An Ion Sensitive Organic Field-Effect Transistor Incorporating the Ionophore Valinomycin

Supachai Ritjareonwattu, Youngjun Yun, Christopher Pearson and Michael C. Petty

Abstract — **We report on the effect of depositing the ionophore valinomycin onto the polymethylmethacrylate (PMMA) gate insulator of an ion-sensitive organic field-effect transistor (ISOFET) based on poly(3-hexylthiophene). The ionophore was deposited onto the PMMA using the Langmuir-Blodgett (LB) technique; thin films based on pure valinomycin and those in which valinomycin was mixed with arachidic acid were investigated. The pH sensitivity of the reference ISOFET could be improved significantly when the devices were coated with an LB film of arachidic acid. However, the response to K^+ was low. By adding a small amount (5% w/w) of the ionophore valinomycin to the fatty acid LB film, an improved response to potassium ions was achieved, but no selectivity over sodium. It was necessary to use an LB membrane of pure valinomycin in order to realise an ISOFET with some K^+ selectivity. We suggest that the presence of the ionophore in the fatty acid matrix disrupts the packing of the hydrocarbon chains in the mixed LB film and that the monovalent ion response originates from interactions with the carboxylic acid groups in the fatty acid. In contrast, for the case of the pure valinomycin coating, it is thought that K^+ response is controlled by complex formation with the ionophore.**

Index Terms— **Organic thin film transistor, pH sensor, potassium sensor, Langmuir-Blodgett valinomycin film.**

I. INTRODUCTION

SENSORS for the identification of ionic species in solution have been available since the early 20th century [1]. The pH meter – for the measurement of hydrogen ion concentration – was, arguably, the first commercial product. Although instruments are available to detect other monovalent ions, such as potassium (K^+) and sodium (Na^+), these are under continuing development for improvements to accuracy, manufacturing cost and portability.

The ion-sensitive field-effect transistor (ISFET) was introduced in the 1970s [2], [3]. This solid-state device, usually based on silicon, is simple, relatively inexpensive to fabricate and can be used in a number of measurement situations where conventional glass electrodes are too bulky. Devices that respond to ions other than H^+ have been reported, although problems with selectivity still remain [4], [5].

Plastic electronics technology, where the active components are fabricated from organic (e.g. polymeric) materials, offers additional benefits such as mechanical flexibility [6], [7] and, possibly, integration with textiles and biological structures. In previous work, we have reported on an ion-sensitive organic field-effect transistor (ISOFET) in which polythiophene was used as the semiconductor while polymethylmethacrylate (PMMA) formed the gate dielectric. Enhanced sensitivity to hydrogen ions was achieved by coating the gate insulator with a Langmuir-Blodgett (LB) film of a fatty acid [8]. Here, we report on an extension to this work by incorporating the ionophore valinomycin into the LB membrane.

II. MATERIALS AND METHODS

A. Materials and fabrication techniques

In this study, valinomycin (val, $C_{54}H_{90}N_6O_{18}$, TLC, ≥ 98.0%) was purchased from Fluka, while poly(3-hexylthiophene) (P3HT, Molecular Weight 25,000 – 35,000, purity ~ 99.995 %), PMMA (Molecular Weight 93,000) and arachidic acid (AA, 99% purity) were bought from Sigma-Aldrich. Chloroform (CH_3Cl, Trace Analysis Grade, > 99.5%) was obtained from Fisher Scientific and used without further purification. Test solutions were prepared from Analytical Grade acetic acid (CH_3COOH, >98% BDH). The pH of the solution was monitored with a Philips PW9420 pH meter and adjusted by adding small amounts of acetic acid to deionised (DI) water.

