

# Behavior of Excess Electrons in Supercritical Fluids

## -Electron Attachment-

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### Abstract

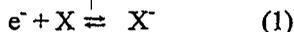
The behavior of excess electrons in supercritical ethane was investigated by measuring mobility and reaction rates. Mobilities were measured by means of a time-of-flight method at 306–320K as a function of pressure. Mobility values decreased at all temperatures with increasing pressure, but showed a small minimum or a shoulder at the pressure where the compressibility  $\chi_T$  has a peak.

Electron attachment to  $\text{CO}_2$ , NO, pyrimidine and  $\text{C}_2\text{F}_4$  over the same temperature range was studied as a function of pressure. Both attachment rate constants  $k_a$  for NO and  $\text{C}_2\text{F}_4$ , and equilibrium constants  $K(=k_a/k_d)$  for  $\text{CO}_2$  and pyrimidine increased sharply at pressures of  $\chi_T$  peaks. Activation volumes  $V_a^*$  and reaction volumes  $\Delta V_r$  are very large and negative in the critical region. The volume change is mainly due to electrostriction around ions formed. The results are compared to volume changes predicted by a compressible continuum model.

### Introduction

The utilization of supercritical fluids (SCF) in processes that involve charged species requires knowledge about the physical properties of such species in the SCF. In particular, SCF's are characterized by high compressibilities near the critical region and the compressibility affects both the mobility and reactivity of electrons. Prior to our studies little was known how these properties behave, and specifically how the partial molar volumes and polarization energies of ions in non-polar SCF change with temperature and pressure.

In the method used, electrons are generated from a short X-ray pulse. The mobility is determined by measuring the drift time by means of a time-of-flight method [1]. The reaction rate with added solute, X, is determined from the decay of the current following the pulse.



For those solutes where the reaction is reversible, that is detachment of electrons from  $X^-$  can be observed,

the free energy of reaction 1,  $\Delta G_r$ , can be obtained. In general  $\Delta G_r$  decreases with increasing pressure due to the increase in polarization energy,  $P^-$ , and changes in the energy level of the electron,  $V_o + E_i$ , according to:

$$\Delta G_r = \Delta G_r(\text{gas}) + P^- - (V_o + E_i) \quad (2)$$

The volume change in reaction 1 is obtained from the derivative of  $\Delta G_r$  with respect to pressure:

$$\Delta V_r = d\Delta G_r/dP \quad (3)$$

### Electron Mobility

Electron mobility  $\mu$  decreases with increasing pressure at all temperatures (see Figure 1), but goes

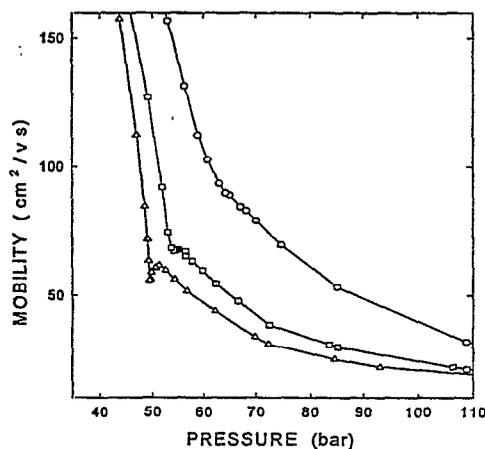


Fig 1. Electron mobility versus pressure at  $\Delta$  306 K,  $\square$  310 K and  $\circ$  320 K.

through a small minimum, or inflection, at the pressure where  $\chi_T$  has its peak value. The position of the minimum changes to an inflection point moving away from the critical temperature. With increasing temperature the peak value of  $\chi_T$  decreases. This correspondence of the depth of the minimum with the magnitude of the compressibility suggests that a deformation potential model is applicable in this region.

## Electron Attachment Reactions

Rate constants for electron attachment are in the range  $10^{10}$ – $10^{11} \text{ m}^{-1} \text{ s}^{-1}$  for  $\text{CO}_2$  [1] and  $\text{C}_2\text{F}_4$  [2],  $10^{10}$ – $10^{12} \text{ m}^{-1} \text{ s}^{-1}$  for  $\text{NO}$  [3] and,  $10^{13} \text{ m}^{-1} \text{ s}^{-1}$  for pyrimidine [4]. These rates are well below the diffusion-controlled limit estimated from the electron mobility. The difference in the reaction rates does not scale with the electron affinity (EA) values, since EA (in eV) for pyrimidine is  $-0.33$ , for  $\text{NO}$  is  $0.026$ , and for  $\text{CO}_2$  is  $-0.60$ . EA values listed for  $\text{C}_2\text{F}_4$  are  $-3.0$  and  $0.11 \text{ eV}$  [5], neither one of which seems to be consistent with its reactivity toward electrons.

