

Potentiometric pH Response of Membranes Prepared with Various Aminated-Poly(Vinyl Chloride) Products*

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Abstract. The preparation and potentiometric pH response properties of membranes formulated with various aminated-poly(vinyl chloride) (PVC-NH₂) products are described. Products containing secondary and/or primary amino functional groups are obtained by modifying PVC with mono- and/or diamines, respectively. Blank membranes prepared with either type of aminated-polymer exhibit nearly Nernstian potentiometric pH responses over different pH ranges. In general, membranes based on diamino products exhibit pH response over a wider range (5–10.5) than membranes formulated with monoamino products (<8.0). These potentiometric results are used to estimate the basicity of the various primary and secondary amino sites in the membrane phases.

Key words: aminated poly(vinyl chloride), pH sensors, neutral carriers, polymer membrane electrodes.

For more than a decade, a variety of liquid/polymeric membrane-based pH sensors have been studied as alternatives to conventional glass pH electrodes [1–11]. Because of their ease of preparation, low electrical resistance and flexibility, these sensors are potentially valuable in certain clinical applications, such as intravascular and intraluminal pH measurements. Liquid membrane pH electrodes employing 3-hydroxy-*N*-dodecylpicolinamide or similar compounds [1–4] have been studied and applied for measurement in physiological samples [5–7]. Similarly, polymeric membranes doped with various amino-based proton carriers have been reported by Simon and co-workers [3–4, 8–10]. The pH response ranges of such membranes varied depending on the basicity of the nitrogen centered ion-carriers doped into the membrane, i.e. the higher the pK_a of the nitrogen center, the higher the linear pH response range [10].

Among the neutral proton carriers reported to date, tridodecylamine (TDDA)-based membranes exhibit high selectivity and have been widely used to prepare

* Dedicated to Professor W. Simon on the occasion of his 60th birthday

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micro pH electrodes for intracellular as well as extracellular studies [8, 11], polymeric membranes for blood pH measurements [12], and as transduction elements for a variety of other assay methods [13–17]. More recently, a wide range of different species including alkyl primary, secondary and tertiary amines have been investigated [18]. Plasticized poly(vinyl chloride) (PVC) membranes doped with these amines were also found to respond to pH in different ranges. In all cases where polymeric membranes are doped with mobile proton carriers, high lipophilicity of these carriers is required to ensure working electrodes with extended lifetimes [10, 19].

Recently, we reported on the potentiometric ion response properties of ionophore (nonactin and tridodecylamine) doped membranes prepared with aminated-PVC [20]. In that same work we provided preliminary results regarding the pH response of blank (no added ionophore) aminated-PVC membranes. The purpose of this report is to provide results from more detailed studies of the pH responses of aminated-PVC membranes prepared with products formed from the reaction of different di- and monoamines with PVC. Such studies include the effect of amine structure, membrane plasticizers and lipophilic salt additives on the slopes and pH response ranges of the electrodes, as well as an evaluation of the selectivity of such aminated-PVC membranes for protons over other cationic species.

Experimental

Reagents

Poly(vinyl chloride) (PVC) (MW 110,000) was a product of PolySciences Inc. (Warrington, PA). Aminated-PVC was synthesized in our laboratory by a modification of [21]. One mole equivalent of PVC was added into a round-bottom flask containing five mole equivalents of alkyl mono- or diamines, and appropriate amount of methanol solvent (about 50 ml of methanol for 2.8 g of PVC). The reaction mixture was refluxed for 3–45 h depending on the particular amine used as the reactant (see Table 1). After the reaction mixture cooled to room temperature, the product was washed alternately with methanol, water, and dilute sodium hydroxide solution, then dried under vacuum overnight and kept in a desiccator until use. Elemental analysis on the final products was performed either in-house or by Galbraith, Inc. (Knoxville, TN).

