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Influence of proton ionophore and negative sites on the dielectric behavior of plasticized poly(vinyl chloride)s[1]

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Abstract

The dielectric behavior of a 50/50 blend of two poly(vinyl chloride) molecule weight standards was measured, both before and after being plasticized with 200 parts per hundred of *o*-nitrophenyl octyl ether. To these dummy membranes were added the proton ionophore, tridodecylamine (TDDA), in the amounts of 0.01, 0.1, 1, and 10 wtwt^{-1}% as well as a source of negative sites, potassium tetrakis-4-chlorophenyl borate (KTpClPB), in relative proportions (TDDA/KTpClPB) of 1:0, 1:1, 1.5:1, and 3:1. Because replicate membranes were cast from parent THF solutions, compositional changes were not a factor. Using a TA Instruments' DEA 2970 equipped with parallel plate sensors, nominally 0.15 mm thick films were scanned at 3°C min^{-1} in the dry and hydrated conditions from −100 to +100°C at seven frequencies (0.1, 1, 10, 100, 1000, 10 000 and 100 000 Hz). By 100°C, permittivity and loss factor increased with TDDA concentration more than 1000-fold over values measured at the glass transition temperature of ca. −75°C. Permittivity and loss factor also increased six orders of magnitude over a six orders of magnitude decrease in frequency. The absolute magnitudes of tan δ at the peaks decreased with increasing TDDA loading. In the wet conditions, tan δ converged to a single value of six at 10 wtwt^{-1}% TDDA, regardless of the proportion of TDDA/KTpClPB and test frequency. The ionic conductivities at the temperature at which the peak of tan δ occurs were independent of TDDA concentration but increased with increasing frequency. Above a minimum of 1.5:1, the relative proportion of TDDA/KTpClPB was not as significant as the absolute amount of TDDA and/or KTpClPB present, and hydration had little overall effect on the dielectric properties.

Keywords: DETA; Membrane; Tridodecylamine; Poly(vinyl chloride); Loss factor; Permittivity; Ionic conductivity; Tan δ

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1. Introduction

Polymer-based sensors may be divided into two classes, those with fixed-site carriers and those with mobile-site carriers. In the latter a highly plasticized system is often selected that is based on the polymer, poly(vinyl chloride) (PVC) [1]. This polymer is favored because of its capacity to be miscible with hundreds of parts of a plasticizer, while still meeting the structural requirements of a sensor. Simultaneously, the plasticizer lowers the glass transition temperature (T_g) of the solvated PVC to sub-ambient temperatures, thereby placing the material in the rubbery-flow or viscous-flow regions near ambient temperatures [2]. The intrinsic compliance of this dummy membrane is crucial to its later functioning as an ion-selective sensor, since the carriers must be mediated via the mobility afforded by the plasticizer. Note that, in this initial material selection process, the plasticizer must not be so mobile that its molecules actually migrate out of the sensor [3] nor the polymer so elastic that its physical entanglements cause syneresis of the plasticizer to occur [4].

Having established a satisfactory dummy membrane, the ionophore and negative sites must be added in order to provide the appropriate selectivity and sensitivity. In a mobile-site proton carrier, the ionophore can be a neutral carrier that is proton selective, e.g. a hydrophobic amine such as tridodecylamine (TDDA) [5]. However, when these protons enter the membrane and complex with the ionophore, the appropriate number of negative sites must be available by the dissociation of a lipophilic salt, e.g. a borate compound such as potassium tetrakis-4-chlorophenyl borate (KTpClPB) in order to maintain charge neutrality and reduce the membrane resistance, anion interferences, and electrode response time [6].

Since the early 1940s, the response of pure and plasticized PVC to cyclic electrical stress has been investigated [7,8]. Much of this work has been directed towards the search for better wire insulators [9–11]. The correlation of the basic dielectric properties of capacitance and conductance to the molecular dynamics of pure polymers, plasticized polymers, and polymers with additives has broader applicability [12–15].

Recently the dielectric properties of dummy membranes were studied that were formed from PVC and two of the plasticizers (dioctyl sebacate and *o*-nitrophenyl octyl ether), which are used in ion-selective electrodes [16]. The dielectric properties of the dioctyl sebacate plasticized PVC were highly influenced by interactions between the nonpolar plasticizer and the PVC. In contrast, the properties of the *o*-nitrophenyl octyl ether plasticized membranes were dominated by this highly polar plasticizer, and no interactions were observed between the plasticizer and PVC.