The ISOFETs were fabricated on a slide glass, which was cleaned in an ultrasonic bath and rendered hydrophobic in dimethyldichlorosilane solution (~2%w/v, in 1,1,1-trichloroethane, BDH Chemicals). Fig. 1a depicts a schematic structure of the top-gate devices. Chromium

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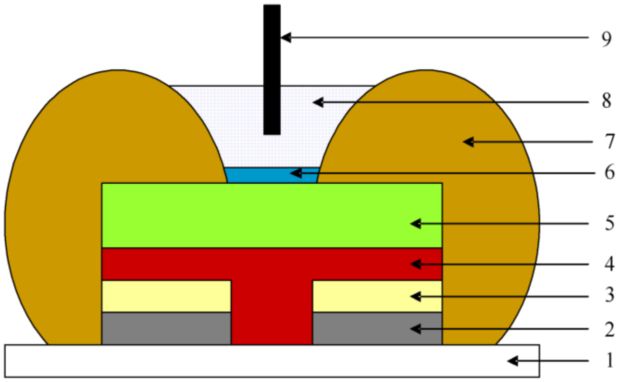
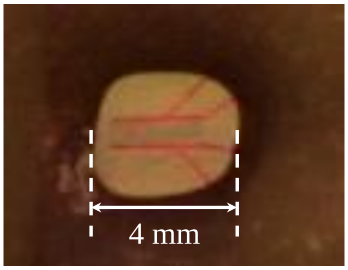
(thickness 20 nm) and gold (thickness 20 nm) were thermally evaporated to form the source and drain electrodes on the slide glass. A simple electrode pattern was produced using a shadow mask. In this case, the electrode width, W, was 2000 µm and the electrode gap, L, was 50 µm. In contrast, photolithography was used to transfer an interdigitated pattern of electrodes, with W = 22,000 µm, L = 25 µm, onto the substrates.



(a)



(b)

Fig. 1. (a) Schematic diagram showing the ISOFET structure; 1 glass substrate, 2 chromium, 3 gold, 4 P3HT, 5 PMMA, 6 LB film, 7 epoxy resin, 8 electrolyte solution, 9 reference (gate) electrode. (b) An actual device after encapsulation with epoxy resin. The source and drain electrodes are evident in the unencapsulated area.

Using spin-coating, the organic semiconductor (P3HT, thickness ~ 40 nm) and the gate dielectric (PMMA, thickness ~ 150 nm) layers were sequentially deposited onto the glass substrate. After each spin-coating step, the devices were annealed in a vacuum oven at 135 °C to evaporate excess solvent. Further fabrication details can be found in our previous publication [8].

An active membrane was deposited onto the PMMA layer of some ISOFET devices using the LB technique. In the case of pure arachidic acid and a mixture of arachidic acid and valinomycin (5 % w/w valinomycin), 10 LB monolayers (Y-type deposition) were transferred onto the PMMA dielectric at a constant surface pressure of 27 mN/m. The approximate thickness of these membranes is 25 nm. However, it was sometimes found difficult to stabilise the surface pressure of a pure valinomycin monolayer in order for the normal LB deposition process to be used [9]. Consequently, an excess of valinomycin solution (approximately 20 µl of a chloroform solution with concentration 1 mg/ml) was dispersed over the subphase surface and left for 30 minutes. It was then found to be possible to transfer this floating layer (now significantly more than a monolayer in thickness) by raising and lowering the substrate through the floating valinomycin/air interface (Y-type deposition). The estimated membrane thickess is 7 – 10 nm.

The final ISOFET devices were then encapsulated by hand using an epoxy resin to leave only a small active gate area (approximately 3 mm x 4 mm) with direct contact to the measuring solution. Fig 1b shows a typical edge definition of the actual device after encapsulation with epoxy resin. Some of the transistors were fabricated using conventional aluminum gate electrodes; these were used as reference OFET devices. All the ISOFETs and OFETs were stored in a desiccator at room temperature until required for use in the experiments.

B. *Electrical measurements*

The reference OFETs (with no encapsulation) were measured in air within a sealed sample chamber. The electrical characteristics of the ISOFETs were monitored in DI water, in some cases with the addition of Na^+ or K^+ ions. A standard double junction silver/silver chloride (Ag/AgCl) electrode was used as the gate. The solution pH was kept below 7 to avoid the formation of silver hydroxide (AgOH), which can occur in basic solutions and affect the potential across the Ag/AgCl electrode. To avoid any interference from chloride ions, sodium sulphate and potassium sulphate (anhydrous, ACS reagents, ≥ 99.0%) were used to prepare test solutions. Both sulphate salts were dissolved in DI water to concentrations of 50, 10, 5, 1 and 0.5 mg/ml. To maintain the stability of the pH during the measurements, the solutions were covered by parafilm (a mixture of paraffin wax and polyolefins) and left overnight at room temperature before use in the experiments.

