0.24 < \sigma_m < 0.35$ Å^2 to be compared to the value $\sigma_m \approx 0.1$ Å^2 of the momentum transfer scattering cross section of gaseous Ar at the Ramsauer minimum.

It has to be noted that the energy transfer cross section is much larger than the momentum transfer one. At thermal energy the ratio of the two is of the order of 10^2. This is not surprising because for thermal electrons the efficiency in energy transfer is greater by the factor $1/S(0) \approx 10^2$ [10] for a liquid.
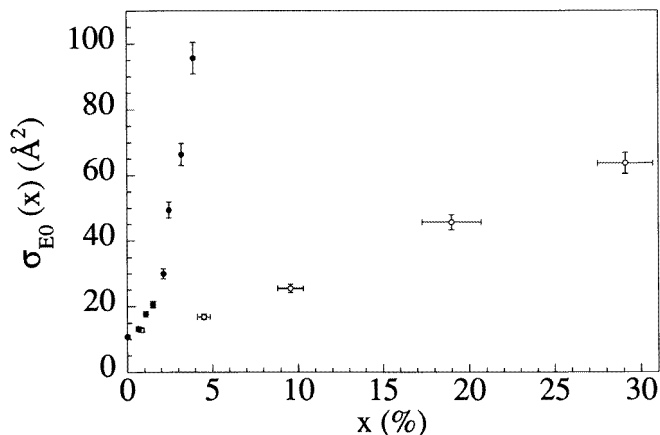
Figure 6. Energy transfer scattering cross section for the mixture Ar–Kr (open circles) and for Ar–Xe (solid circles) as a function of the solute (Kr or Xe) concentration.
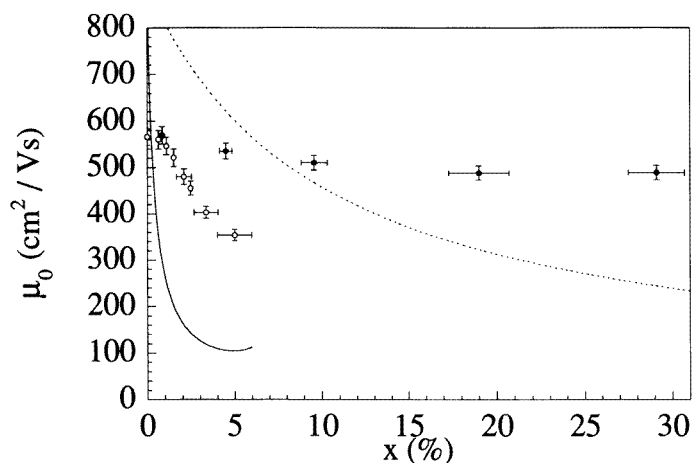

Figure 7. Results of the deformation potential model adapted to binary mixtures for the zero-field mobility μ_0. Experimental data: Ar–Kr (closed circles), Ar–Xe (open circles). Model results: Ar–Kr (dotted line), Ar–Xe (solid line). x is the concentration of either Kr or Xe.

It is also interesting to note that both scattering cross sections (for momentum and energy transfer) increase with increasing solute concentration and this means that the addition of an atomic solute increases the chance of an electron undergoing scattering.

As a conclusion, we can stress the fact that upon a reasonable choice of the scattering cross sections the mobility data can be described with relevant accuracy by this gas-kinetic approach over the whole electric field range.

5. Deformation potential model for binary mixtures

Recently the original deformation potential model was adapted to the case of binary mixtures [12]. Now, beside density–density fluctuations, also concentration–concentration

fluctuations are to be considered, as well as crossed density–concentration fluctuations. The scattering potential is due to fluctuations of the energy at the bottom of the conduction band, V_0, that depends now on both density and concentration. By calculating the scattering matrix element in the Born approximation and by taking suitable averages, the deformation potential theory for binary mixtures yields the following expression for the zero-field mobility

$$\left[\mu_0 \left(\frac{3m^2}{2e\hbar} \right) \left(\frac{mk_BT}{2\pi} \right)^{1/2} \right]^{-1} = \left(\frac{\partial V_0}{\partial N} \right)^2 (N^2 k_B T \chi_T + N\theta^2 x(1-x))$$
$$+ \left(\frac{\partial V_0}{\partial x} \right)^2 x(1-x)/N - 2 \left(\frac{\partial V_0}{\partial N} \right) \left(\frac{\partial V_0}{\partial x} \right) \theta x(1-x). \tag{10}$$

The previous equation is obtained by assuming that the mixtures behave ideally. χ_T is the isothermal compressibility, $\theta = N(v_H - v_S)$, where v_H and v_S are the molar volumes of the solute and solvent, respectively. The mixture properties are calculated from the properties of the pure fluids again by assuming that the mixtures are ideal [12]. The properties of the solutes Kr and Xe have been calculated by extrapolating thermodynamic data [13] to the working temperature.

In figure 7 we show the results of this model. It can be seen that the agreement of the model is very poor and this may depend on the fact that the agreement of the original deformation potential for pure liquid is in strong quantitative disagreement with the pure fluid data [2]. Moreover, this model is not suited to describe the field dependence of the mobility.

6. Conclusions

The transport properties of excess electrons in non-polar liquids are far from being satisfactorily understood. The present two different theoretical approaches to this problem assume very different scattering mechanisms. We have carried out electron drift mobility measurements in liquid mixtures of noble gases to ascertain the influence of additional scattering sources in order to clarify the scattering mechanisms that determine the mobility. The addition of an atomic solute does indeed increase the overall scattering rate of excess electrons. We have extended the gas-kinetic approach to a binary mixture by taking into account the fact that the excess electrons may collide with two different types of scatterer. The agreement of this model with the data is fairly good, even though we have to rely on adjustable parameters (the scattering cross sections). Nonetheless, the physical meaning of this picture (a modified single-scattering picture) is very easy to grasp.

On the other hand, the deformation potential approach is in very poor agreement with the experimental data, and has the great limit that it cannot account for the electric field dependence of the data. The disagreement with the experiments can be probably traced back to two different factors. First of all, even for pure fluids this model does not agree with the data. Secondly, the approximation of ideal mixtures might not be verified. As a result, we believe that the deformation theory should be greatly improved in order to compare favourably with the gas-kinetic approach.

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