In the present work the influences of TDDA and/or KTpClPB on the dielectric behavior of a dummy membrane of plasticized PVC are investigated as a function of the absolute amounts of TDDA and KTpClPB and the relative proportions of TDDA/KTpClPB. By casting duplicate membranes from the same composition, the influence of hydration as a function of frequency and temperature is also investigated. From these dielectric measurements, both the permittivities due to the alignment of induced dipoles and the ionic conductance associated with the loss factor increase with the addition of TDDA and the relative proportions of ionophore/negative sites.

2. Materials and methods

2.1. Test material

A stock solution was made using a 50:50 blend of two PVC molecular weight standards (M_w = 77 300 and 194 000, Scientific Polymer Products) and a polar low molecular weight plasticizer, *o*-nitrophenyl octyl ether (*o*-NPOE; M_w = 251, Fluka) [17] in HPLC grade tetrahydrofuran (THF, Mallinckrodt). The standard composition of 200:100 parts of plasticizer polymer was used for these plasticized PVC membranes (0_P) [18]. As summarized in Table 1 the proton ionophore, TDDA (Fluka), was added to equal parts of this stock solution in the amounts of 0, 0.01, 0.1, 1, and 10 wtwt^{-1}% as well as a source of negative sites, KTpClPB (Fluka), in relative weight proportions (TDDA/KTpClPB) of 1:0, 1:1, 1.5:1, and 3:1. Each solution that was comprised of PVC, *o*-NPOE, TDDA, and KTpClPB was divided in half. Following the general procedure of Moody et al. [19] one membrane was obtained from each half, after the THF was evaporated. Before testing via thermal analysis, one membrane was stored in a vacuum oven at 21°C ("dry"), and the other membrane was hydrated in a buffer solution (pH 7) for 24–36 h ("wet"). The pure PVC (0_{NP}) was also tested in the dry condition without any plasticizer, TDDA, or KTpClPB.

2.2. DETA instrumentation

All membranes were run in a TA Instruments' DEA 2970 using ceramic parallel plate sensors. After DETA calibration, each membrane was positioned in the DETA and purged for at least 3 min with dry nitrogen at a flow rate of 2.0 l min^{-1}. The surfaces of the hydrated membranes were blotted with lens paper just prior to placement in the DETA. A ram pressure of 200 N was applied and the sample was cooled down to −100°C by a modified Liquid Nitrogen Cooling Accessory. Using a rate of 3°C min^{-1}, the sam-

Table 1

Summary of sample compositions and conditions tested

TDDA in wtwt^{-1}%	Pure PVC				Proportion of TDDA/KTpClPB in *o*-NPOE plasticized PVC							
	0_{NP}[a]		0_P[b]		1:0[c]		1:1		1.5:1		3:1	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
0	X		X	X								
0.01					X	X	X	X	X	X	X	X
0.1					X	X	X	X	X	X	X	X
1					X	X	X	X	X	X	X	X
10					X	X	X	X	X	X	X	X

[a] Contains no plasticizer, TDDA, or KTpClPB.

[b] Contains *o*-NPOE plasticizer, but no TDDA or KTpClPB.

[c] Contains *o*-NPOE plasticizer and TDDA, but no KTpClPB.

ples were heated to +100°C while exposing one of the parallel plates to alternating electric fields of 0.1, 1, 10, 100, 1000, 10 000, and 100 000 Hz. The 2000 System Controller monitored the current in the opposing parallel plate and the phase angle shift (δ) between the applied voltage and the measured current. The dissipation factor ($\tan\delta$), the capacitance (C), and the resistance (R = l/conductance) were computed from these measurements. By knowing the electrode plate area (A), the plate spacing (d), the frequency (f), and the absolute permittivity of free space ($e_0 = 8.85$ pF m^{-1}), the permittivity (e') and the loss factor (e'') were determined using Eqs. (1) and (2). The e' values indicate the amount of dipole alignment in the samples, and e'' is a measure of the actual energy necessary to align the dipoles and move ions. The ionic conductivity (σ) was derived from e'' when $T > T_g$ (Eq. 3) [14]; the $\tan\delta$ equaled the quotient of the loss factor divided by the permittivity (Eq. 4). In all, four quantities were monitored (e', e'', σ, and $\tan\delta$) to analyze these 32 runs at the seven frequencies in the dry and wet conditions.