The proton carrier, tridodecylamine (TDDA), was purchased from Eastman Kodak (Rochester, NY), while sodium tetraphenylborate (NaTPB), potassium tetrakis-(*p*-chlorophenyl)borate (KTPCIPB), dioctylsebacate (DOS), dibutylsebacate (DBS) and *o*-nitrophenyloctylether (O-NPOE) were products of Fluka (Ronkoka, NY). Dioctyladipate (DOA) was from ICN (Plainview, NY). The salts, dimethyldioctadecylammonium tetraphenyl-(*p*-chlorophenyl)borate (DMDODA-TpCIPB), tetraethylammonium tetraphenylborate (Et₄NTPB), and trimethylphenylammonium tetraphenylborate (Me₃PNTPB), were isolated in the following manner: NaTPB or KTPCIPB was dissolved or suspended in water (~10 mM) and the bromide or chloride salts of the alkylammonium ions were dissolved in chloroform (~10 mM). The two phases were vigorously shaken, the organic phase was separated, and the chloroform was evaporated to yield the desired lipophilic salts.

Tetrahydrofuran (THF) was doubly distilled. All other chemicals used were analytical reagent grade. Standard solutions and buffers were prepared with deionized water.

Apparatus

The potentiometric response of each membrane electrode was determined relative to an saturated calomel reference electrode (SCE). All cell emf values were recorded at room temperature (22°C) in 100 ml of sample solution. The ISEs and external reference were connected through high-impedance

amplifiers to a Zenith Z-100 PC computer equipped with a Data Translations (DT 2801) analog to digital converter.

Membranes with different compositions were cast on glass slides as described in [22]. Smaller disks were punched from these larger membranes and mounted in Philips electrode bodies (IS-561; Glasblaserei Moller, Zurich). The inner solution was a pH 6.58 buffer containing 0.25 M KH_2PO_4 , 0.25 M Na_2HPO_4 and 0.1 M NaCl for all membranes prepared with TDDA and blank PVC-NH₂.

The direct current (dc) resistance of each of the membranes was measured with a Keithley Model 610B electrometer (Columbus, OH). Values reported in Tables 2, 4 and 5 represent absolute resistances. For comparison purposes, the active area and thickness of the membranes evaluated were typically 0.126 cm² and 130 μm, respectively. Transmission infrared spectra of membranes were obtained with a Nicolet 5-DX FT-IR instrument.

Evaluating the pH Response and Selectivity of Membranes

The potentiometric pH response of various blank aminated-PVC or TDDA/PVC membranes was evaluated in an universal buffer electrolyte background containing 11.4 mM boric acid, 6.7 mM citric acid, and 10.0 mM NaH_2PO_4 . The calibration pH response plots were obtained by the addition of HCl or NaOH into 100 ml of background electrolyte at room temperature. The solutions were magnetically stirred throughout and the equilibrium potentials were recorded (typically, seconds after addition of hydrochloric acid). In most instances, selectivity data for the proton selective membranes were obtained via the fixed interferent method [23], using 1 M of interferent cations (as chloride salts). Similarly, the pH of the solution was adjusted with dilute HCl. The pH of all solutions was monitored simultaneously with a combination glass membrane pH electrode (Fisher Accu-pHast, Fisher Scientific, Detroit, MI). Unless otherwise noted, membranes were conditioned prior to use by soaking in inner filling buffer solution.

Results and Discussion

Characteristics of Aminated-PVC Products

The reaction scheme used to prepare various aminated-PVC products is shown in Fig. 1. The degree of amination of different products was estimated based on the

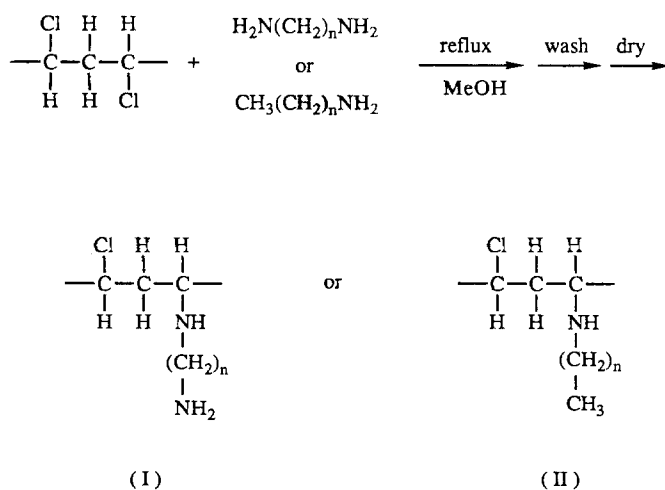


Fig. 1. Schematic diagram of reaction sequence used to couple mono- and diamines to PVC