All electrical measurements were undertaken in the dark and at room temperature. The electrical characteristics of the devices were recorded using a Keithley 485 picoammeter and 2400 source meter.

III. RESULTS AND DISCUSSION

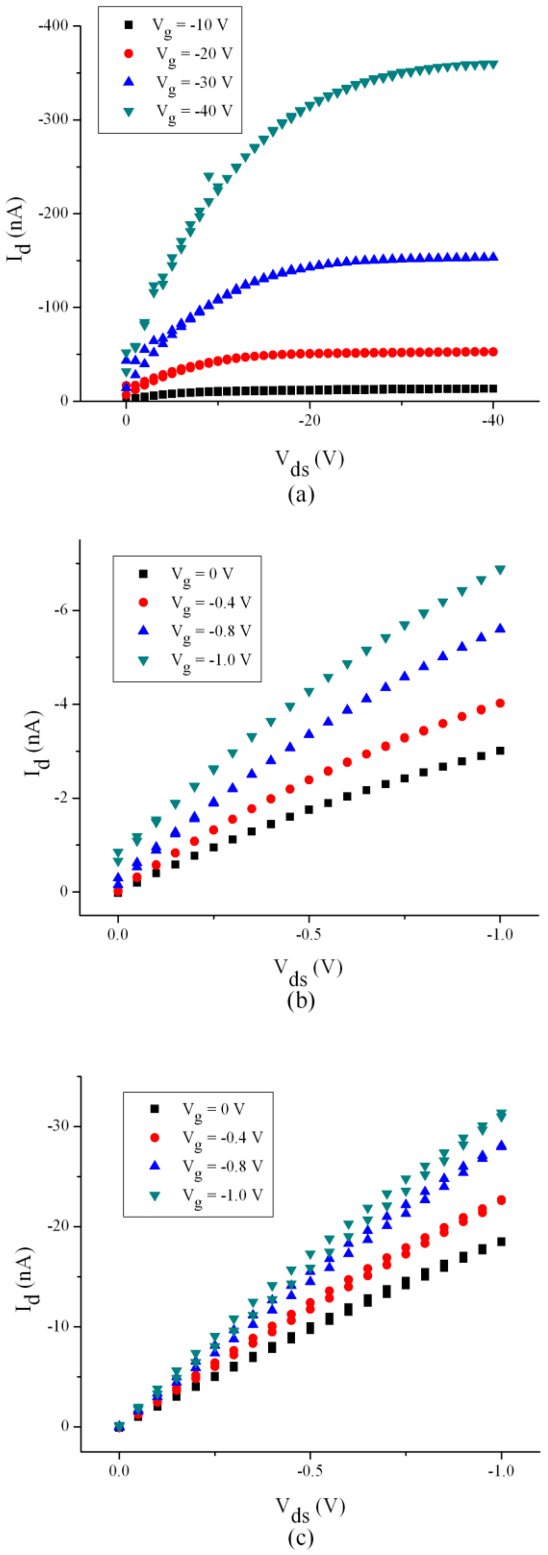
Fig. 2 shows the output characteristics of the organic field-effect transistors used in this work; data for both increasing and decreasing the drain-source voltage, V_{ds}, are given. The results for the reference OFET (i.e. with an Al gate) are depicted in Fig. 2a. Good transistor behavior is evident with saturation of the drain current, I_d, on increasing V_{ds}. Moreover, very little hysteresis is seen on reversing the direction of V_{ds}. The results are consistent with previous reports and indicate that the PMMA gate insulator is suited to the fabrication of FETs [10], [11].

For measurements in aqueous environments, applied voltages were kept below 1 V to avoid unwanted electrochemical reactions, which were found to lead to device instability. The output characteristics of the device with the simple pattern of source and drain electrodes are shown in Fig 2b; the current versus voltage characteristics are, again, shown for both increasing and decreasing V_{ds}. Following each non-zero gate voltage measurement, V_g was returned to 0 V, and V_{ds} was then scanned between 0 and -0.2 V for several cycles until a stable (reference) output curve was obtained [8].