$$\text{Permittivity:} \quad e' = Cd(e_0A)^{-1} \tag{1}$$

$$\text{Loss factor:} \quad e'' = d(RA2\pi fe_0)^{-1} \tag{2}$$

$$\text{Ionic conductivity:} \quad \sigma = e''2\pi fe_0 \tag{3}$$

$$\text{Dissipation factor:} \quad \tan\delta = e''e'^{-1} \tag{4}$$

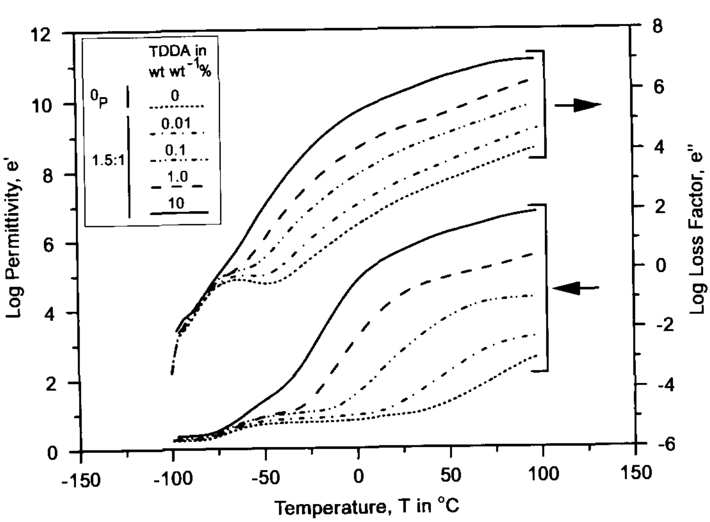

Fig. 1. Influence of TDDA loading in wtwt^{-1}% on the temperature dependence of the e' and e'' for o-NPOE plasticized PVC membranes in the dry condition at a relative proportion of TDDA/KTpClPB equal to 1.5:1 at 10 Hz.

3. Results

Fig. 1 shows the typical molecular motion of these highly plasticized, proton-conductive, PVC membranes in the dry condition for a relative proportion of TDDA/KTpClPB equal to 1.5:1 at a frequency of 10 Hz. As the amount of TDDA increased from 0 to 10 wtwt^{-1}%, the values of e' and e'' increased by more than 1000-fold. In both dry and wet conditions at relative proportions equal to 1:1 (Fig. 2, dry) and 1.5:1 (Fig. 3, wet) at 37°C (representing the temperature that implanted sensors would experience), e' and e'' increased with lower frequencies. With the exceptions of a few permittivity values in the wet condition ($f \geq 100$ Hz), e' and e'' increased with increased loading of TDDA at all frequencies. The corresponding magnitudes of the pure PVC (0_{NP}) were superposed on the dry results (Fig. 2) as solid circles.

From 3-D plots of the TDDA loading and the relative proportion of TDDA/KTpClPB at 10 Hz and at the same physiologically significant temperature (37°C), e' and e'' were found to reach either a maximum or a steady state value at a relative proportion equal to 1:1 in the dry condition (Fig. 4) and either 1:1 or 1.5:1 in the wet condition (Fig. 5). In all cases e' and e'' increased with TDDA loading. Again, the results for the pure PVC (0_{NP}) were superposed on the dry plots (Fig. 4) as solid circles.

Table 2

Selected dielectric properties of PVC membranes

TDDA in wtwt^{-1}%	Frequency in Hz	Temperature in °C	Dry		Wet	
			$\log e'$	$\log e''$	$\log e'$	$\log e''$
0_{NP}[a]	10	0	0.297	−1.708	NT[b]	NT
0_{NP}	10	37	0.500	−0.466	NT	NT
0_{NP}	10	100	0.966	2.142	NT	NT
0_{NP}	1	0	0.304	−1.656	NT	NT
0_{NP}	1	37	0.572	−0.060	NT	NT
0_{NP}	1	100	1.239	3.120	NT	NT
0_{NP}	0.1	0	0.311	−1.661	NT	NT
0_{NP}	0.1	37	0.730	0.294	NT	NT
0_{NP}	0.1	100	2.307	3.983	NT	NT
0_{P}[c]	10	0	0.811	1.481	1.015	1.214
0_{P}	10	37	1.048	2.646	1.125	2.457
0_{P}	10	100	2.569	4.030	1.977	3.696
0_{P}	1	0	1.185	2.457	1.251	2.358
0_{P}	1	37	2.294	3.626	1.912	3.438
0_{P}	1	100	4.078	4.982	3.544	4.668
0_{P}	0.1	0	2.358	3.425	2.087	3.330
0_{P}	0.1	37	3.894	4.551	3.566	4.392
0_{P}	0.1	100	5.156	5.801	4.692	5.538

[a] Contains no plasticizer, TDDA, or KTpClPB.

[b] Not tested in the wet state,

[c] Contains *o*-NPOE plasticizer, but no TDDA or KTpClPB.

