LETTERS

Double Layer Structure in a Supercritical Fluid

Andrew P. Abbott* and Christopher A. Eardley

Chemistry Department, The University of Leicester, Leicester, LE1 7RH, U.K.

Received: May 25, 1999

This work reports the first double layer capacitance measurements in a polar supercritical fluid. The capacitance of a tetrabutylammonium tetrafluoroborate (TBA BF_4) electrolyte in supercritical difluoromethane (HFC 32) at a platinum electrode is shown to be strongly dependent on fluid density. At high pressures the capacitance−potential plots exhibit a double layer response similar to that in the liquid state, but as the pressure is lowered toward the critical value the diffuse layer collapses and a pure Helmholtz response is observed.

Supercritical (sc) fluids are extremely attractive solvation media because the solvent properties can be dramatically changed with only modest adjustments to the temperature or pressure. Consequently, these solvent systems have been utilized in many applications, such as extraction, chromatography, and chemical reaction.[1]

Since the early 1980s, electrochemistry has been thoroughly investigated in supercritical media. The low viscosity of sc fluids leads to enhanced mass transport both to and from the electrode surface. It was recognized that the tuneability and improved mass transport conditions associated with sc solvents held clear advantages for electrosynthesis. Silvestri and co-workers were the first to report on the validity of performing electrosyntheses in sc solvents.[2] Bard and co-workers, however, have performed the most extensive work on electrochemistry in sc fluids.[3] By predominantly using polar sc solvents such as NH_3 and H_2O, they probed the thermodynamics and kinetics of a variety of electrode processes in order to test the viability of electrosynthesis in these media.

Previous studies in sc fluids have found that artifacts similar to those caused by uncompensated *iR*, are frequently observed close to p_c.[4,5] To elucidate the origin of these artifacts a knowledge of the double layer structure at the electrode/electrolyte interface is required.

Generally the higher the polarity of a substance, the higher the critical temperature. Difluoromethane (HFC 32) has recently been shown[5] to be an excellent solvent in which to perform sc electrochemistry, since it exhibits mild critical constants (T_c = 351.26 K, p_c = 57.82 bar) and relatively high polarity at the critical point (ϵ_c = 6.0).[6] In the current work the double layer properties of TBA BF_4 in both liquid and supercritical HFC 32 have been investigated. The studies were performed on platinum electrodes to allow direct comparison with electron transfer data recently published on this surface.[5]

The solvent HFC 32 (ICI Klea group, 99.99%) was used as received. The TBA BF_4 electrolyte (Fluka, Electrochemical grade) was dried in vacuo prior to use. The high-pressure cell design was similar to that employed previously.[7] A novel electrochemical cell design was required due to the low capacitance of the electrolyte solutions in the liquid and supercritical phase. Two rectangular stainless steel plates (28 mm × 11 mm × 1 mm) were held in a parallel plate design by Teflon spacers. The separation between the two electrodes was 4 mm. Both plates were coated with a layer of platinum black, electrodeposited by the standard technique.[8] These plates formed the working and counter electrodes of the cell. Platinization of the steel plates led to a significant increase in the surface area of the working electrode and, therefore, a desired rise in the measured double layer capacitance. The area of the working electrode was calculated via voltammetry, using an aqueous

* Author to whom correspondence should be addressed. Fax: +44 116 252 3789. E-mail: apa1@le.ac.uk.
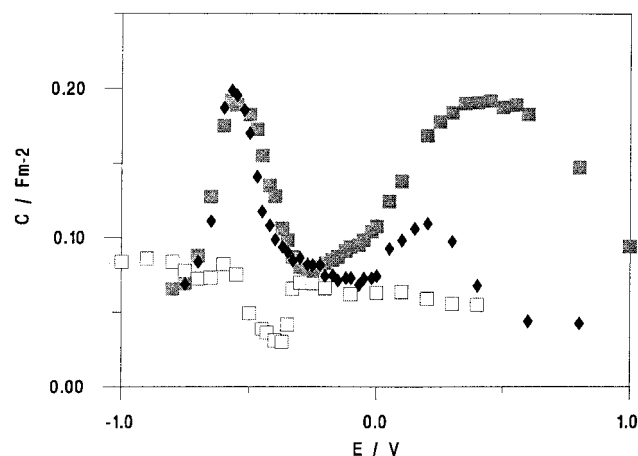
Figure 1. Double layer capacitance of a Pt electrode in a solution of TBA BF$_4$ (0.02 mol dm^{-3}) in liquid and supercritical HFC 32. (□) 30 °C and 200 bar, (◆) 70 °C and 135 bar (both liquid), (■) 90 °C and 260 bar (supercritical).