The data in Fig. 2b reveal that, due to the restricted voltage measurement range, the FET is operating in its linear regime. The measured currents are significantly less than those shown for the Al-gate FET in Fig. 2a. A small offset in the drain current for a zero drain-source voltage is also evident in Fig. 2b. This is observed in other organic field-effect transistors and thought to result from leakage currents flowing through the gate dielectric to an expanded semiconductor accumulation layer [10].

To improve the sensitivity of the ISOFETs, we have used an interdigitated pattern of source and drain electrodes. The output characteristics, shown in Fig. 2c, reveal a marked increase in the drain current; the device also shows a much reduced drain-current offset to that measured for the ISOFET with the standard pattern of source/drain electrodes, Fig. 2b. One disadvantage of the interdigitated electrode device was found to be the longer recovery times following an I_d versus V_{ds} scan. For example, the time taken for the device to recover completely (to the reference scan of V_{ds} at V_g = 0 V) following measurements at V_g = -1.0 V was 19 minutes compared to 6 minutes following measurements at V_g = -0.4 V. The increased recovery times are probably related to the larger channel width, and hence the greater accumulated channel charge, of the interdigitated transistor. For this reason, V_g was set at -0.2 V for all of the measurements in this work.

In our previous work, we have shown how the pH sensitivity of the ISOFET may be enhanced by coating the PMMA gate dielectric with several LB layers of arachidic acid [8]. Here, we have repeated this work and, in addition, measured the pH responses of ISOFETs coated with a 10-layer AA film containing 5 % (w/w) valinomycin (val) and devices in which 10 layers of pure valinomycin have been deposited on top of the PMMA gate. The influence of the solution pH on I_d for an ISOFET incorporating the LB membrane consisting of 10 layers of (95% AA + 5% val) is shown in Fig. 3. The measurement sequence, 0, 1, 3 etc., is indicated on the abscissa of the graph. The pH of the solution was deliberately alternated between high and low values in order to reveal a true pH effect, rather than that due to a change (drift) in the ISOFET characteristics over time.



(a)

(b)

(c)

Fig. 2. Output characteristics: (a) ISOFET with Al gate electrode, measured in air. (b) ISOFET with ordinary pattern of source and drain electrodes, measured in DI water using an Ag/AgCl reference electrode. (c) ISOFET with interdigitated pattern of source and drain electrodes, measured in DI water using an Ag/AgCl reference electrode.

A real pH response is, indeed, suggested from the data in Fig. 3, which show that the magnitude of I_d increases with increasing pH. This is consistent with our previous results and may be explained by the fact that an increase in the pH (i.e. to a more basic solution) will decrease the positive charge density, leading to an increase in the density of holes in the accumulation layer of the P3HT [7]. As a consequence, the magnitude of the drain current increases.

