



Anion dependence of camel-shape capacitance at the interface between mercury and ionic liquids studied using pendant drop method



Naoya Nishi*, Shunsuke Yasui, Atsunori Hashimoto, Tetsuo Sakka

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, 615-8510, Japan

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ABSTRACT

The electrocapillarity and zero-frequency differential capacitance, C_d , have been studied using pendant drop method, at the Hg interface of an ionic liquid (IL), 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide, $[\text{C}_2\text{mim}^+][\text{TfSA}^-]$, and have been compared with those of $[\text{C}_2\text{mim}^+]\text{BF}_4^-$, an IL with the common cation and a different anion, to focus on the anion dependence of zero-frequency C_d . The Hg interface of $[\text{C}_2\text{mim}^+][\text{TfSA}^-]$, the IL of the larger anion in the present study, exhibits greater zero-frequency C_d than that of $[\text{C}_2\text{mim}^+]\text{BF}_4^-$, the IL of the smaller anion. This behavior contradicts a simple expectation in which larger ion leads to smaller C_d . This apparent contradiction is explained by proximity of the charged moiety of TfSA^- to the electrode surface compared with that of BF_4^- . The potential dependence of zero-frequency C_d for the two ILs both exhibits one-hump camel shape around the potential of zero charge (E_{pzc}), which has been predicted to be specific behavior of the electrical double layer of ILs by theory and simulation. The humps are located at potentials more negative than E_{pzc} . From a mean-field lattice-gas theory for the EDL in ILs, this negative shift can be interpreted that the charged moiety for C_2mim^+ is more easily condensed in the EDL than those for BF_4^- and TfSA^- .

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1. Introduction

Ionic liquids (ILs) are liquid salts that are composed of cations and anions and the possible electrochemical applications of ILs have recently accelerated studies on the structure of the electrochemical interface of ILs [1–4]. The differential capacitance (C_d) reflects the interfacial structure and its potential dependence, i.e., the behavior of ions in the electrical double layer (EDL). Since ILs are entirely composed of ions without neutral solvent molecules, the potential dependence of C_d has been predicted [3,5,6] to be different from that of the Gouy-Chapman-Stern (GCS) model [7–9], which has successfully modeled the EDL for dilute electrolyte solutions where neutral solvent molecules are the major components. The mean-field lattice-gas model for the EDL in ILs proposed by Kornyshev [5] illustrates the peculiar camel-shape potential dependence of C_d : either of one-hump or two-hump shape around the potential of zero charge (E_{pzc}) depending on the size of charged and neutral moieties of IL ions [10–13], in contrast to the U shape behavior for the GCS model. The one-hump camel shape is for ILs composed of small

ions and can be explained by excluded volume not only between electrode and ions, but also between neighboring ions in the EDL, the latter of which was not taken into account in the GCS model. The two-hump camel shape is for ILs with relatively large ions having neutral moiety and is similar to the one-hump shape except around E_{pzc} where the potential dependence of C_d returns to the GCS behavior, showing negative curvature. This is due to the neutral moiety in IL ions that can play a role as “latent void” [10,11] to be replaced with charged moiety in IL ions at the first ionic layer when the interface becomes charged from E_{pzc} .

Experimentally, C_d can be measured by using electrochemical impedance spectroscopy (EIS) at a frequency or a range of frequency and by adopting one of probable equivalent circuit models. The EIS C_d for the electrochemical interface of ILs has been intensively reported [14–24]. However, the EIS C_d is known to have strong frequency dependence [25–32] and also hysteresis effect [25,33–35], both of which seem to result from the structural ordering of IL interface [36–42] and the ultraslow dynamics [43–50] of such ordered structure. This makes it difficult to compare the EIS C_d with C_d from theory and simulation, latter of which is C_d in equilibrium, i.e., zero-frequency C_d . This problem has been pointed out by Fedorov and Kornyshev in their recent review [3] as “The fact that impedance measurements cannot reliably assess equilibrium characteristics is not

* Corresponding author.

E-mail address: nishi.naoya.7e@kyoto-u.ac.jp (N. Nishi).

Table 1

Volume of ions by quantum chemical calculation in the level of B3LYP/6-311++G**.

Ion	V_i ($\text{cm}^3 \text{ mol}^{-1}$)
TFSA ⁻	123 ^a , 128 ^b
BF ₄ ⁻	45
C ₂ mim ⁺	88

^a C₁ conformer.

^b C₂ conformer.

a problem of the EDL theory that operates with equilibrium properties, but rather a problem of experimental techniques available these days." Therefore, the experimental method that can evaluate zero-frequency C_d would be desirable to compare experimental and theoretical zero-frequency C_d , extract the characteristics of the EDL in ILs from the comparison, and furthermore provide feedbacks for the improvement of the theory of the EDL in ILs.

Recently, we experimentally obtained zero-frequency C_d from the thermodynamic analysis of the electrocapillarity (interfacial tension as a function of electrode potential) at the IL|Hg interface measured using the pendant drop method [51]. Since the pendant drop method is a static method, the measurements are not affected by the ultraslow dynamics of the interfacial structure of ILs, enabling us to experimentally evaluate zero-frequency C_d and to directly compare it with the prediction by theory and simulation. It should be noted that similar methods to measure electrocapillarity such as drop time method [15,52–57] and drop weight method [58] previously reported for IL|Hg interface, are dynamic ones, which cannot escape from the slow dynamics problem. The potential dependence of zero-frequency C_d obtained using the pendant drop method exhibited remarkable dependence on alkyl chain length of IL cations. [C₂mim⁺][BF₄⁻], IL of cation having short alkyl chain, showed the one-hump potential dependence, whereas [C₈mim⁺][BF₄⁻] with long alkyl chain, i.e., large neutral moiety, showed two-hump camel shape (C_nmim⁺: 1-alkyl-3-methylimidazolium). These findings experimentally proved the validity of the prediction by theory and simulation [3,5,10].