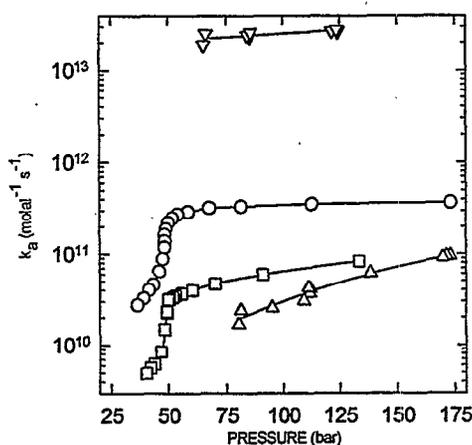


Fig. 2 Rate constant for electron attachment to pyrimidine ( $\nabla$ ),  $\text{NO}$  ( $\circ$ ),  $\text{C}_2\text{F}_4$  ( $\square$ ), and  $\text{CO}_2$  ( $\Delta$ ) at 310K.

With  $\text{NO}$  and  $\text{C}_2\text{F}_4$  as solutes,  $k_a$  increases sharply in the region where  $\chi_T$  goes through a maximum. With pyrimidine, however,  $k_a$  stays almost constant over the pressure range 70–125 bar and is temperature-independent.  $k_d$  decreases rapidly with increasing pressure, and has an activation energy of about  $1 \text{ eV}$ . Thus the equilibrium constant  $K$  increases also rapidly in this pressure region.

With  $\text{CO}_2$  as solute,  $k_a$  increases and  $k_d$  decreases with pressure, consequently  $K$  increases also with pressure. The individual rate constants could only be resolved at pressures greater than 80 bar for  $\text{CO}_2$  and 70 bar for pyrimidine. At lower pressures, the detachment rate becomes too large and  $K$ -values were estimated from mobility values assuming a two-state model.

$\ln k_a$  depends linearly on  $\Delta G_r$  according to eq 4.

$$\ln k_a = a\Delta G_r + b \quad (4)$$

For  $\text{CO}_2$  the slope,  $a$ , was found to be  $-20 \text{ eV}^{-1}$ , but for pyrimidine the slope is nearly zero. Thus for  $\text{CO}_2$ , the rate of electron attachment behaves similarly to rates observed for electron transfer [6], while  $\ln k_a$  for pyrimidine exhibits a different trend.

## Free Energy Changes

The free energy changes for these electron attachment reactions in SC ethane depend on the polarization energy of the ion formed,  $P^-$ , and the energy of the electron in the fluid,  $V_o + E_r$ , as given by eq 2. As the pressure increases the ion is stabilized; that is, the value of  $P^-$  decreases, while the electron is destabilized; that is, the value of  $V_o$  tends to increase. The reaction with  $\text{CO}_2$  in SC ethane is least favorable; values of  $\Delta G_r$  range from  $-0.09$  to  $-0.25$ , which is consistent with its EA of  $-0.60 \text{ eV}$ . The reaction with pyrimidine is more favorable; values of  $\Delta G_r$  range from  $-0.28$  to  $-0.39 \text{ eV}$  since the EA is  $-0.33 \text{ eV}$ . The reaction of the electron with  $\text{NO}$  is most favorable. In this case  $\Delta G_r$  was not measured but was calculated using eq 2; at 310 K and 80 bar  $\Delta G_r = -0.89 \text{ eV}$ . This value corresponds to a very large equilibrium constant which explains why this reaction is not reversible. At this temperature and pressure the magnitude of the polarization energy of the negative ion,  $\text{NO}^-$ , is large,  $-1.23 \text{ eV}$ , because of the small size of the ion. This value is based on a compressible continuum model calculation that takes into account the clustering of ethane molecules around the ion. (See eq 7 below)