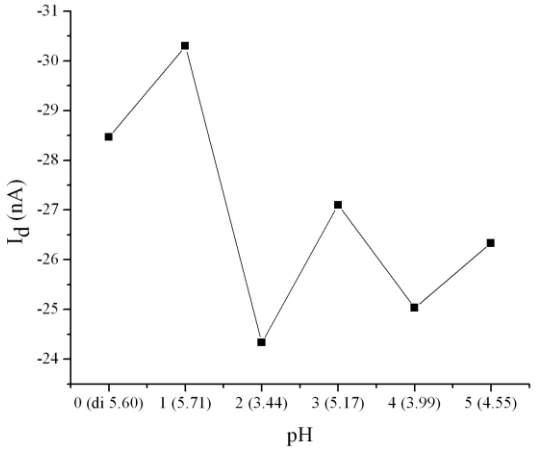
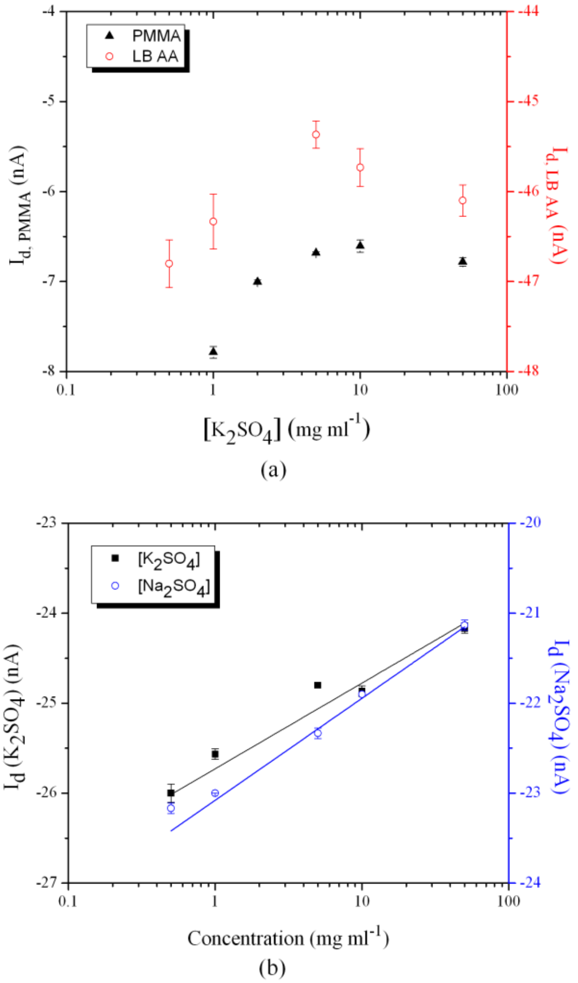


Fig. 3. Measuring sequence for testing the ISOFET pH response. The order of the experiments is indicated by 1, 2, 3 on the abscissa, with the pH value given in brackets. The particular ISOFET device under test included a LB membrane of 10 layers of (95% AA+5% val) deposited on top of the PMMA gate insulator.

TABLE I
THE SENSITIVITY OF THE ISOFETS

Device	Sensitivity		
	pH (nA/pH)	$[K^+]$ (nA/decade)	$[Na^+]$ (nA/decade)
ISOFET	0.5 ± 0.1	0.5 ± 0.1	0.6 ± 0.1
ISOFET/LB AA	3.4 ± 0.1	< 0.5	-
ISOFET/LB 5%val+95%AA	2.3 ± 0.1	0.9 ± 0.1	1.0 ± 0.1
ISOFET/LB val	1.8 ± 0.1	1.5 ± 0.1	0.5 ± 0.1

The pH sensitivities of the ISOFETs coated with different organic membranes are compared in Table 1. The error bars reflect approximately five measurements using the same device. In general, the absolute values of the drain currents varied between different batches of devices by up to 20% and the absolute sensitivities by up to 50%. However, the relationship between the sensitivities of the devices to different ions was the same (e.g. for pH, the basic ISOFET showed the smallest sensitivity while the highest sensitivity was recorded for the ISOFET coated with the AA membrane). In Table I, the pH sensitivity of the device without an additional LB membrane is about 0.5 ± 0.1 nA/pH, very similar to the value found in our previous study [8]. This relatively low sensitivity to pH suggests that the force attracting the hydrogen ions in the solution to the surface of the PMMA polymer is not strong. However, the response of the device is improved significantly when its active area is coated by an LB membrane of AA, (95%AA + 5% val), or pure val. Thermodynamically, the hydrated H^+ and water molecules are small and able to move freely through the LB membrane. As suggested in our previous study [8], the carboxylic head groups within the organic multilayer film can ionize and generate a stronger force for attracting H^+ than the ester groups in the PMMA. This explains the enhanced pH sensitivity of the AA and (95% AA + 5% val) ISOFETs. In the case of the device with the pure valinomycin outer layer, we suggest that the higher sensitivity is related to the presence of twelve ester groups in one molecule of the ionophore.



(a)

(b)

Fig. 4. (a) The pK responses of the uncoated ISOFET device and a structure with 10 LB monolayers of AA (some error bars are smaller than the data symbols). (b) Responses for an ISOFET coated with 10 LB monolayers of (95% AA + 5% val) to different concentrations of Na^+ and K^+ in solution (some error bars are smaller than the data symbols).

