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STUDY ON SURFACE ADSORPTION FROM CATIONIC SURFACTANT-ELECTROLYTE MIXED AQUEOUS SOLUTION INCLUDING BF$_4^-$ ION

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ABSTRACT

The surface tension of aqueous mixtures of dodecyltrimethylammonium tetrafluoroborate (DTABF$_4$) and sodium tetrafluoroborate (NaBF$_4$) was measured as a function of total molality and composition of DTABF$_4$ at 298.15K. The

results were analyzed by originally developed thermodynamic equations and compared

with those of dodecyltrimethylammonium bromide (DTAB)- sodium bromide (NaBr)

mixed system.   It was indicated that BF_4^- ions reduce the repulsion between DTA^+

ions more effectively than Br^- ions in the adsorbed film.   To investigate this difference

more closely, the surface tension of DTAB-$NaBF_4$ and $DTABF_4$-NaBr mixed system

was also measured.   The data analysis revealed that BF_4^- ions are adsorbed positively

even for the pure $NaBF_4$ system and preferentially to Br^- ions in these mixtures.

Furthermore it was concluded that the side-by-side arrangement suggested in the

adsorbed film of 1-hexyl-3-methylimidazolium tetrafluoroborate ($HMIMBF_4$) is due to

not only the positive adsorption of BF_4^- ions but also the capability of hydrogen bond

formation between imidazolium ion and BF_4^- ions.

Keywords

INTRODUCTION

For past decades, ionic liquids have been received increasing attention as a substitute for existing reaction solvents because of their low vapor pressure, non-flammability, and good solvent ability for a wide range of materials [1-3] and as a novel media for batteries, fuel cells, and solar cells because of their high conductivities and wide electrochemical windows [4-6]. The ionic liquids based of 1-alkyl-3-methylimidazolium ion have been investigated recently as short-chain cationic surfactant in the field of colloid and interface science because the imidazolium cations have an amphiphilic structure and their assembled states is, at least partly, similar to structure of neat ionic liquids [7-11]. We have previously studied the surface property of the aqueous solutions of 1-hexyl-3-methylimidazolium tetrafluoroborate (HMIMBF$_4$) and a usual cationic surfactant with BF$_4^-$ as its counter anion, dodecyltrimethylammonium tetrafluoroborate (DTABF$_4$), by employing the surface thermodynamics and X ray absorption fine structure under total reflection condition (TRXAFS) [12,13]. It was demonstrated that for example, the surface pressure π

vs. the average area per molecule A curve of the HMIMBF$_4$ system is almost vertical,

which suggests an incompressible adsorbed film, at the saturation adsorption whereas

those of DTABF$_4$ and dodecyltrimethylammonium bromide (DTAB) systems show a

higher compressibility even at their saturation adsorption (Fig. 1).   Furthermore in

the adsorbed film of the HMIMBF$_4$ - 1-hexyl-3-methylimidazolium bromide (HMIMBr)

mixture, BF$_4^-$ ions are rather near cations but Br$^-$ ions are distributed in the electric

double layer and thus, a segregation of BF$_4^-$ and Br$^-$ ions takes place in the adsorbed

film [13].   Such counterion distribution is probably examined employing the theory

of Ivanov et al. [14].

For the neat ionic liquid surface, it is indicated that the BF$_4^-$ ion occupies the surface

at the same level of the imidazolium ring because the BF$_4^-$ ion forms two hydrogen

bonds with C(2)-H and –CH on the side chain and as a result, it positions on top of the

imidazolium ring [15-17].   From the fact that the compressibility of the film is very

low irrespective of that the observed minimum occupied area of HMIMBF$_4$ is still

larger than the expected area for the fully packed monolayer of HMIM$^+$ ions (0.36 nm^2),

we have concluded that the adsorbed film has similar structure to the neat ionic liquid

surface.   Probably, the adsorption of imidazolium cations at the air/water interface

plays an important role for providing the environment where BF_4^- ions are highly concentrated as the neat ionic liquid surface.

In the present study, in order to examine this unique adsorption behavior, we will focus on the effect of the counterions and the role of imidazolium cation on the adsorption behavior.   For this purpose, we adopted the dodecyltrimethylammonium ion (DTA^+ ion) as a surfactant cation which is less capable of forming hydrogen bonds than imidazolium ion and measured the surface tension of the $DTABF_4$-$NaBF_4$, $DTAB$-$NaBF_4$, and $DTABF_4$-$NaBr$ systems.   It was found that BF_4- ion adsorbs at the air/water interface preferentially to Br^- ion and the capability of hydrogen bond formation between imidazolium ion and counterion works effectively for the side-by-side arrangement in the adsorbed film of $HMIMBF_4$.

EXPERIMENTAL

Material: Sodium tetrafluoroborate ($NaBF_4$) was purchased from Kanto Kagaku Co., Ltd. (98%) and recrystallized from water and then baked at $170\,°C$ for 7 hours under

reduced pressure.   Sodium bromide (NaBr) was purchased from Wako Pure Chemical

Industries (99.9%) and used as received.   Dodecyltrimethylammonium bromide

(DTAB) purchased from Wako Pure Chemical Industries (99%) was purified by

recrystallizing it five times from the mixture of acetone and ethanol (1:5 volume ratio).

Dodecyltrimethylammonium tetrafluoroborate (DTABF$_4$) was synthesized from DTAB

with equimolar amount of NaBF$_4$ in the aqueous solution and then recrystallized twice

from water.   These purities were checked by elemental analysis.   Water used for all

experiments was distilled three times; the second and third stages were done from

alkaline permanganate solution.

Surface Tension Measurement: The surface tension γ of the aqueous solutions was

measured by the drop volume method at 298.15K under atmospheric pressure.   The

total molality $\hat{m}$ and mole fraction of surfactant $\hat{X}_2$ were adopted as the

experimental concentration variables, where they are defined as

$$\hat{m} = \left(m_{1+} + m_{1-} \right) + \left(m_{2+} + m_{2-} \right) \tag{1}$$

and

$$\hat{X}_2 = \left(m_{2+} + m_{2-}\right)/\hat{m} \tag{2}$$

Here, m_{1+} and m_{1-} represent the molalities of cationic and anionic ions dissociated from inorganic salts, and m_{2+} and m_{2-} those from ionic surfactants, respectively.

The γ value was calculated by the following equation [18, 19]

$$\gamma = \frac{V \Delta \rho g}{r} F \,, \tag{3}$$

where V is the volume of a drop, g the local acceleration of gravity, r the capillary radius, and F the correction factor calculated from the following equation,

$$F = 0.1482 + 0.27896(r/V^{1/3}) - 0.166(r/V^{1/3})^2 \tag{4}$$

and $\Delta\rho$ the density difference between air and aqueous solution. The densities of aqueous solutions of NaBr and NaBF$_4$ ρ_{solution} were measured by the oscillating tube method (Anton Par, D60/602) and shown in Fig. 2. It was found that ρ_{solution} increases linearly with molality as

$$\rho_{\text{solution}} = \rho_{\text{water}} + a\hat{m} \tag{5}$$

Where ρ_{water} was 0.997047 g cm^{-3}, and $a = 7.65052 \times 10^{-5}$ (NaBr), 6.69881×10^{-5} (NaBF$_4$), respectively.

The experimental error of the surface tension measurement was within 0.05 mN m^{-1}.