Table 1. Reaction time and nitrogen content of various PVC-NH₂ products

Amines reacted	Reaction time	% N of product
1,2-Diaminoethane	11 h	0.20
1,4-Diaminobutane	3.5 h	0.81
1,6-Diaminohexane	6 h	0.86
1,12-Diaminododecane	8 h	0.74
Hexylamine	35 h	—
Butylamine	41 h	0.17
Octadecylamine	45 h	0.10
4,4'-Methylenedianiline	8 h	0.83

results from elemental analysis (see Table 1). Among the mono- and diamines studied, 1,4-diaminobutane (1,4-DAB), 1,6-diaminohexane (1,6-DAH), and 1,12-diaminododecane (1,12-DADD) were found to be the most reactive with PVC. The reactivity of amines decreased dramatically when 1,2-diaminoethane (1,2-DAE) or various monoamines were used (as indicated by longer reaction times to gain detectable amination). The degree of reaction seems to depend predominantly on the steric arrangement of the amine molecules in the reaction solvent (methanol), but not on the basicity of the free amino functional groups. Indeed, the pK_a values (from literature) of various amines examined (see Table 1) are all quite similar in aqueous solution (~ 10.5) [24].

When PVC reacts with alkyl monoamines, the product ((I) in Fig. 1) contains only secondary amino functional groups. On the other hand, when PVC is reacted with diamines, both primary and secondary amino functional groups are obtained ((II) in Fig. 1). This is clearly illustrated in Fig. 2 which shows the infrared transmission spectra of different polymeric membranes prepared with mono- and diamino products (only partial spectra are shown). The IR spectrum of starting material, underivatized PVC, shows a clear window in the regions of interest, i.e. N–H stretch (around 3,300 cm⁻¹) and NH₂ bend (scissoring, around 1,600 cm⁻¹, Fig. 2 a). The secondary amino functional groups generated by the PVC reaction with monoamine, e.g. octadecylamine (C₁₈H₃₇NH₂), shows an N–H stretching band at 3,269 cm⁻¹ and no absorption in the region between 1,500 and 1,700 cm⁻¹ (Fig. 2 b). However, both bands appear in the spectra of the diamino (e.g. 1,6-DAH) reaction products (Fig. 2 c).

While testing the solubilities of the various aminated-PVC products in THF (the most common organic solvent used in casting ISE membranes), it was found that some particles, particularly from the products of 1,4-diaminobutane and 1,6-diaminohexane reactions, were not soluble but merely swelled. These particles may be materials containing amino-group cross-linked PVC rather than the desired products (see Fig. 1). Since these small particles were separated from the bulk solution and were not part of the solution used to cast ISE membranes, no further analysis was performed on these materials. However, gel permeation chromatography (GPC) of the soluble material (in THF) showed an almost identical chromatogram (results not shown) compared to that of dissolved underivatized starting material, PVC.