solution of 2 mM K$_3$Fe(CN)$_6$, 2 mM K$_4$Fe(CN)$_6$, and 0.1 M KNO$_3$ at 25 °C. The reference electrode was a length of silver wire run through parallel holes in the Teflon spacers. This gave a grill-shaped reference electrode lying centrally between the two platinum plates.

An ac impedance method was used to measure the capacitances, employing a 1286 potentiostat and a 1254 frequency response analyzer (both Solartron Instruments) controlled by ZPLOT software. A 20 mV ac amplitude was used to record impedance spectra in the frequency range 65000 to 1 Hz. The acquired data were analyzed using ZVIEW software, where the electrochemical system was modeled as a parallel RC circuit. Double layer capacitance values were subsequently obtained by computer-generated fits to the observed semi-circular Nyquist plots. All values of solvent relative permittivity, ϵ, were taken from the literature.[6]

The capacitance of liquid HFC 32 at 30 °C and 220 bar (ϵ = 14.1) containing 20 mM TBA BF$_4$ at a platinum electrode as a function of potential is shown in Figure 1. The decrease in capacitance at -0.37 V is indicative of a diffuse layer minimum.[9] In the present study the potential of zero charge (PZC) will be assumed to be close to the capacitance minimum. The shape of this plot is remarkably similar to those observed for NaF in aqueous solutions at low concentrations at 25 °C.[9] This suggests that the TBA$^+$ and BF$_4^-$ ions are insignificantly adsorbed at potentials close to the PZC. The capacitance values, however, are much lower than those of NaF in aqueous solution at potentials both positive and negative of the PZC, as expected in view of the reduced relative permittivity. Furthermore, the capacitance values at extreme positive potentials (E > 0 V) are less than those at extreme negative potentials (E < -0.8 V). The capacitances at these potentials correspond well to a compact layer of ions where the capacitance, C_H, is given by

$$C_H = \frac{\epsilon \epsilon_0}{d} \qquad (1)$$

where ϵ_0 is the permittivity of free space (8.854 × 10^{-12} F m^{-1}) and d is the distance between the center of the ions and the electrode surface.

Assuming that the relative permittivity close to the electrode surface is approximately equal in both cation and anion adsorption, the capacitance values indicate a larger value of d in the latter case. The ionic radii of 0.413 and 0.202 nm for TBA$^+$ and BF$_4^-$, respectively,[10] therefore, imply that the BF$_4^-$

anion remains solvated within the compact layer precluding specific adsorption.

Figure 1 also shows the capacitance plot for the same solution at 70 °C and 135 bar where the solvent relative permittivity is 9.6. The capacitance minimum has now shifted to a more positive value of -0.07 V. The effect is most probably dominated by the change in reference potential with temperature. The shape and magnitude of the capacitance−potential plot are similar to those observed for TBA BF$_4$ in dichloroethane (ϵ = 10.27) and anisole (ϵ = 4.33) at both mercury and platinum electrodes.[11] The major difference here is that the cathodic peak at -0.57 V is larger than the anodic peak at 0.2 V. Such capacitance humps have been observed in both aqueous and nonaqueous media such as dimethylsulfoxide and *N*-methyl acetamide.[11] The capacitance humps are generally ascribed to the reorientation of polar solvent molecules adjacent to the electrode surface as a result of the change in surface charge. Capacitance studies in cyclohexane, however, have also yielded anodic humps,[11] and it was suggested that the specific adsorption of ion aggregates and not solvent reorientation can cause the capacitance hump effect.