RESULT AND DISCUSSION

The results of surface tension measurements of the aqueous solutions of the DTABF$_4$-NaBF$_4$ mixtures were plotted against $\hat{m}$ at fixed mole fractions of DTABF$_4$ $\hat{X}_2$ in Fig. 3. The γ value decreases with increasing $\hat{m}$ and the shape of γ vs. $\hat{m}$ changes regularly with $\hat{X}_2$. We have previously proved that the break points on these curves are corresponding to the phase transition of the adsorbed film from the gaseous to the expanded states [20]. It should be noted that the γ values of the aqueous solution of NaBF$_4$ slightly decreases with $\hat{m}$, in contrast to that of NaBr, as shown in the wide concentration ranges in Fig. 4.

The total differential of surface tension at constant temperature and pressure is given by [21]

$$d\gamma = -\left(RT\,\hat{\Gamma}^{\mathrm{H}}/\hat{m}\right)d\hat{m} - \left(RT\,\hat{\Gamma}^{\mathrm{H}}/2\hat{X}_1\hat{X}_2\right)\left(\hat{X}_2^{\mathrm{H}} - \hat{X}_2\right)d\hat{X}_2 \qquad (6)$$

where the total surface density of ions and the surface composition of the second surfactant, DTABF$_4$. are defined as

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$$\hat{\varGamma}^{\mathrm{H}} = \varGamma_{\mathrm{DTA}^+}^{\mathrm{H}} + \varGamma_{\mathrm{Na}^+}^{\mathrm{H}} + \varGamma_{\mathrm{BF}_4^-}^{\mathrm{H}} = 2\left(\varGamma_{\mathrm{DTA}^+}^{\mathrm{H}} + \varGamma_{\mathrm{Na}^+}^{\mathrm{H}}\right) \tag{7}$$

where the electroneutrality condition $\varGamma_{\mathrm{DTA}^+}^{\mathrm{H}} + \varGamma_{\mathrm{Na}^+}^{\mathrm{H}} = \varGamma_{\mathrm{BF}_4^-}^{\mathrm{H}}$ is taken into account, and

$$\hat{X}_2^{\mathrm{H}} = 2\varGamma_{\mathrm{DTA}^+}^{\mathrm{H}} \big/ \hat{\varGamma}^{\mathrm{H}} \tag{8}$$

respectively.   From Eq. (6), the surface density of surfactant was calculated by using

$$\hat{\varGamma}^{\mathrm{H}} = -\left(\hat{m}/RT\right)\left(\partial\gamma/\partial\hat{m}\right)_{T,p,\hat{X}_2} \tag{9}$$

and shown in Fig. 5.   From the linear decrease of γ with $\hat{m}$ for the pure NaBF$_4$

solution, it was noticed that NaBF$_4$ adsorbs positively at the air/water interface and its

amount increases with increasing $\hat{m}$.   It is well known that Na$^+$ ion shows negative

adsorption due to the image force from the interface, hence, it was revealed that BF$_4^-$

ion adsorbs positively in the pure NaBF$_4$ system.   On the other hand, $\hat{\varGamma}^{\mathrm{H}}$ of DTABF$_4$

and the mixtures increases with increasing $\hat{m}$ and shows the discontinuous change at

the phase transition concentrations.

Next, let us evaluate the compositions of DTABF$_4$ in the adsorbed film $\hat{X}_2^{\mathrm{H}}$ by

plotting $\hat{m}$ values against $\hat{X}_2$ at fixed γ and then applying

$$\hat{X}_2^{\mathrm{H}} = \hat{X}_2 - \left(2\hat{X}_1\hat{X}_2/\hat{m}\right)\left(\partial\hat{m}/\partial\hat{X}_2\right)_{T,p,\gamma} \tag{10}$$

to the $\hat{m}$ vs. $\hat{X}_2$ curves. The results were drawn in the form of the phase diagram

of adsorption (PDA) in which the composition in the bulk solution and that in the

adsorbed film were represented together (Fig. 6).

It is worth noting that the value of $\hat{X}_2^{\mathrm{H}}$ is larger than unity in the whole bulk

composition range. Considering that $\hat{X}_2^{\mathrm{H}}$ is rewritten from Eqs. (7) and (8) as

$$\hat{X}_2^{\mathrm{H}} = \frac{\varGamma_{\mathrm{DTA}^+}^{\mathrm{H}}}{\varGamma_{\mathrm{DTA}^+}^{\mathrm{H}} + \varGamma_{\mathrm{Na}^+}^{\mathrm{H}}} \qquad (11)$$

it can be understood that one of the reason for this is the negative value of $\varGamma_{\mathrm{Na}^+}^{\mathrm{H}}$, that is,

exclusion of Na^+ ions from the surface region by the electrostatic repulsion toward

DTA^+ ions adsorbed at the interface. Figure 7 represents the surface densities of DTA^+

ion evaluated by combining the $\hat{\varGamma}^{\mathrm{H}}$ values in Fig. 5 and $\hat{X}_2^{\mathrm{H}}$ values in Fig. 6, where

the results of the DTAB-NaBr system [22] is also drawn. The $\varGamma_{\mathrm{DTA}^+}^{\mathrm{H}}$ value increases

with decreasing $\hat{X}_2$, but its dependence on $\hat{X}_2$ is much weaker than that observed in

the DTAB-NaBr mixtures. These results clearly demonstrate that the shielding effect

of BF_4^- ion on the electrostatic repulsion between DTA^+ ions is quite effective compared

with that of Br^- ion and the electric charge of DTA^+ ions is almost completely shielded

even in the pure DTABF_4 system. Therefore, the further adsorption of BF_4^- ion does

not take place when $NaBF_4$ is added.

Furthermore, the investigation of adsorption behavior of the DTAB-$NaBF_4$ system revealed that BF_4^- ion adsorbs at the air/water interface preferentially to Br^- ion as follows. Figures 8 and 9 show the γ vs. $\hat{m}$ curves and the PDA for the DTAB-$NaBF_4$ mixtures. It should be noted in Fig. 8 that the γ vs. $\hat{m}$ curve at a given $\hat{X}_2$ moves to the left from $\hat{X}_2 = 1$ (DTAB) to $\hat{X}_2 = 0.5$ and then turns to the right with decreasing $\hat{X}_2$. The $\hat{m}$ vs. $\hat{X}_2$ curves at given surface tensions (solid curves in Fig. 9) demonstrates this situation more clearly; the curves have a minimum at around $\hat{X}_2 = 0.5$. The $\hat{X}_2^H$ values calculated from the solid curves are shown by the broken lines, which form the PDA together with the $\hat{m}$ vs. $\hat{X}_2$ curves. There are two important points. First the PDA exhibits a negative azeotropic point and thus, two components are mixed favorably in the adsorbed film in the whole range of $\hat{X}_2$. Secondary the $\hat{X}_2^H$ values are around $\hat{X}_2^H = 0.5$ irrespective of $\hat{X}_2$ when $\hat{X}_2 < 0.5$. Taking account of the relation $\hat{X}_2^H = X_{DTA^+}^H + X_{Br^-}^H$ from Eq. (8) and

$$X_{Na^+}^H + X_{DTA^+}^H + X_{BF_4^-}^H + X_{Br^-}^H = 1 \tag{12}$$

and supposing that $X_{Na^+}^H \approx 0$, we have $X_{DTA^+}^H + X_{Br^-}^H = 0.5$ and $X_{BF_4^-}^H = 0.5$ when

$\hat{X}_2^{\mathrm{H}} = 0.5$. Therefore, the electroneutrality condition $X_{\mathrm{DTA}^+}^{\mathrm{H}} = X_{\mathrm{BF}_4^-}^{\mathrm{H}} + X_{\mathrm{Br}^-}^{\mathrm{H}}$ yields

$X_{\mathrm{Br}^-}^{\mathrm{H}} = 0$; it is suggested that the adsorbed film is almost composed of DTA$^+$ and BF$_4^-$

ions when $\hat{X}_2 < 0.5$. This is demonstrated more precisely by combining the results of

the DTAB-NaBF$_4$ system with those of the DTABF$_4$-NaBr system as shown later.