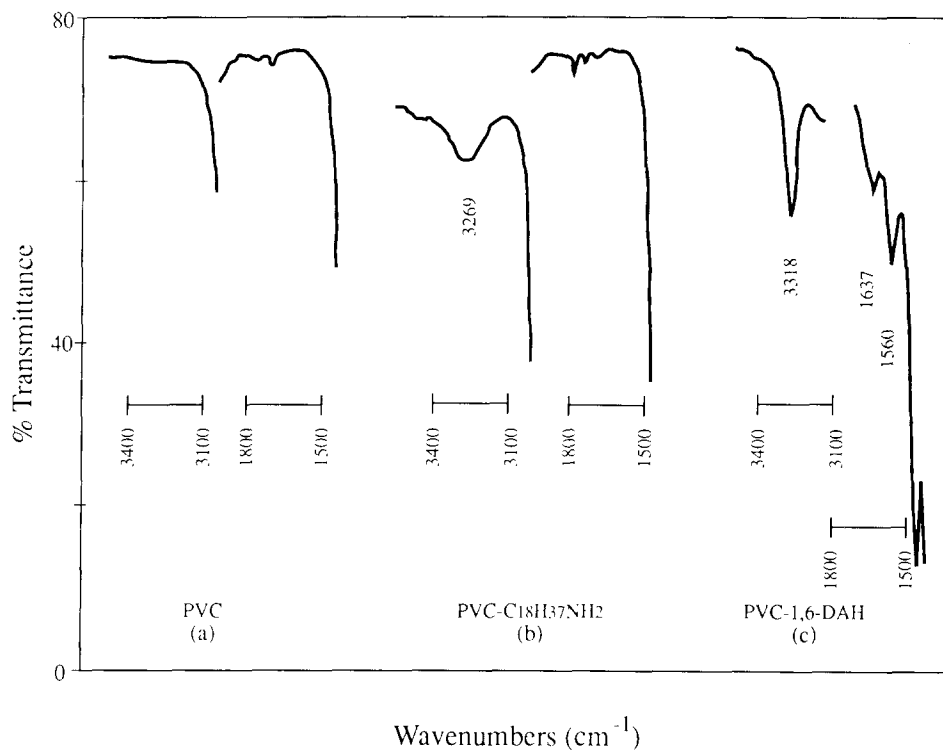


Fig. 2. Fourier transform infrared spectra of various polymeric membranes: (a) starting material, dry underivatized PVC; (b) dry PVC-C₁₈H₃₇NH₂ membrane; (c) dry PVC-1,6-DAH membrane

This suggests relatively little crosslinking is present in the soluble products of the diamine-PVC reaction.

Products of 1,12-diaminododecane and monoamines were as soluble in THF as underivatized PVC. However, the products of 1,2-diaminoethane, 1,4-diaminobutane and 1,6-diaminohexane were less soluble than normal PVC. Indeed, in general, the higher the degree of amination the less soluble the products (in THF). These highly aminated products (not shown in Tables 1 and 2) are not suitable for casting pH sensitive membranes.

pH Response Characteristics of Blank Aminated-PVC Membranes

The pH response of membranes based on TDDA/PVC or various aminated-PVC products are summarized in Table 2. For the most part, membrane compositions of the various aminated-PVC products were similar to that used to cast TDDA-2 membrane (i.e., 51 mg PVC-NH₂, 132 mg DBS and 1.4 mg NaTPB). The molar amounts of different amines are calculated based on %N obtained from elemental analysis (see Table 1). The amount of NaTPB incorporated into such aminated-PVC membranes was kept constant (at 1.4 mg). While optimum for TDDA/PVC membrane (TDDA-2), this quantity was found to be in excess for certain aminated-PVC membranes. Indeed, the excess NaTPB will leach out from the aminated-PVC membranes while conditioning these membranes in the internal filling buffer solution before measurements. The duration of pretreatment for membranes to achieve

Table 2. Potentiometric response characteristics, resistances and compositions of membranes prepared with TDDA/PVC and PVC-NH₂^a

Membranes ^{b,c}	Linear range after conditioning (slope) ^d	Day ^e	Mole ratio of NaTPB/amine (wt% of amine in membrane) ^f	Membrane resistance ($\times 10^6$ ohm)	
				Initial	Conditioned ^g
TDDA-1	5.5–10.2 (56.0)	1 d	1.07 (1%)	1.1	3.0
TDDA-2	5.5–10.7 (56.6)	1 d	0.21 (5%)	2.0	3.0
TDDA-3	5.5–10.7 (57.2)	1 d	0.11 (10%)	2.4	2.4
PVC-1,2-DAE	5.2– 8.3 (44.2)	6 d	1.12 (0.1%)	1.1	3.4
PVC-1,4-DAB	5.0–10.5 (55.1)	1 d	0.28 (0.7%)	60	60
PVC-1,6-DAH	5.0– 9.0 (47.9)	1 d	0.26 (1.0%)	69	39
PVC-1,12-DADD	5.0– 9.0 (49.9)	2 d	0.30 (1.4%)	1.7	17
PVC-4,4'-MDA	8.0–12.0 (24.0)	1 d	0.27 (5.9%)	130	180
PVC-C ₄ H ₉ NH ₂	4.7– 8.2 (53.9)	Initial	0.09 (0.2%)	14	—
PVC-C ₁₈ H ₃₇ NH ₂	5.0– 7.0 (52.3)	11 d	1.14 (1.0%)	0.6	32

^a All values reported are an average of three determinations using different disks cut from one large membrane

^b Membranes TDDA-1, 2, and 3 were prepared with various wt% of TDDA and normal PVC; ~26 wt% PVC, ~66 wt% DBS and ~0.7 wt% NaTPB