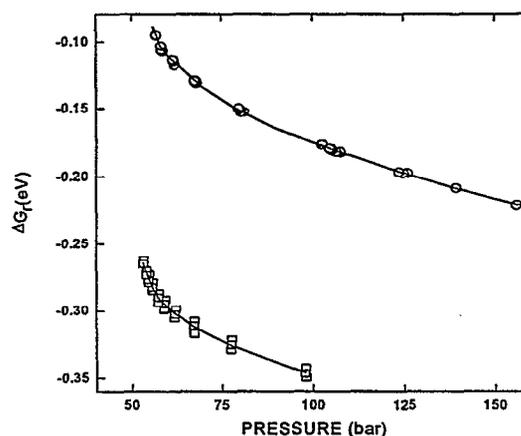


Fig. 3.  $\Delta G_r$  vs. pressure for reaction 1 at 310K  
X=pyrimidine ( $\square$ ), X= $\text{CO}_2$  ( $\circ$ )

## Volume Changes

Volume changes  $\Delta V_r$  and activation volumes  $V_a^*$  for reaction 1 are calculated from the derivatives of  $\Delta G_r$  (Fig. 3) and  $-RT \ln k_a$ , respectively, with respect to pressure. For  $\text{CO}_2$ , values of  $\Delta V_r$  range from  $-19.0$  to  $-0.5 \text{ l/mol}$ , depending on pressure and temperature.  $V_a^*$  for attachment is approximately  $\Delta V_r/2$ .

For pyrimidine,  $\Delta V_r$  values are in the range  $-9.0$  to  $-0.4 \text{ l/mol}$ . Values of  $V_a^*$  are, however, practically zero over the pressure range 55–130 bar as can be seen from fig. 2.  $V_a^*$  values for  $\text{NO}$  are quite large and negative, particularly at the pressure of the  $\chi_T$  peak;

-27, -9.2 and -2.3 l/mol at 306, 310 and 320K, respectively.

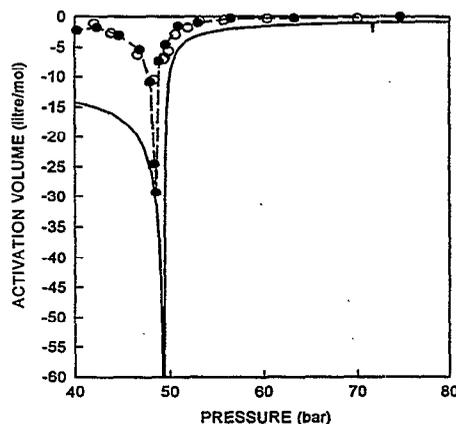


Fig. 4.  $V_a^*$  for electron attachment to NO(●) and  $C_2F_4$ (○) at 306K  
— compressible continuum model

These negative volume changes are primarily ascribed to electrostriction around the negative ions formed. In fact, electrostriction volumes,  $V_{el}$ , calculated by a compressible continuum model agree with experimental  $\Delta V_r$  values for  $CO_2$  and pyrimidine. However, the reaction volume also includes the partial molar volume for the neutral species,  $v(x)$ , (see eq 5). For  $X = CO_2$  this term can be neglected [1], but is expected to be significant for larger molecules especially when  $\chi_T$  is large.

$$\Delta V_r = \bar{v}(X^-) - \bar{v}(X) - \bar{v}(e^-) \quad (5)$$

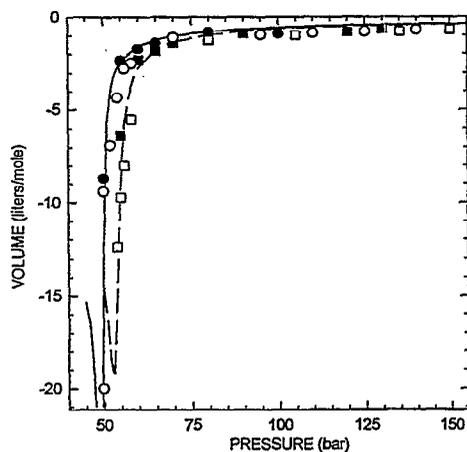


Fig.5.  $\Delta V_r$  for  $CO_2$  (● 306K, ○ 310K) and pyrimidine(■ 306K, □ 310K), compressible continuum model(— 306K, --- 310K)

The same model when applied to NO gives approximately twice as large values as experimentally

observed  $V_a^*$  values. These larger calculated values correspond to electrostriction around the stable ion, but  $V_a^*$  is for the activated complex. Thus, it seems reasonable to assume that the electron attachment to NO is similar to electron attachment to  $CO_2$  in that  $V_a^*$  is one half  $\Delta V_r$ . The fact that  $V_a^*$  is nearly zero for pyrimidine suggests that the structure of the transition state is close to that of the reactants.