We have previously reported that the Br$^-$ ions in the adsorbed film of DTAB aqueous

solution have two hydration states by the TRXAFS measurement [12]: one

corresponding to the Br$^-$ ions with smaller hydration number of 3 to 4 distributed near

the surfactant head groups (bound ions) and the other the Br$^-$ ions with hydration

number of 6 similar to those in the bulk solution (free ions).   The fraction of the free

ions decreases with increasing $\Gamma_{\mathrm{DTA}^+}^{\mathrm{H}}$ and the fraction of the bound ions increases

instead.   However, in the mixed adsorbed film of HMIMBF$_4$-HMIMBr system, the

TRXAFS revealed that the Br$^-$ ions are all in the free states at almost all the bulk

compositions [13].   Taking these results into consideration, it is indicated that the

fraction of the bound-BF$_4^-$ is considerably high even in the pure DTABF$_4$ system and

Br$^-$ ions distribute mainly in the electrical double layer as the free ion.

Finally let us calculate the ratio of BF$_4^-$ ion and Br$^-$ ion in the mixed adsorbed film.

Here it should be remembered that the surface densities of the respective ions cannot be

calculated in principle for the binary ionic surfactant mixture without common ions like

the DTAB-NaBF$_4$ system [21]. However, they can be evaluated at $\hat{X}_2 = 0.5$ by

combining the results of the DTABF$_4$-NaBr system as follows. Figures 10 and 11

show the γ vs. $\hat{m}$ curves and the PDA for the DTABF$_4$-NaBr mixtures. The γ vs.

$\hat{m}$ curve gradually changes its position from $\hat{X}_2 = 1$ (DTABF$_4$) by adding NaBr,

which gives the similar feature to that of the DTABF$_4$-NaBF$_4$ mixture in Fig. 3, but the

different one from that of the DTAB-NaBF$_4$ mixture in Fig. 8. Since the numbers of

constituent ions are the same for the DTABF$_4$-NaBr and DTAB-NaBF$_4$ systems at a

given $\hat{m}$ and at $\hat{X}_2 = 0.5$, we have four equations; the one is Eq. (12) from the mass

balance relation and other three are

$$\hat{X}_2^{\mathrm{H}} = X_{\mathrm{DTA}^+}^{\mathrm{H}} + X_{\mathrm{Br}^-}^{\mathrm{H}} \quad \text{(DTAB-NaBF}_4 \text{ system)} \tag{13}$$

$$\hat{X}_2^{\mathrm{H}} = X_{\mathrm{DTA}^+}^{\mathrm{H}} + X_{\mathrm{BF}_4^-}^{\mathrm{H}} \quad \text{(DTABF}_4\text{-NaBr system)} \tag{14}$$

and

$$X_{\mathrm{DTA}^+}^{\mathrm{H}} + X_{\mathrm{Na}^+}^{\mathrm{H}} = X_{\mathrm{BF}_4^-}^{\mathrm{H}} + X_{\mathrm{Br}^-}^{\mathrm{H}} \tag{15}$$

from the electroneutrality condition in adsorbed film. The $X_\alpha^{\mathrm{H}}(\alpha$; DTA$^+$, Na$^+$, Br$^-$,

BF$_4^-$) values thus estimated are listed at $\gamma = 65$ and 46 mN m^{-1} in Table 1. It is evident

that the ratio $X_{\mathrm{Br^-}}^{\mathrm{H}} / X_{\mathrm{BF_4^-}}^{\mathrm{H}} = 0.099$ and 0.053 and thus the adsorbed film is almost

composed of $\mathrm{DTA^+}$ and $\mathrm{BF_4^-}$ ions when $\hat{X}_2 = 0.5$. This is in accord with the

suggestion obtained from the PDA of the DTAB-NaBF$_4$ system and the examination on

it by supposing $X_{\mathrm{Na^+}}^{\mathrm{H}} \approx 0$.

In the present study, for the purpose of examining the side-by-side arrangement of

HMIMBF$_4$ in the adsorbed film, we investigated the counterion effect on surface

adsorption of the several cationic surfactants. The important conclusions are as

follows: BF$_4^-$ ions show strong shield effect on the electric repulsion between surfactant

ions and they are preferentially adsorbed at the air/water interface even when the bulk

solutions are enriched with Br$^-$ ion. Taking into account that the BF$_4^-$ ion adsorbs

positively while Br$^-$ ion negatively at the air/water interface in the respective pure

inorganic electrolyte solutions, the differences in adsorption behavior observed in the

binary mixtures of DTABF$_4$-NaBF$_4$, DTAB-NaBF$_4$, and DTABF$_4$-NaBr are partially

attributable to the difference in surface activity of the counterions. Although the

adsorption ability of BF$_4^-$ ion is undoubtedly important factor in governing the

adsorption behavior of cationic surfactant having BF$_4^-$ as counter anion, the interaction

between the surfactant cation and BF$_4^-$ is also essential in the adsorption behavior.

For example, the side-by-side arrangement is suggested due to the ion-paring between HMIM$^+$ and BF$_4^-$ ions in the adsorbed film, whereas DTABF$_4$ itself does not show such arrangement as examined from the π vs. A curves (Fig. 1). Therefore, it is indicated that the capability of hydrogen bond formation between imidazolium ion and counterion works effectively for the side-by-side arrangement.

ACKNOWLEDGEMENT

REFERENCES

1. Wasserscheid P, Welton T (2003) Ionic Liquids in Synthesis. Wiley, New York

2. Welton T (1999) Chem Rev 99:2071

3. Wasserscheid P, Keim W (2000) Angew Chem Int Edi 39:3773

4. Bonhote P, Dias A, Papageorgiou N, Kalyanasundaram K, Gratzel M (1996) Inorg Chem 35:1168

5. Fuller J, Breda AC, Carlin RT (1998) J Electroanal Chem 459:29

6. Quinn BM, Ding ZF, Moulton R, Bard AJ (2002) Langmuir 18:1734

7. Firestone MA, Dzielawa JA, Zapol P, Curtiss LA, Seifert S, Dietz ML (2002) Langmuir 18:7258

8. Dong B, Zhao XY, Zhang J, Li N, Inoue T (2008) 317:666

9. Bowers J, Butts CP, Martin PJ, Vergara-Gutierrez MC, Heenan RK (2004) Langmuir 20:2191

10. Jiang W, Wang YT, Voth GA (2007) J Phy Chem B 111:4812

11. Vanyur R, Biczok L, Miskolczy Z (2007) Colloids Surfaces A-Physico Eng Asp 299:256

12. Aratono M, Shimamoto K, Onohara A, Murakami D, Tanida H, Watanabe I Ozeki T, Matsubara H, Takiue T (2008) Anal Sci 24:1279

13. Shimamoto K, Onohara A, Takumi T, Watanabe I, Tanida H, Matsubara H, Takiue T, Aratono M (2009) Langmuir 25:9954

14. Ivanov IB, Marinova KG, Danov KD, Dirnitrova D, Ananthapadmanabhan KP, Lips A (2007) Adv Colloid Interface Sci 134:105