^c All other membranes were prepared with ~28 wt% PVC-NH₂, ~71 wt% DBS, and ~1 wt% NaTPB

^d Optimum slope is after required conditioning

^e Days of soaking required to achieve optimum pH response

^f Based on the %N from elemental analysis of each PVC-NH₂ product; the wt% of amine relative to the total weight of membrane composition was determined by calculating the number of moles of original amine compound within the weight of PVC-amine product used to prepare the membrane phase

^g After soaking in internal buffer, pH 6.58 for at least 1 day

optimum pH response depends, therefore, on the degree of amination of the polymer. More highly aminated-products required less time for the conditioning effect to be observed. As shown in Table 2, a longer time is needed when there is a higher ratio of NaTPB/amine, as in the case of 1,2-diaminoethane and octadecylamine aminated membranes. A comparison showing the increase in slope after various durations of membrane conditioning is illustrated in Fig. 3. Membranes prepared with 1,6-diaminohexane product containing lower ratio of NaTPB/amine (0.28) need less conditioning time (1 day). However, membranes prepared with the octadecylamine product containing a higher ratio of NaTPB/amine (1.14) require a significantly longer period (11 days) pretreatment before observing optimum pH response (see Table 2).

The effect of different levels of NaTPB was studied by adding various (less than 1.4 mg) amounts of NaTPB to aminated-PVC membranes based on the product of the 1,6-diaminohexane reaction. As shown in Fig. 4, the linear response ranges and slopes increase as the amount of NaTPB decreases. The optimum amount of NaTPB is approximately 0.14 mg/membrane (i.e., 0.08 wt% NaTPB/membrane). Similar

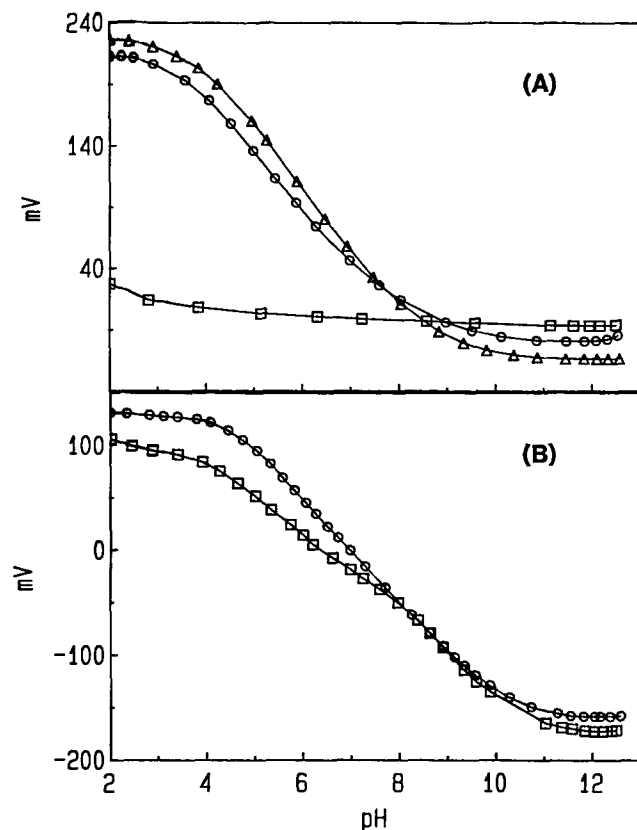


Fig. 3. Effect of conditioning time and mole ratio of NaTPB/amine membrane formulation on the pH response of various membranes: **A** membrane based on $C_{18}H_{37}NH_2$ product; 0 day (\square), 2 days (\circ), 11 days (Δ); **B** membrane based on 1,6-DAH product; 0 day (\square), 1 day (\circ)