### Compressible Continuum Model

The classical Drude-Nernst model for electrostriction [7] gives the following formula:

$$V_{el} = -[e^2/(6r_{ion}\epsilon^2)] \chi_T(\epsilon + 2)(\epsilon - 1)/\epsilon^2 \quad (6)$$

where the bulk value for the dielectric constant  $\epsilon$  is assumed. Because extensive clustering is expected to take place around ions in SCF due to large  $\chi_T$ , eq 6 cannot be a good approximation. In the compressible continuum model, described elsewhere [1,3], the clustering is taken into account. In short, attractive interaction between ions and the induced dipole of solvent molecules gives rise to the local pressure around the ion and by means of an equation of state [8], local density is calculated, which gives the value of local  $\epsilon$  values. By utilizing local  $\epsilon$  values, pressure, and thus density values  $\rho(r)$  as a function of distance from the ion are calculated iteratively, until  $\rho(r)$  becomes invariant. The electrostriction volumes in this model, obtained by:

$$V_{el} = 4\pi \int_{r_{ion}}^{\infty} \left[ \frac{v(r)}{V_o} \right] r^2 dr \quad (6)$$

agree with experimental  $\Delta V_r$  values including the position of the minima.

The polarization energy  $P^-$  used in eq 2 is given in this model by:

$$P^- = 4\pi \int_{r_{ion}}^{\infty} (1/2)\epsilon_0\epsilon(r)[E(r)]^2 r^2 dr - e^2/8\pi\epsilon_0 r_{ion} \quad (7)$$

The density profile  $\rho(r)$ , calculated by this model, gradually decreases in the higher pressure region with distance from the ion. However, in the low pressure region, the difference between that around the ion and the bulk is large and  $\rho(r)$  shows an almost vertical drop near the edge. In this case the cluster extends almost to 2 nm (see Fig. 6). The positive ion mobility measured in SC ethane yields similar values by means of the Stokes-Einstein equation [2].

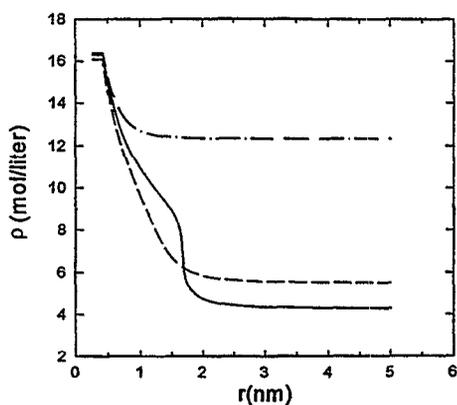


Fig.6. Density profile around a pyrimidine anion  
 — 306K, 48bar, — 318K, 59bar, -.- 310K, 120bar

### Conclusion

These studies have demonstrated that clustering of ethane molecules takes place around ions in the supercritical fluid state. The density is enhanced over the average density to distances of 1.8 nm from the center of the ion. This clustering explains the large volume changes observed in electron attachment reactions and accounts for the sharp increases in  $K_1$  and  $k_a$  that takes place in the pressure region where  $\chi_T$  goes through a maximum. Also the polarization energy of ions in SCFs must take these density changes into account to explain free energy shifts.

### Acknowledgment

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### References

1. M. Nishikawa, K. Itoh, R. A. Holroyd, *J. Phys. Chem.* 1999, **103**, 550.
2. R. A. Holroyd, M. Nishikawa, K. Itoh, unpublished.
3. M. Nishikawa, R. Holroyd, K. Itoh, *J. Phys. Chem.* 1998, **102**, 4189.
4. R. Holroyd, M. Nishikawa, K. Itoh, *J. Phys. Chem.* (submitted).
5. *Electron Affinities of Atoms, Molecules and Radicals*, Ed. L. G. Christophorou et al ORO-4703-39, 1983.
6. R. A. Marcus, *Rev. Mod. Phys.* 1993, **65**, 599.
7. P. Drude, W. G. Nernst, *Z. Phys. Chem.* 1894, **15**, 79.
8. B. A. Younglove, J. F. Ely, *J. Phys. Chem. Ref. Data*, 1987, **16**, 577.