15. Jeon Y, Sung J, Seo C, Lim H, Cheong H, Kang M, Moon B, Ouchi Y, Kim D (2008) J Phys Chem B 112:4735

16. Jeon Y, Sung J, Bu W, Vaknin D, Ouchi Y, Kim D (2008) J Phys Chem C 112:19649

17. Kolbeck C, Cremer T, Lovelock KRJ, Paape N, Schulz PS, Wasserscheid P, Maier F, Steinruck HP (2009) J Phys Chem B 113:8682

18. Harkins WD, Brown FE (1919) J Am Chem Soc 41:499

19. Lando JL, Oakley HT (1967) J Colloid Interface Sci 25:526

20. Motomura K, Iwanaga S, Hayami Y, Uryu S, Matsuura R (1981) J Colloid Interface Sci 80:32

21. Aratono M, Villeneuve M, Takiue T, Ikeda N, Iyota H (1998) J Colloid Interface Sci 200:161

22. Kashimoto K, Takata Y, Matsuda T, Ikeda N, Matsubara H, Takiue T, Aratono M,

Tanida H, Watanabe I (2006) Langmuir 22:8403
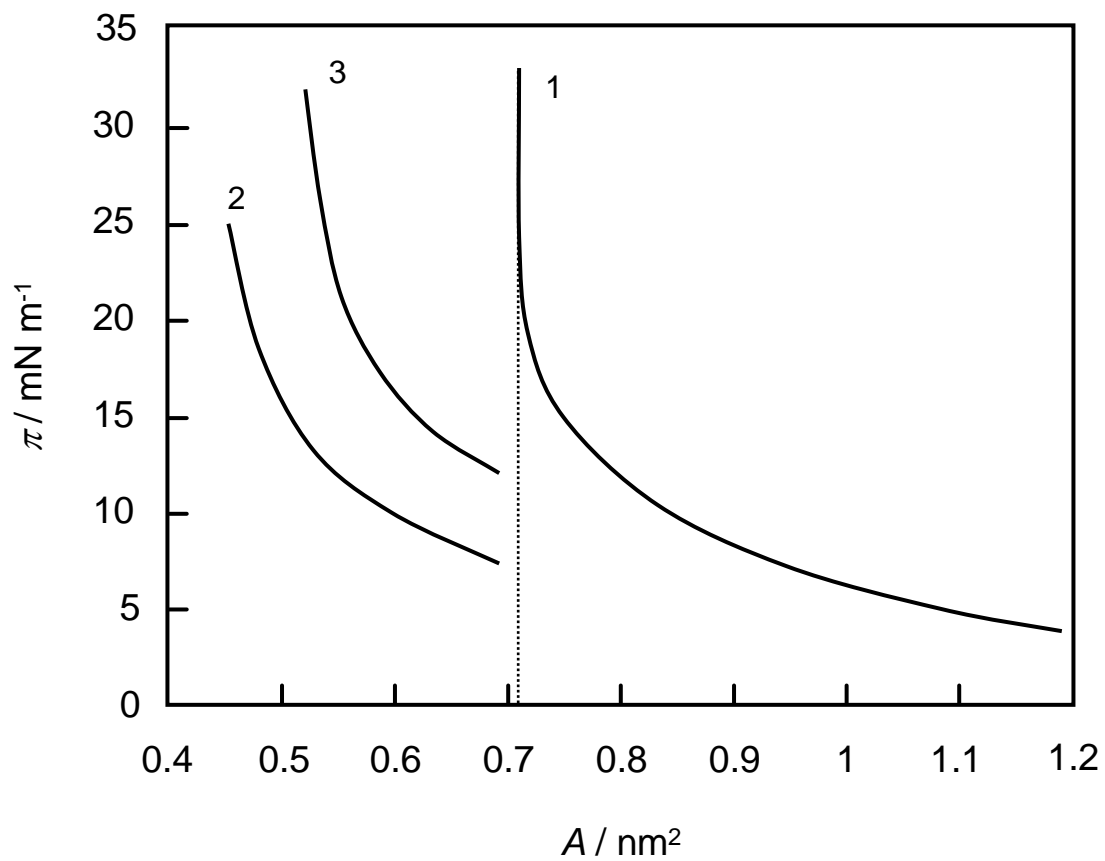
Fig. 1 Surface pressure vs. area per molecule curves: (1) HMIMBF$_4$, (2) DTABF$_4$, (3) DTAB
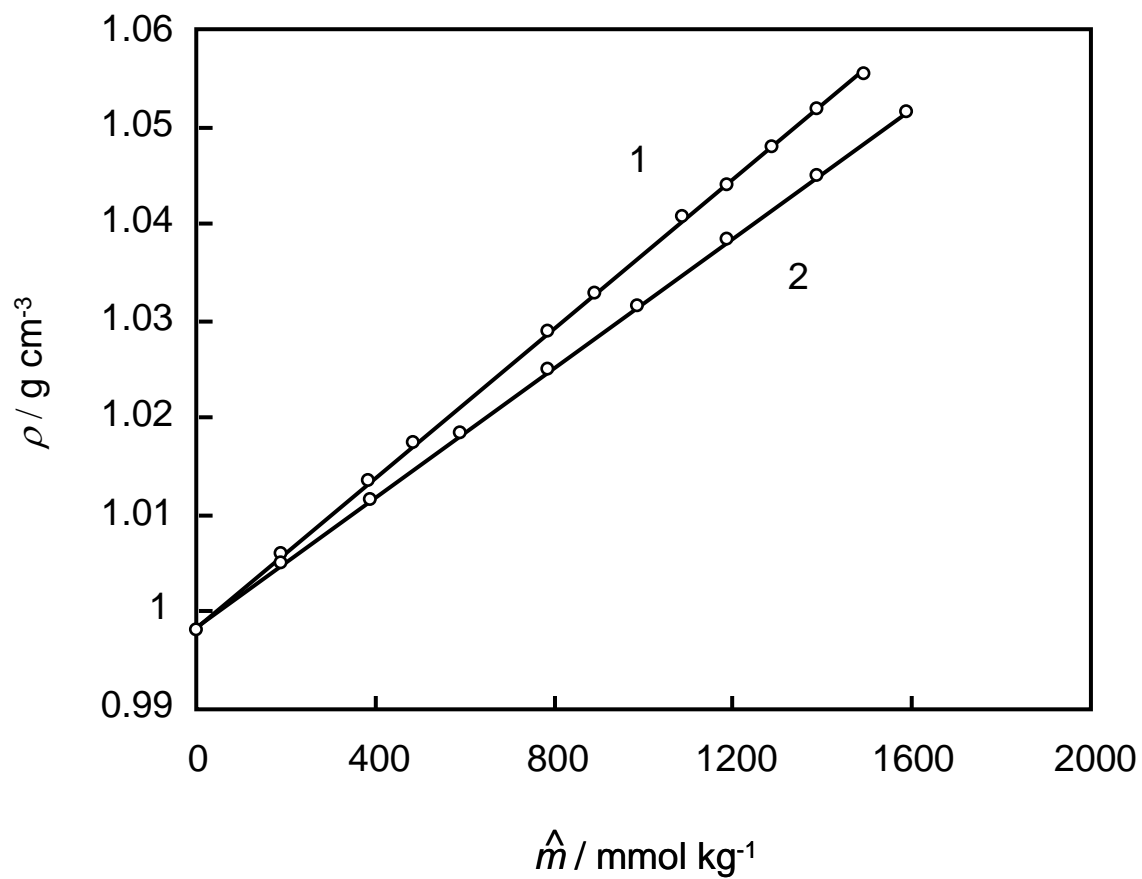