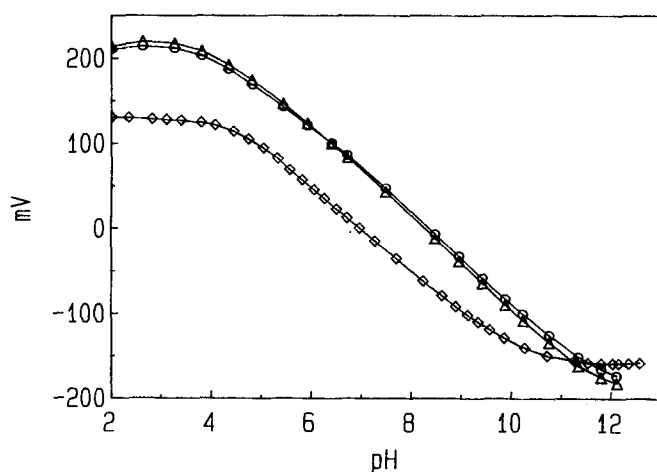


Fig. 4. Effect of various amounts of additive, NaTPB, to the emf response of the electrodes based on PVC-1,6-DAH membrane: 1.4 mg (\diamond , slope = 48.7 at pH 5.5–9); 0.47 mg (\circ , slope = 52.1 at pH 5.5–11); 0.14 mg (Δ , slope = 54.1 at pH 5.5–11). Membrane: ~ 28 wt% PVC- NH_2 , < 1 wt% NaTPB and ~ 71 wt% DBS

results were obtained with TDDA/PVC membranes. As shown in Table 2, when the ratio of NaTPB/amine exceeds optimum composition, such as in membrane TDDA-1, a narrower linear response range occurs and the slope of pH response decreases. These observations are in good agreement with the known role of NaTPB additives in neutral carrier membranes as a means of decreasing counter anion partitioning into the membrane phases [25].

As shown in Table 2, membranes based on diamino products have wider pH response ranges than membranes based on monoamino products. The latter usually

exhibit linear response below pH 8. Typical pH response characteristics and curves of different membranes are summarized in Table 2 and shown in Fig. 5 A, B. The blank aminated-PVC membranes usually exhibit slopes between 47 and 55 mV/decade in their respective linear response ranges (except for membranes cast with the product of 4,4'-methylenedianiline (4,4'-MDA) which yielded only ~ 20 mV/decade in the range of pH 8–12). A further comparison of the linear ranges of different membranes (Fig. 6), suggests that the secondary amino groups present in both mono- and diamino products are sensitive to pH changes at lower pH ranges

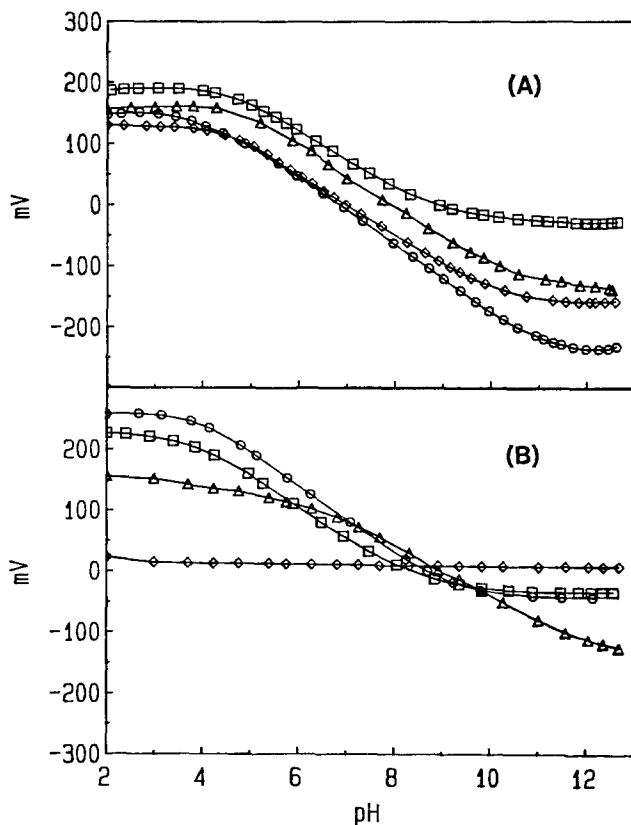


Fig. 5. Comparison of pH response ranges of different membranes based on various aminated-PVC products or free amines incorporated within underivatized PVC: **A** blank membranes from PVC-NH₂ product of diamines; 1,2-DAE (\square), 1,4-DAB (\circ), 1,6-DAH (\diamond), 1,12-DADD (\triangle); **B** blank membrane containing free monoamines or based on product of monoamine reactions; PVC-C₄H₉NH₂ (\circ), PVC-C₁₈H₃₇NH₂ (\square), free C₄H₉NH₂ (\diamond), free C₁₈H₃₇NH₂ (\triangle). Membrane: ~ 28 wt% polymer, < 1 wt% NaTPB, ~ 71 wt% DBS, < 1 wt% covalent amines or ~ 1 wt% free amines

