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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 χ_T has a peak.

Electron attachment to CO_2, NO, pyrimidine and C_2F_4 over the same temperature range was studied as a function of pressure. Both attachment rate constants k_a for NO and C_2F_4, and equilibrium constants $K(=k_a/k_d)$ for CO_2 and pyrimidine increased sharply at pressures of χ_T peaks. Activation volumes V_a^* and reaction volumes ΔV_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.

$$e^- + X \rightleftarrows X^- \qquad (1)$$

For those solutes where the reaction is reversible, that is detachment of electrons from X^- can be observed, the free energy of reaction 1, ΔG_r, can be obtained. In general ΔG_r decreases with increasing pressure due to the increase in polarization energy, P^-, and changes in the energy level of the electron, $V_o + E_t$, according to:

$$\Delta G_r = \Delta G_r(gas) + P^- - (V_o + E_t) \qquad (2)$$

The volume change in reaction 1 is obtained from the derivative of ΔG_r with respect to pressure:

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

Electron Mobility

Electron mobility μ decreases with increasing pressure at all temperatures (see Figure 1), but goes through a small minimum, or inflection, at the pressure where χ_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 χ_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.

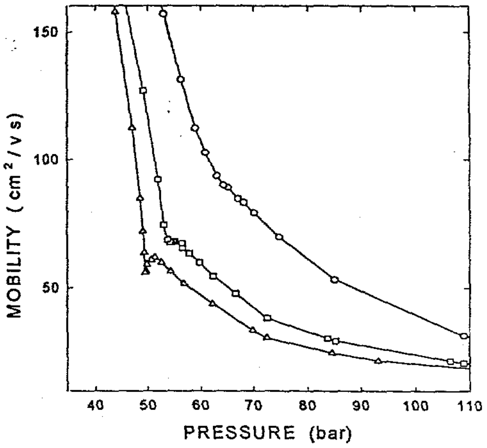

Fig 1. Electron mobility *versus* pressure at Δ 306 K, □ 310 K and O 320 K.

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Electron Attachment Reactions

Rate constants for electron attachment are in the range 10^{10}–$10^{11} m^{-1}s^{-1}$ for CO_2 [1] and C_2F_4 [2], 10^{10}–$10^{12} m^{-1}s^{-1}$ for NO [3] and, $10^{13} m^{-1}s^{-1}$ 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 NO is 0.026, and for CO_2 is –0.60. EA values listed for C_2F_4 are –3.0 and 0.11eV[5], neither one of which seems to be consistent with its reactivity toward electrons.

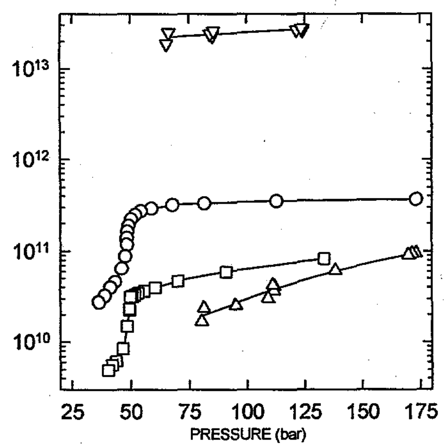

Fig. 2 Rate constant for electron attachment to pyrimidine (∇), NO (o), C_2F_4 ( ), and CO_2 (Δ) at 310K.

With NO and C_2F_4 as solutes, k_a increases sharply in the region where χ_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 1eV. Thus the equilibrium constant K increases also rapidly in this pressure region.

With CO_2 as solute, k_a increases and k_d decreases with pressure, consequently K_l increases also with pressure. The individual rate constants could only be resolved at pressures greater than 80 bar for CO_2 and 70 bar for pyrimidine. At lower pressures, the detachment rate becomes too large and K_l-values were estimated from mobility values assuming a two-state model.

Ln k_a depends linearly on ΔG_r according to eq 4.

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

For CO_2 the slope, a, was found to be –20 eV^{-1}, but for pyrimidine the slope is nearly zero. Thus for 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, $V_o + E_t$, 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 CO_2 in SC ethane is least favorable; values of ΔG_r range from –0.09 to –0.25, which is consistent with its EA of –0.60 eV. The reaction with pyrimidine is more favorable; values of ΔG_r range from –0.28 to –0.39 eV since the EA is –0.33 eV. The reaction of the electron with NO is most favorable. In this case ΔG_r was not measured but was calculated using eq 2; at 310 K and 80 bar ΔG_r = –0.89 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, NO^-, is large , –1.23 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)