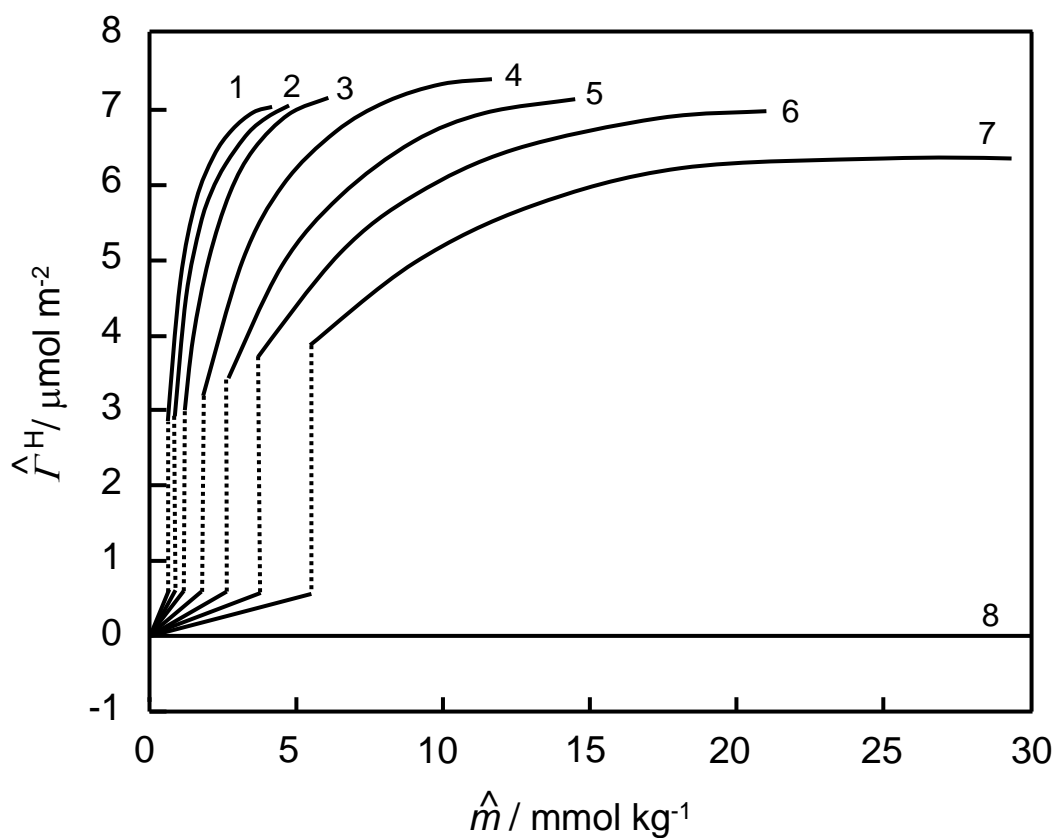**Fig. 2** Density of aqueous solution vs. molality curves: (1) NaBr, (2) NaBF$_4$
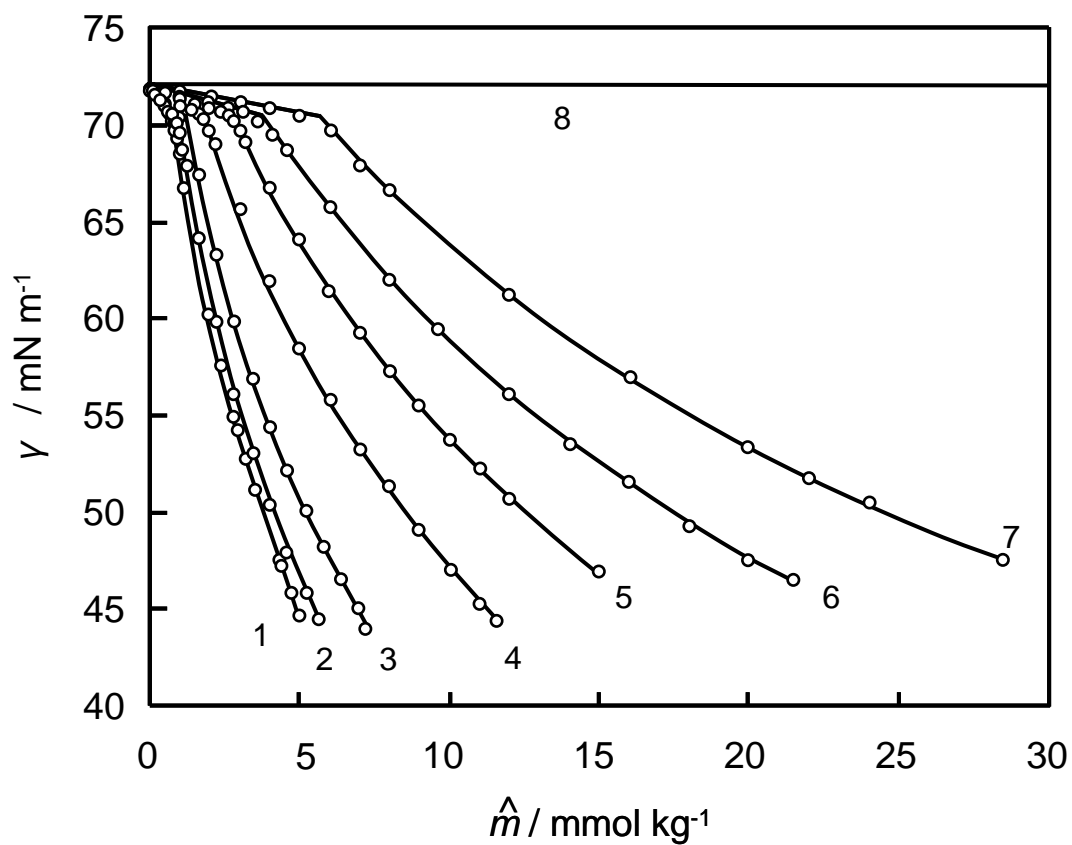
Fig. 3 Surface tension vs. total molality curves of DTABF$_4$-NaBF$_4$ system at constant bulk compositions: (1) $\hat{X}_2$=1 (DTABF$_4$), (2) 0.8, (3) 0.5, (4) 0.2, (5) 0.1, (6) 0.05, (7) 0.03, (8)0 (NaBF$_4$)
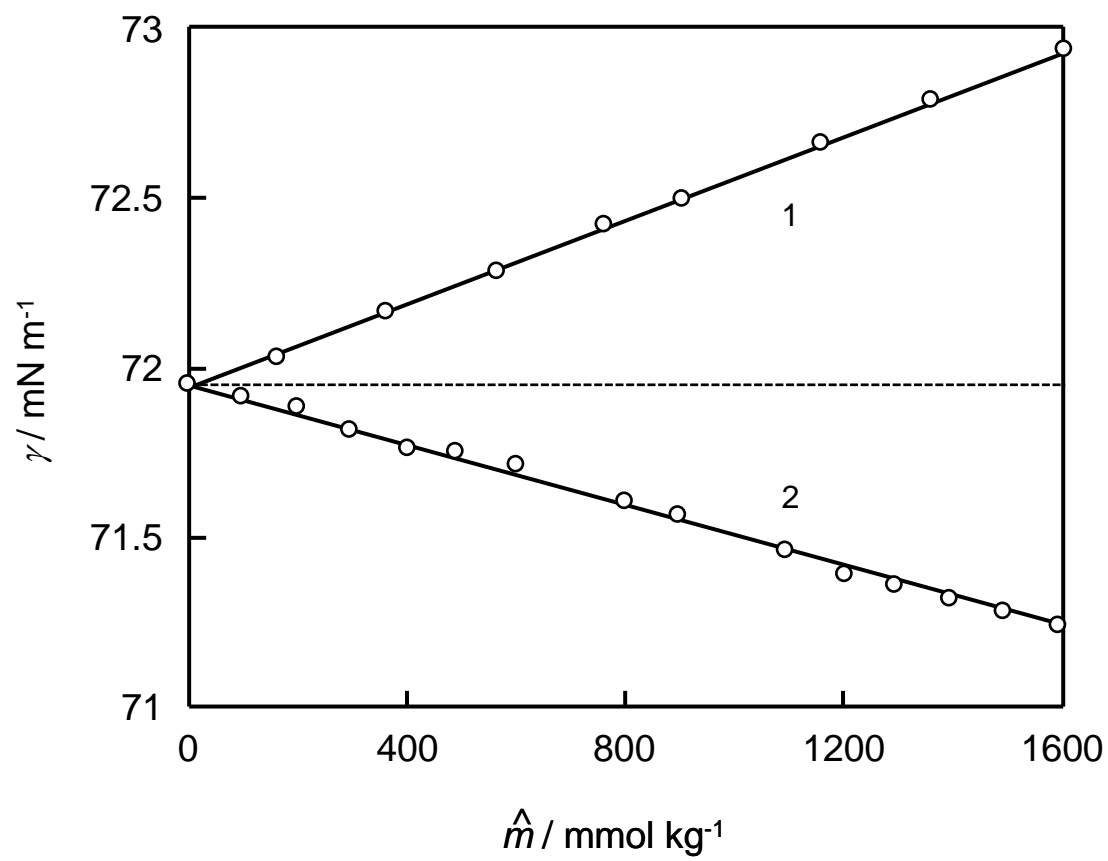
Fig. 4 Surface tension vs. molality curves of electrolyte solutions: (1) NaBr, (2)
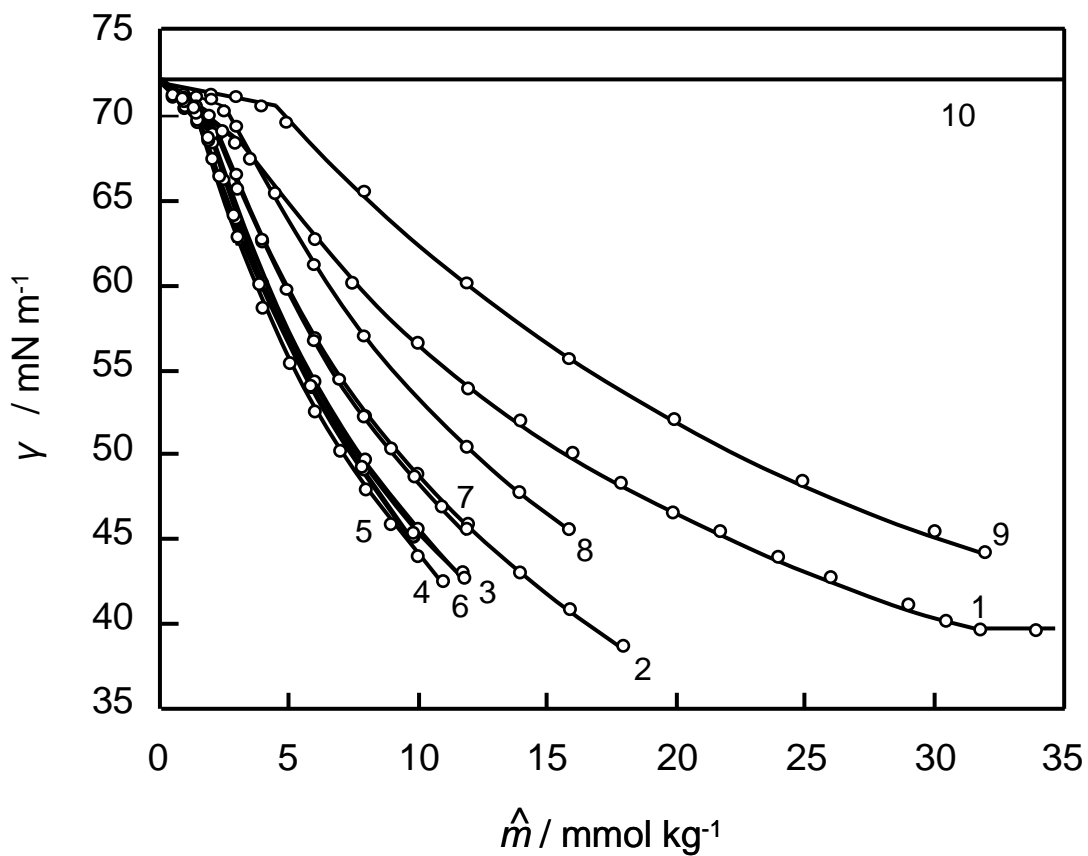
$NaBF_4$