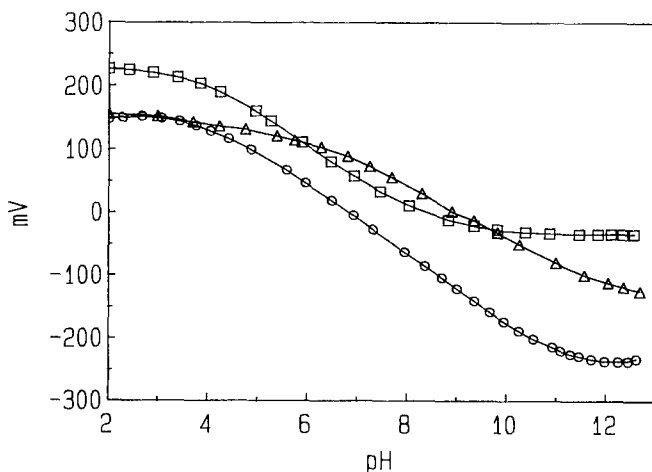


Fig. 6. More direct comparison of pH response ranges of selected membranes (from Fig. 5 A, B): PVC-1,4-DAB (\circ); PVC-C₁₈H₃₇NH₂ (\square); free C₁₈H₃₇NH₂ (\triangle)

while the primary amino groups in the diamino products are sensitive to pH changes in higher pH ranges. Simon et al. [10] have reported that the dynamic ranges shift to higher pH values as the pK_a of the proton ionophore in the membrane increases. Thus, our observations of the shift in pH response range may indicate that the basicity of the secondary amino groups has decreased after the amination reaction. Indeed, the amino groups in diamino products have two different pK_a values and this may be the reason that membranes prepared with these materials exhibit a wider range of linear pH response (see Fig. 5). The decreased basicity of secondary amino groups directly attached to the PVC chain may be due to the electronegative environment arising from the abundant electron withdrawing chlorine atoms on the polymer backbone. Both inductive and hydrogen bonding effects could contribute to the decrease of secondary amino groups' basicity [26]. The effects on the terminal primary amino groups however may be weak, depending on the length of the alkyl chain. The longer the carbon chain, the less inductive effect on the primary amino group. This rationale is supported by the fact that membranes cast from the 1,2-diaminoethane product exhibit response in a more acidic pH range than those prepared with the other diamino products (see Table 2 and Fig. 4).

Plasticized blank, underivatized PVC membranes, and membranes with physically tapped free diamines or butylamine (C₄H₉NH₂ in Fig. 4 B), yield no potentiometric pH response in the range of pH 2–12. However, linear pH response at pH > 7 was obtained with a membrane containing free octadecylamine. This is probably due to the fact that short alkyl chain amines or diamines are less lipophilic, and therefore, are not retained in the polymeric matrix, PVC. Homogeneous membranes with these carriers could not be obtained because such membranes contained small particles suspended in the polymeric matrix. It's been reported by Fiedler and Ruzicka [27], based on studies with PVC membranes, that one of the fundamental requirements for a viable polymer membrane system is that both the ionophore and polymer must be soluble in the solvent mediator and the proportions of the components must be such as to give a single-phase system. The longer alkyl chain, e.g. of octadecylamine, allows it to be relatively soluble in the membrane phase, enough to form a homogeneous pH responsive membrane.

Table 3. Selectivity of proton-sensitive PVC-NH₂ membrane electrode compared to conventional TDDA/PVC membrane^a

Metal ion	Log $K_{H^+,M}^{pot}$	
	PVC-NH ₂ membrane	TDDA membrane ^d
Na ^{+,b}	-9.5	-11.2
K ^{+,b}	-9.2	-10.5
Ca ^{++^c}	< -9.6	< -10.7