In the present study, we further explore the dependence of zero-frequency C_d on ionic species of ILs, by studying the electrocapillarity and the zero-frequency C_d at the Hg interface of [C₂mim⁺][TFSA⁻] (TFSA⁻: bis(trifluoromethanesulfonyl)amide) and by comparing them with those of [C₂mim⁺][BF₄⁻] previously studied by us [51]. Although we previously used the mean-field lattice-gas theory for ILs composed of same size ions for analysis, in the present study we used an extended version of the theory recently proposed by Han et al. [59] where the size of IL ions can be different. The theory enables us to discuss the difference in the behavior of cation and anion in the EDL from the zero-frequency C_d data. TFSA⁻ is one of the most frequently used IL anions and the behavior of [C₂mim⁺][TFSA⁻] at the electrode interface has been studied by experiment [15,37,41,55,57,58,60,61] and simulation [62–66]. TFSA⁻ has three-time larger volume than BF₄⁻ (Table 1), and has asymmetric structure and localized charge distribution compared with BF₄⁻. We will discuss the effect of these difference of the molecular structure on the macroscopic zero-frequency C_d behavior.

2. Experimental

For the preparation of [C₂mim⁺][TFSA⁻], equimolar amount of synthesized [51] [C₂mim⁺][Br⁻] and purchased Li⁺[TFSA⁻] (Central Glass Co.) were dissolved in water and [C₂mim⁺][TFSA⁻] in the aqueous solution was extracted to dichloromethane. Dry Na₂SO₄ and MgSO₄ solids were added to the dichloromethane solution to remove

water and the solids were then filtered off. [C₂mim⁺][TFSA⁻] dissolved in dichloromethane was purified by column chromatography with activated carbon and silica gel as the stationary phase [43,67]. Dichloromethane was removed using an evaporator and a rotary oil pump, and [C₂mim⁺][TFSA⁻] was obtained as colorless liquid.

The details of the pendant drop method have been reported previously [51]. A pendant drop of Hg hanging from a glass tube immersed in [C₂mim⁺][TFSA⁻] was illuminated and the shape of the Hg drop was imaged. The outline of the drop was fitted with the theoretical curve of Bashforth-Adams equation. In the fitting the densities, ρ , of the two liquids were fixed and the interfacial tension, σ , was evaluated from one of the variable parameters [51]. The ρ value for [C₂mim⁺][TFSA⁻] was measured to be 1.520 g cm⁻³ at 25.0 °C by using a density meter (DA-505, KEM), which agrees with literature values [68,69]. The ρ value for Hg was adopted to be 13.5336 g cm⁻³ at 25.0 °C from literature [70]. The potential at the IL|Hg interface was controlled with a three-electrode electrochemical system. A Ag wire coated with AgCl was directly immersed in the IL as a quasi-reference electrode (QRE), and a Pt coiled wire as a counter electrode (CE). The potential of the Hg working electrode (WE) with respect to the Ag/AgCl QRE, denoted as E , was controlled using a PC-controlled potentiostat (HA1010mM1A, Hokuto Denko). At each potential, measurements were continued for sufficiently long time, typically more than 5 min to equilibrate the interfacial structure at the IL|Hg interface [51]. The σ value that became independent of time was adopted as σ in equilibrium at the potential. Measurements were performed at 25.0 ± 0.1 °C. The surface charge density on Hg, q_M , was evaluated from the numerical differentiation of the E dependence of σ in the same manner as previously reported [51]. Similarly, the zero-frequency C_d was evaluated from the numerical differentiation of the potential dependence of q_M with respect to E .

To compare with the zero-frequency C_d , the EIS C_d was also measured. A hanging mercury drop electrode (WK2, Institute of Physical Chemistry Polish Academy of Sciences) was used as WE. The surface area of Hg, A , was 0.024 cm². QRE and CE are the same as those in the pendant drop method. The EIS measurements were performed with a PC-controlled potentiostat (CompactStat, Ivium Technologies) with the ac potential amplitude of 10 mV and the frequency range from 10 to 1000 Hz. For the analysis of impedance spectra we used equivalent circuit composed of constant phase element (CPE), whose impedance is $\frac{1}{(i\omega)^p T}$ where ω is angular frequency, in series with a solution resistance. When needed, an electron-transfer resistance was added in parallel with CPE. The EIS C_d was evaluated as

$$C_d = \frac{T\omega^{p-1}}{A}. \quad (1)$$

As shown in Eq. (1), C_d of CPE depends on the frequency. As a representative data we chose C_d at 100 Hz, which corresponds to the midpoint of the measurement frequency range in logarithmic scale. Before measurements at each dc potential, we applied the dc potential for 60–100 s to minimize the effect of the ultraslow dynamics of EDL.

3. Results and discussion

The electrocapillary curve at the [C₂mim⁺][TFSA⁻]|Hg interface is shown in Fig. 1 as solid circles. The shape of σ as a function of E is parabolic and the potential at the apex of the parabola around -0.4 V, is the potential of zero charge, E_{pzc} , where the interface is not charged ($q_M = 0$). In Fig. 1 also shown is the electrocapillary curve at the [C₂mim⁺][BF₄⁻]|Hg interface (solid squares) from our previous study [51]. The σ value for [C₂mim⁺][TFSA⁻] at E_{pzc} , 355 mN m⁻¹, which is 34 mN m⁻¹ less than that for [C₂mim⁺][BF₄⁻]. The interfacial tensions of the free surface (IL|air interface) of the two

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