Fig. 5 Total surface density vs. total molality curves of $DTABF_4$-$NaBF_4$ system at constant bulk compositions: (1) $\hat{X}_2$=1 ($DTABF_4$), (2) 0.8, (3) 0.5, (4) 0.2, (5) 0.1, (6) 0.05, (7) 0.03, (8)0 ($NaBF_4$)
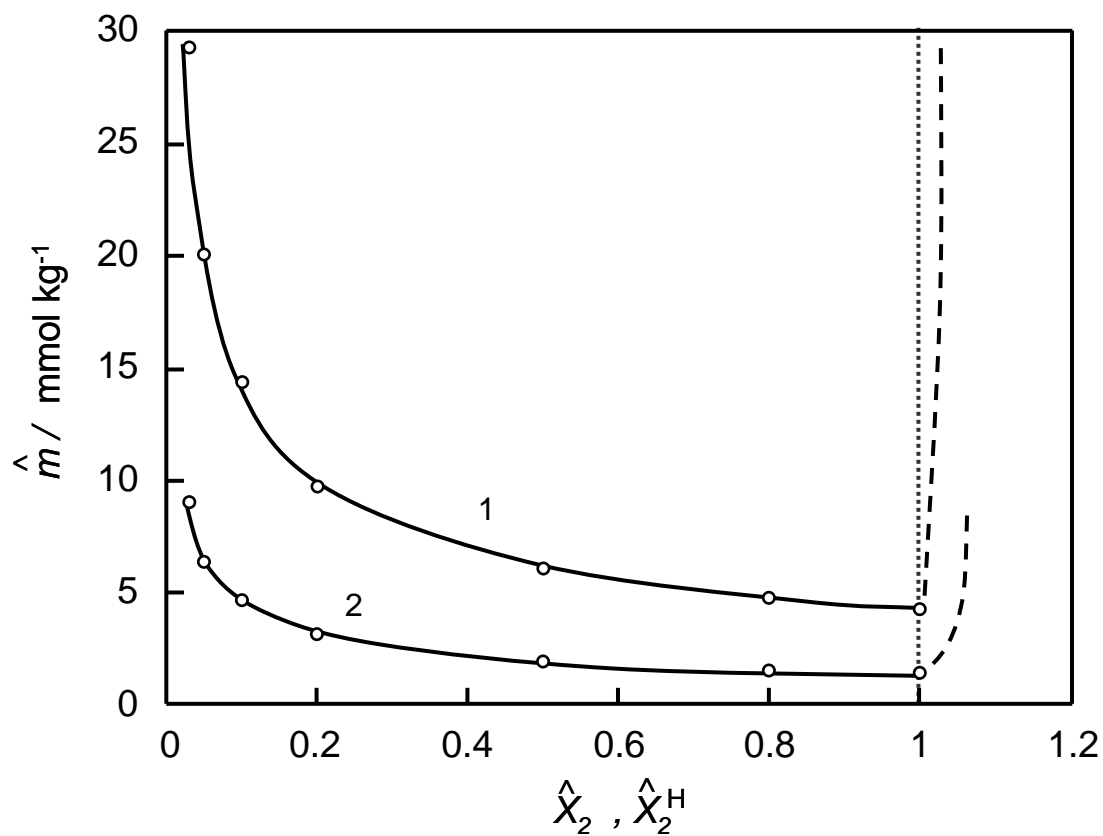
Fig. 6 Total molality vs. composition curves of DTABF$_4$-NaBF$_4$ system at constant surface tensions: (1) $\gamma = 47.5$ mN m^{-1}, (2) $\gamma = 65$ mN m^{-1}; (solid line) $\hat{m}$ vs. $\hat{X}_2$, (broken line) $\hat{m}$ vs. $\hat{X}_2^H$
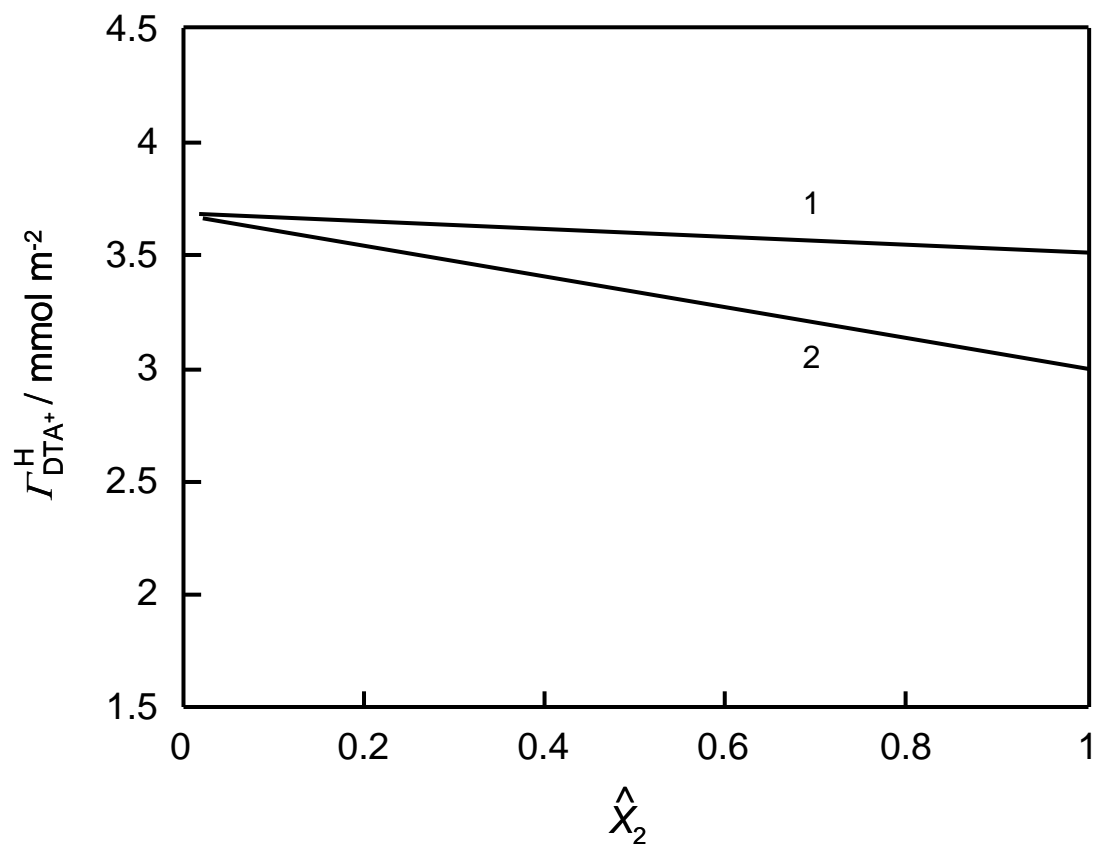
Fig. 7 Surface density of DTA$^+$ ion vs. bulk composition at $\gamma = 47.5$ mN m^{-1}: (1)