Also shown in Figure 1 is the capacitance−potential plot for 20 mM TBA BF$_4$ in supercritical HFC 32 at 90 °C and 260 bar, where the solvent relative permittivity is 9.5. Anodic and cathodic capacitance humps are again observed, on either side of the capacitance minimum at -0.25 V. This is an important result as it shows that the double layer structure is present in supercritical fluids at high pressures. Voltammetric studies in supercritical HFC 32 at similar conditions have already shown the ferrocene/ferrocinium couple to behave reversibly at a platinum microelectrode.[5] Ion adsorption, therefore, was not expected at these conditions.

The ionic strength and hence the capacitance will clearly be determined by the relative permittivity of the solution. Extensive ion pairing is prevalent for TBA BF$_4$ in HFC 32 but the capacitance plots at 90 and 70 °C can be compared because the solutions have the same relative permittivity. Indeed both plots are similar, except that at supercritical conditions displays a significantly larger anodic capacitance hump that has a magnitude similar to that of the cathodic hump. Interestingly, both plots display a cathodic capacitance hump peak at -0.57 V. A more detailed interpretation of the capacitance data presented here requires the consideration of ion pairing but these should be similar to those recently published in nonpolar liquid solutions.[11]

Figure 2 shows the effect of pressure on the double layer capacitance plots for a supercritical HFC 32 solution at 90 °C. Upon decreasing the pressure from 260 to 160 bar (ϵ = 8.5) there is a decrease in the height of the cathodic capacitance hump and a complete disappearance of the anodic hump. A further reduction in pressure to 135 bar, where the solution relative permittivity is 8.1, leads to a complete removal of the cathodic capacitance hump.

At 135 bar the capacitance-potential plot consists of two roughly linear regions divided at approximately -0.55 V. The capacitance in each region is roughly independent of potential, suggesting that ion adsorption is prevalent. It is understandable, therefore, that at such conditions large deviations from Nernstian behavior have been observed with voltammetry.[4,5]

In contrast to the capacitance−potential plot of liquid HFC 32 at 30 °C, the capacitance of the cathodic compact layer is lower than that of the anodic equivalent. Assuming eq 1 again holds, it can be inferred that the TBA$^+$ cations are specifically adsorbed at potentials negative of -0.55 V. It is suggested that

Letters

J. Phys. Chem. B, Vol. 103, No. 30, 1999 **6159**
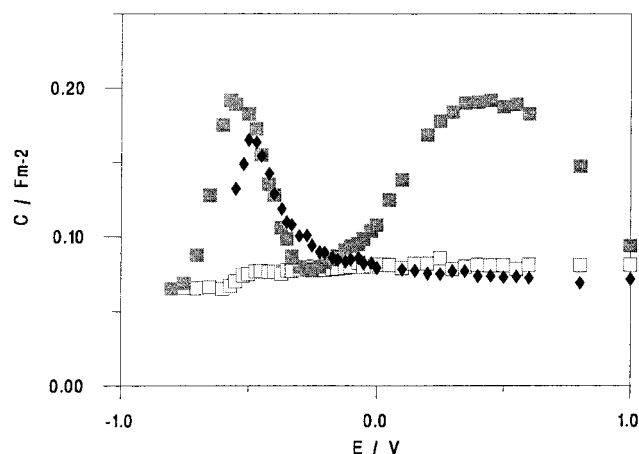
Figure 2. Double layer capacitance of a Pt electrode in a solution of TBA BF$_4$ (0.02 mol dm^{-3}) in supercritical HFC 32 at 90 °C. (□) 135bar, (◆) 160 bar, (■) 260 bar.

at potentials positive of −0.55 V the BF$_4^-$ anions are also specifically adsorbed, as a consequence of the breaking down of the solute−solvent specific interactions implied present in the liquid phase. Hence the double layer structure can be entirely described by the Helmholtz model.

A decrease of the pressure of the sc system at 90 °C from 260 to 135 bar, therefore, apparently causes a diffuse double layer structure to collapse. It is proposed that the increased thermal motion at lower pressures, a consequence of reduced fluid viscosity, prevents the formation of a diffuse layer.

Conversely, the reduced relative permittivity of the medium increasingly favors ion adsorption on the electrode surface, yielding a compact double layer. These results explain the deviations from Nernstian behavior observed for standard redox couples in fluids close to the critical conditions.

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