Fig. 4 shows the responses of the ISOFETs to potassium and sodium ions. The potassium responses of the ISOFETs with and without the AA LB membrane are depicted in Fig 4a. In both cases, the value of I_d increases with K^+ for low potassium concentrations but then saturates for potassium concentrations greater than about 1 mg/ml. However, apart from the higher drain currents noted in the AA-coated device, there is little difference between the K^+ responses for the two devices. The K^+ sensitivity values (~ 0.5 nA/decade) are given in Table 1 and are averages over the entire range of potassium concentrations. These experiments suggest the hydrated K^+ does not penetrate the fatty acid layer as easily as H^+. In the case of uncoated devices, the hydrated K^+ may be adsorbed at ester groups on the surface of the PMMA. However, the sensitivity of the device is low because of the relatively weak attractive force. Although the polar regions of carboxylic head groups within the AA multilayer array will have a strong affinity for K^+, the dense packing of the hydrocarbon chains will block the passage of hydrated potassium ions and prevent these from reaching the polar interface regions within the LB multilayer film. The device coated with AA monolayers shows a small sensitivity to K^+ since the hydrated ions can leak to the polar interface regions through defects in the fatty acid film.

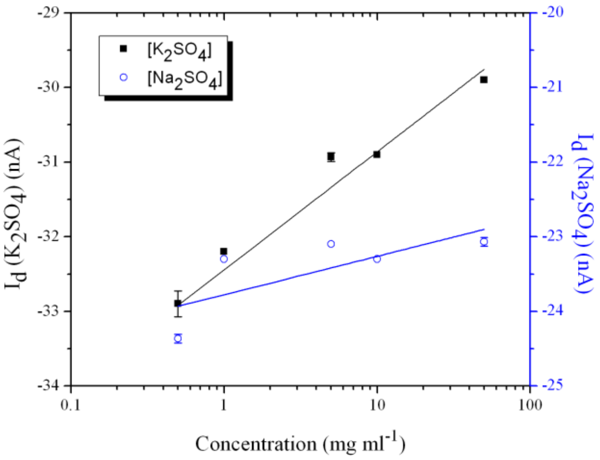
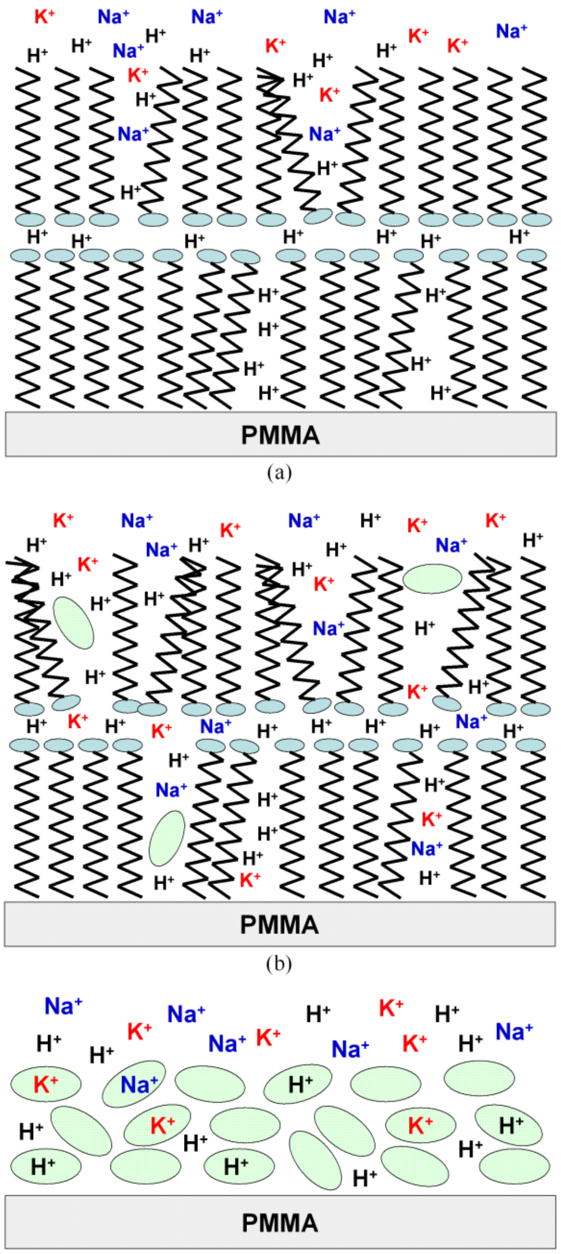


Fig. 5. Responses for an ISOFET coated with 10 LB monolayers of pure valinomycin to different concentrations of Na^+ and K^+ in solution (some error bars are smaller than the data symbols).