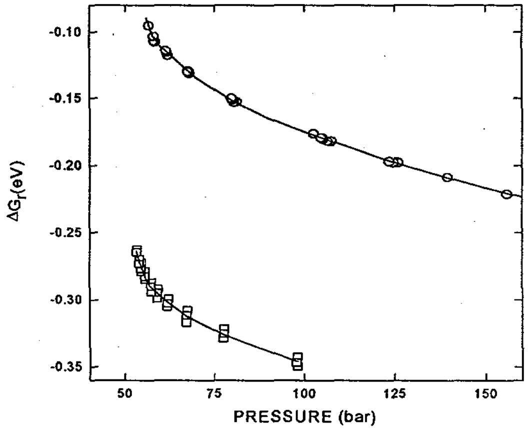

Fig. 3. ΔG_r *vs.* pressure for reaction 1at 310K
X=pyrimidine (□), X=CO_2 (○)

Volume Changes

Volume changes ΔV_r and activation volumes V_a^* for reaction 1 are calculated from the derivatives of ΔG_r (Fig. 3) and –RT$\ln k_a$, respectively, with respect to pressure. For CO_2, values of ΔV_r range from –19.0 to –0.5 *l*/mol, depending on pressure and temperature. V_a^* for attachment is approximately $\Delta V_r/2$.

For pyrimidine, ΔV_r values are in the range –9.0 to –0.4 *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 NO are quite large and negative, particularly at the pressure of the χ_T peak;

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

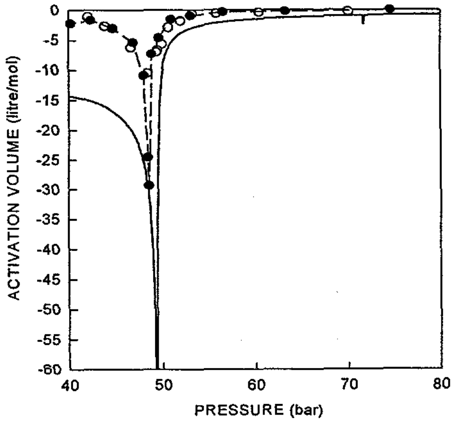

Fig. 4. V_a^* for electron attachment to NO(•) and C_2F_4(○) at 306K
— compressible continuum model

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 ΔV_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 χ_T is large.

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

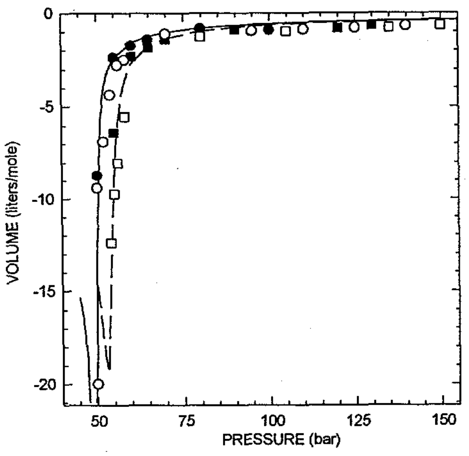

Fig.5. ΔV_r for CO_2 (● 306K, ○ 310K) and pyrimidine(■ 306K, □ 310K), compressible continuum model(—— 306K, – – – 310K)

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 ΔV_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:

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

where the bulk value for the dielectric constant ε is assumed. Because extensive clustering is expected to take place around ions in SCF due to large χ_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 ε values. By utilizing local ε values, pressure, and thus density values ρ(r) as a function of distance from the ion are calculated iteratively, until ρ(r) becomes invariant. The electrostriction volumes in this model, obtained by:

$$V_{el} = 4\pi \int_{r_{ion}}^{\infty} \left[1/V(r) \int_{V_\infty}^{V(r)} dV \right] r^2 dr \qquad (6)$$

agree with experimental ΔV_r values including the position of the minima.

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

$$P^- = 4\pi \int_{r_{ion}}^{\infty} (1/2)\varepsilon_0 \varepsilon(r)[E(r)]^2 r^2 dr - e^2/8\pi\varepsilon_0 r_{ion} \qquad (7)$$

The density profile ρ(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 ρ(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].

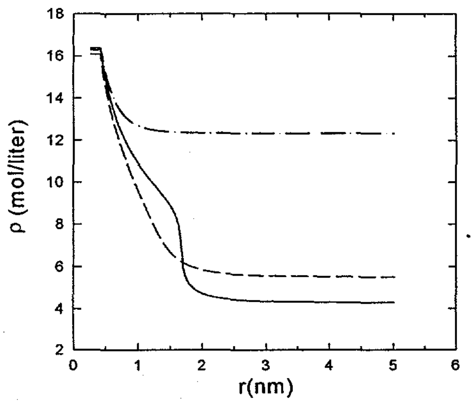

Fig.6. Density profile around a pyrimidine anion
— 306K, 48bar, —318K, 59bar, –·– 310K, 120bar

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_I and k_a that takes place in the pressure region where χ_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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