DTABF$_4$-NaBF$_4$, (2) DTAB-NaBr

Fig. 8 Surface tension vs. total molality curves of DTAB-NaBF$_4$ system at constant bulk compositions: (1) $\hat{X}_2$=1 (DTAB), (2) 0.9, (3) 0.8, (4) 0.65, (5) 0.5, (6) 0.352, (7) 0.2, (8) 0.1, (9) 0.03, (10) 0 (NaBF$_4$)
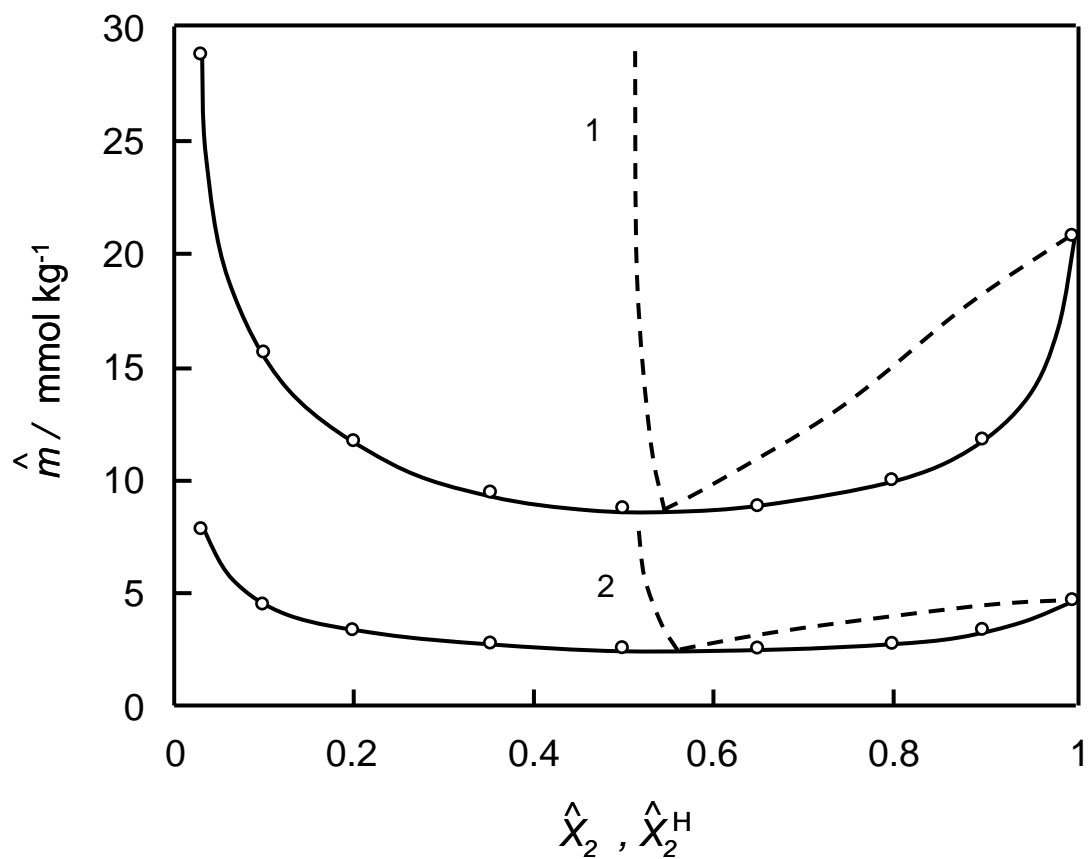
Fig. 9 Total molality vs. composition curves of DTAB-NaBF$_4$ system at constant surface tensions: (1) $\gamma = 46$ mN m^{-1}, (2) $\gamma = 65$ mN m^{-1}; (solid line) $\hat{m}$ vs. $\hat{X}_2$, (broken line) $\hat{m}$ vs. $\hat{X}_2^{\mathrm{H}}$
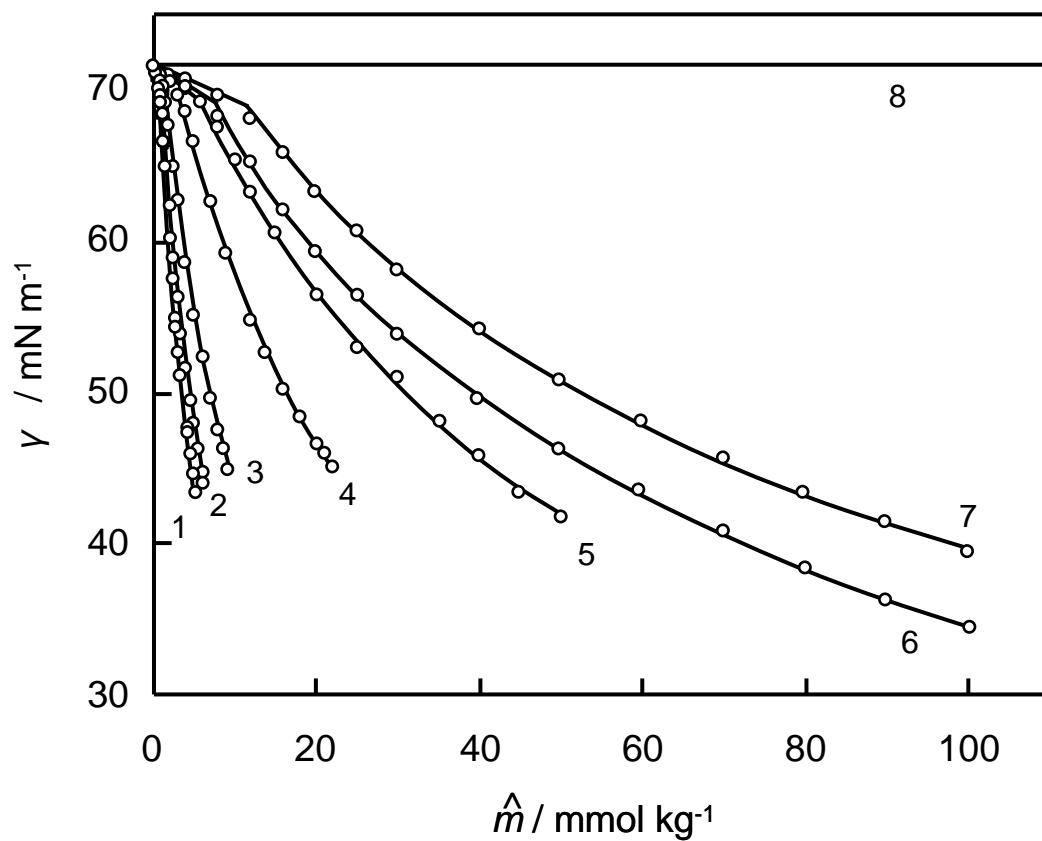
Fig. 10 Surface tension vs. total molality curves of DTABF$_4$-NaBr system at constant bulk compositions: (1) $\hat{X}_2$=1 (DTABF$_4$), (2) 0.8, (3) 0.5, (4) 0.2, (5) 0.1, (6) 0.05, (7) 0.03, (8)0 (NaBr)
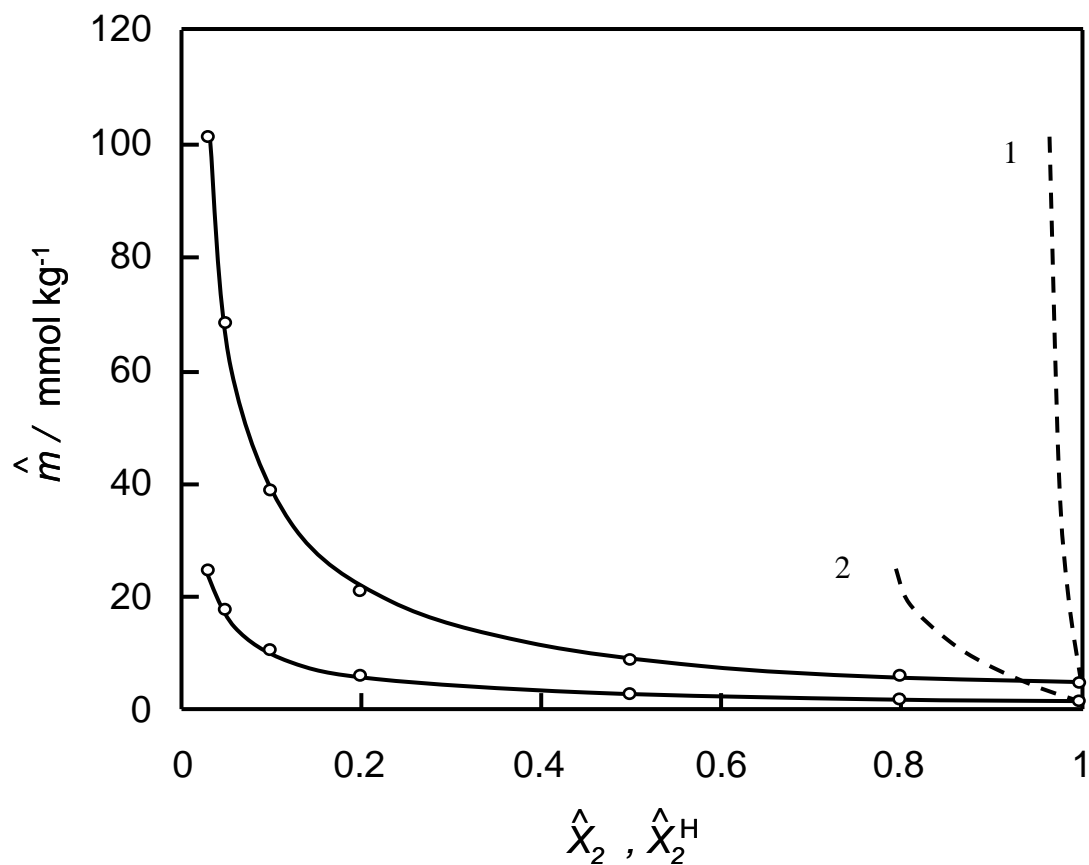
Fig. 11 Total molality vs. composition curves of DTABF$_4$-NaBr system at constant surface tensions: (1) $\gamma = 46$ mN m^{-1}, (2) $\gamma = 65$ mN m^{-1}; (solid line) $\hat{m}$ vs. $\hat{X}_2$, (broken line) $\hat{m}$ vs. $\hat{X}_2^H$

Table 1 Surface compositions of ions at $\hat{X}_2 = 0.5$

γ / mN m^{-1}	$X_{\mathrm{DTA}^+}^{\mathrm{H}}$	$X_{\mathrm{Na}^+}^{\mathrm{H}}$	$X_{\mathrm{BF}_4^-}^{\mathrm{H}}$	$X_{\mathrm{Br}^-}^{\mathrm{H}}$
65	0.525	-0.0250	0.455	0.0450
46	0.515	-0.0150	0.475	0.0250