The K^+ and Na^+ responses of the ISOFET device coated with (95% AA+5% val) are compared in Fig. 4b. These were recorded over the concentration range 0.5 to 50 mg/ml. The average sensitivity values for both devices are similar, about 1 nA/decade, and higher than the responses measured to hydrogen ions. As noted previously [12], the size of the pore in the centre of the valinomycin molecule (around 0.6 nm in diameter) can accommodate a hydrated K^+ ion (0.5 nm diameter) but it is too small to fit a hydrated Na^+ ion (0.65 nm diameter). On this basis, we would expect to see some selectivity to potassium over sodium. We suggest that, instead of acting as traps for the ions, the main effect of the ionophore addition is to disrupt the fatty acid matrix in the LB membrane. Consequently, both potassium and sodium ions can reach the polar interfaces, where they can react (unselectively) with the carboxylic acid groups. The resulting leakages of K^+ and Na^+ ions are similar, leading to an enhanced monovalent ion response over the AA-coated ISOFET, but no selectivity. A somewhat reduced pH response (2.3 nA/pH) was measured for the (95% AA+5% val) - coated ISOFET compared to that for the AA-coated structure.



(a)

(b)

(c)

Fig. 6. Schematic diagrams showing the proposed distribution of monovalent ions for the different devices on exposure to the aqueous solutions: (a) ISOFET coated with LB monolayers of AA. (b) ISOFET coated with LB monolayers of (95% AA + 5% val). (c) ISOFET coated with LB layers of pure valinomycin.

Transistor devices which were coated with 10 layers of pure valinomycin were then tested. These results are shown in Fig. 5 and included in Table 1. An improved sensitivity to K^+ and some selectivity over Na^+ is evident (Fig. 5), although the pH response for the ISOFET coated with pure valinomycin is less than that measured for the AA-coated transistor (Table I). In this case, we think that K^+ is able to interact with valinomycin to form a valinomycin-K^+ complex [13].

There are two possible explanations for the lower, but finite, sensitivity to sodium ions. First, valinomycin molecules may flip inside out, providing polar sites which can then attract Na^+ (and K^+) ions. Secondly, non-hydrated Na^+, which is smaller than hydrated Na^+, may be trapped within the ionophore pores. Such a valinomycin - non-hydrated Na^+ complex will be weakly bound, but could account for the small observed sodium response [13].

The responses of our different ISOFET structures can be understood by reference to the schematic diagrams in Fig. 6. The device without an LB coating exhibits a small response to all of the monovalent ions studied, i.e. H^+, K^+, and Na^+. This is probably because all these ions can become bound to the ester groups on the surface of PMMA. The ISOFET coated with 10 monolayers of AA exhibits the highest sensitivity to H^+ but could not detect K^+ or Na^+.

This suggests that H^+ ions can move freely through the multilayer fatty acid film and interact with the carboxylic head groups within the LB membrane, Fig 6a. In contrast, K^+ and Na^+ ions generally attract water molecules to become hydrated. Due to the size of these complex molecules, they cannot penetrate the densely packed hydrocarbon chain in the LB film. The addition of a small amount of valinomycin improves the response to K^+ and Na^+, but no selectivity is found for one of these ionic species over the other. We suggest that the presence of the ionophore disrupts the packing of the hydrocarbon chains in the mixed LB film, allowing the monovalent ions to move to the interior of the organic multilayer and interact with the polar head groups of the AA, Fig. 6b. Some selectivity to potassium is finally achieved for the ISOFET coated with a pure valinomycin LB film, Fig. 6c. We attribute this to the ability of the hydrated potassium ions to form a stable complex with the ionophore.