^a Prepared with 1,4-diaminobutane product, Table 1

^b Measured at the interfering ion concentration of 1 M

^c Measured at the interfering ion concentration of 0.055 M

^d From membrane TDDA-2, Table 2

The potential analytical utility of the blank aminated-PVC membranes was further tested by measuring the selectivity of the membranes toward some commonly encountered metal cations. As shown in Table 3, the selectivity of blank membranes based on the 1,4-diaminobutane product is about one order of magnitude less than that observed for TDDA-based membranes, at least toward Na^+ , K^+ and Ca^{++} . However, this poorer selectivity should not interfere with the application of this membrane for pH measurements of biological samples where, given the measured selectivity constants, the normal levels of these interfering ions would not be sensed by the membrane. Indeed, the calculated required selectivity factor, $\text{Log } K_{\text{H}^+}^{\text{pot}, \text{M}}$ for interfering M cations Na^+ , K^+ , and Ca^{++} (for a maximally tolerable error of 1% at pH 7.4) are -8.5 , -7.0 and -7.7 , respectively [28].

The resistances of the aminated-PVC membranes (ca. 10^7 ohm) are from a few fold to more than 10 fold higher than those of free TDDA/PVC membranes (ca. 10^6 ohm), particularly after these membranes are soaked in solution for some time (Table 2). These resistances can be reduced by using different plasticizers or additives for membrane casting. As shown in Tables 4 and 5, for membranes prepared with product of 1,6-diaminohexane, the plasticizer O-NPOE and lipophilic salt KTpClPB may be used to replace DBS or NaTPB. Lower membrane resistances will become more important if micro or miniaturized aminated-PVC membrane electrodes are to be fabricated and/or used for *in vivo* measurements.

All of the aminated-PVC membrane electrodes exhibit reproducible potentiometric response with standard deviations of ~ 0.1 mV at pH 6.2 (static measurement over 8 h). The standard deviation is < 0.5 mV for alternating measurements in stirred solutions at pH 6.2 and 12.0. These electrodes have been used frequently during a one month period without deterioration of slope or dynamic response range. The response time ($t_{90\%}$) of the electrodes towards a step change in pH (i.e., via addition of hydrochloric acid to the stirred and buffered sample) has been typically a few seconds (≤ 3 s) in all cases. Moreover, there is no noticeable hysteresis

Table 4. Effect of different plasticizers on resistances and pH response of PVC-1,6-DAH membrane^{a,b}

Plasticizer	Membrane resistance ($\times 10^6$ ohm)		Slope (pH range)
	Initial	Conditioned ^c	
DBS	72	42	47.9 (5.5–8.5)
O-NPOE	1.9	6.2	42.8 (5.5–8.5)
DOS	440	730	42.2 (5.5–8.5)
DOA	33	76	42.1 (5.5–8.5)

^a All values reported are an average of three determinations using different disks cut from one large membrane

^b Membranes were prepared with ~ 28 wt% PVC-NH₂, ~ 71 wt% plasticizer, and ~ 1 wt% NaTPB

^c After soaking in internal buffer, pH 6.58, for one day

Table 5. Effect of different additives on pH response range, slope, and resistance of PVC-1,6-DAH membrane^{a,b}

Additive	Membrane resistance ($\times 10^6$ ohm)		Slope (pH range)
	Initial	Conditioned ^c	
NaTPB	72	42	47.9 (5.5–9.0)
Me ₃ PNTPB	27	23	51.0 (6.0–9.0)
Et ₄ NTPB	8.8	17	32.9 (6.0–9.0)
KTpCIPB	2.6	5.2	53.9 (6.0–9.0)
DMDODA-TpCIPB	3.0	7.5	No response

^a All values reported are an average of three determinations using different disks cut from one large membrane

^b Membranes were prepared with ~ 28 wt% PVC-NH₂, ~ 71 wt% DBS, and ~ 1 wt% additive

^c After soaking in internal buffer, pH 6.58, for one day

observed for any of the electrodes upon switching from low to high or high to low pH samples.

Conclusions

A new type of polymeric pH sensitive membrane based on aminated-PVC has been described. The pH response ranges vary depending on the nature of the alkyl amines used during the amination reaction. Several of the aminated-PVC products provide membranes with pH response similar to that found for conventional underivatized PVC membrane doped with tridodecylamine. This finding may prove valuable in the design of miniaturized pH and pCO₂ sensing catheters suitable for *in vivo* measurements where concerns about the leaching of toxic proton carriers need to be resolved before such devices become widely used.

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