IV. CONCLUSIONS

An ion-sensitive organic field-effect transistor has been fabricated by using P3HT as the semiconductive layer and PMMA as the gate insulator. Such devices respond similarly to the presence of H^+, K^+ or Na^+ in solution. The pH sensitivity could be improved significantly when the ISOFETs were coated with an LB film of arachidic acid. However, the response to K^+ was still low. By adding a small amount (5% w/w) of the ionophore valinomycin to the fatty acid LB film, an improved response to potassium ions was achieved, but no selectivity over sodium. It was necessary to use an LB membrane of pure valinomycin in order to realise an ISOFET with some K^+ selectivity. These results indicate that useful ion sensitive organic transistors may be fabricated by exploiting tailored LB film coatings. Many other sensing architectures may be possible using this approach. However, in order to provide a platform for useful chemical (and, perhaps, biochemical) sensors, the sensitivity of the basic organic transistor structure must first be enhanced.

REFERENCES

[1] J. Koryta, “Ion-selective electrodes,” Ann. Rev. Mater. Sci., vol. 16, pp. 13-27, Aug 1986.

[2] P. Bergveld, “Thirty years of ISFETOLOGY: What happened in the past 30 years and what may happen in the next 30 years,” Sens. Actuators B, vol. 88, no. 1, pp. 1 – 20, Jan. 2003.

[3] J. Janata, “Thirty years of CHEMFETs – a personal view,” Electroanalysis, vol. 16, no. 22, pp. 1831 – 1835, Nov. 2004.

[4] T. Osa, “Potentiometric response of lipid modified ISFET,” Appl. Biochem. Biotechnol, vol. 41, no. 1-2, pp. 35 – 40, Apr.-May 1993.

[5] S. D. Moss, J. Janata, and C. C. Johnson, “Potassium ion-sensitive field-effect transistor,” Anal. Chem., vol. 47, no. 13, pp. 2238 – 2243, Nov. 1975.

[6] J. T. Mabeck, and G. G. Malliaras, “Chemical and biological sensors based on organic thin-film transistors,” Anal. Bioanal. Chem., vol. 384, no. 2, pp. 343 – 353, Jan. 2006.

[7] C. Bartic, and G. Borhs, “Organic thin-film transistors as transducers for (bio) analytical applications,” Anal. Bioanal. Chem., vol. 384, no. 2, pp. 354 – 365, Jan 2006.

[8] S. Ritjareonwattu, Y. Yun, C. Pearson, and M. C. Petty, “Enhanced sensitivity of an organic field-effect transistor pH sensor using a fatty acid Langmuir-Blodgett film,” Org. Electron, vol. 11, no. 11, pp. 1792-1795, Nov. 2010.

[9] V. A. Howarth, M. C. Petty, G. H. Davies, and J. Yarwood, “The deposition and characterisation of multilayers of the ionophore valinomycin,” Thin Solid Films, vol. 160, no. 1-2, pp. 485 – 489, Jun. 1988.

[10] Y. Yun, C. Pearson, and M. C. Petty, “Pentacene thin film transistors with a poly(methyl methacrylate) gate dielectric: optimisation of device performance,” J. Appl. Phys., vol. 105, no. 3, pp. 034508 – 034508-7, Feb 2009.

[11] Y. Yun, C. Pearson, and M. C. Petty, “Bootstrapped inverter using a pentacene thin-film transistor with a poly(methyl methacrylate) gate dielectric,” IET Circ. Dev. & Syst., vol. 3, no. 4, pp. 182 – 186, Aug. 2009.

[12] T. E. Andreoli, M. Tieffenberg, and D. C. Tosteson, “The effect of valinomycin on the ionic permeability of thin lipid membranes,” J. Gen. Physiol., vol. 50, no. 11, pp. 2527 – 2545, Dec. 1967.

[13] S. Varma, D. Sabo, and S. B. Rempe, “K^+/Na^+ selectivity in K channels and valinomycin: over-coordination versus cavity-size constraints,” J. Mol. Biol., vol. 376, no. 1, pp. 13 – 22, Feb. 2008.