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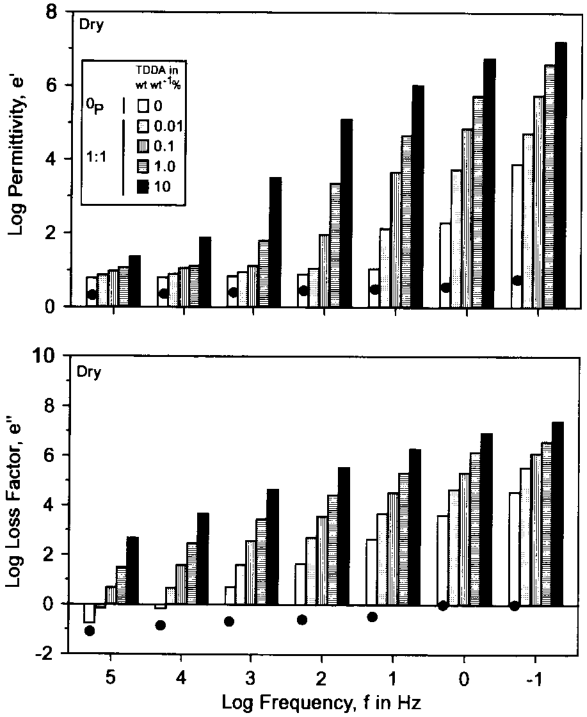

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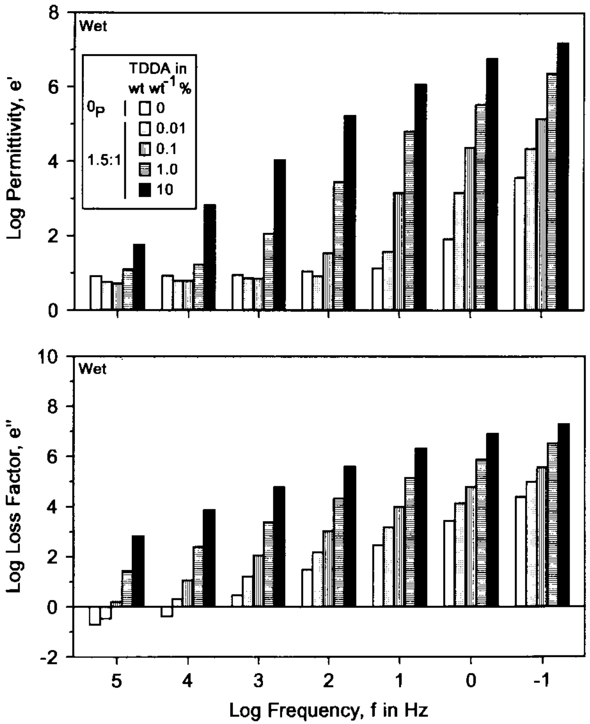

Fig. 2. Influence of frequency and TDDA loading in wt wt^{-1}% on e' and e'' for *o*-NPOE plasticized PVC membranes in the dry condition at a relative proportion of TDDA/KTpClPB equal to 1:1 at 37°C. The solid circles indicate the results for pure, unplasticized PVC, that is, 0_{NP}.

Fig. 3. Influence of frequency and TDDA loading in wt wt^{-1}% on e' and e'' for *o*-NPOE plasticized PVC membranes in the wet condition after hydration in a pH 7 buffer at a relative proportion of TDDA/KTpClPB equal to 1.5:1 at 37°C.

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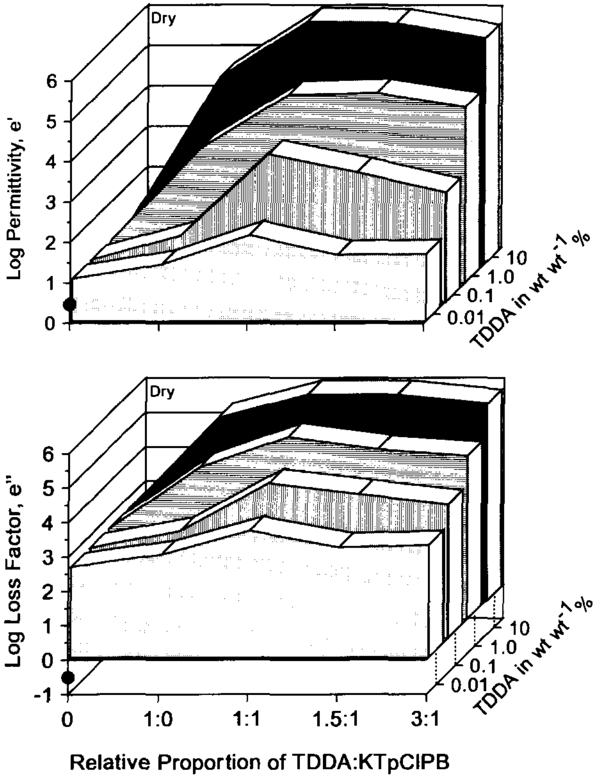

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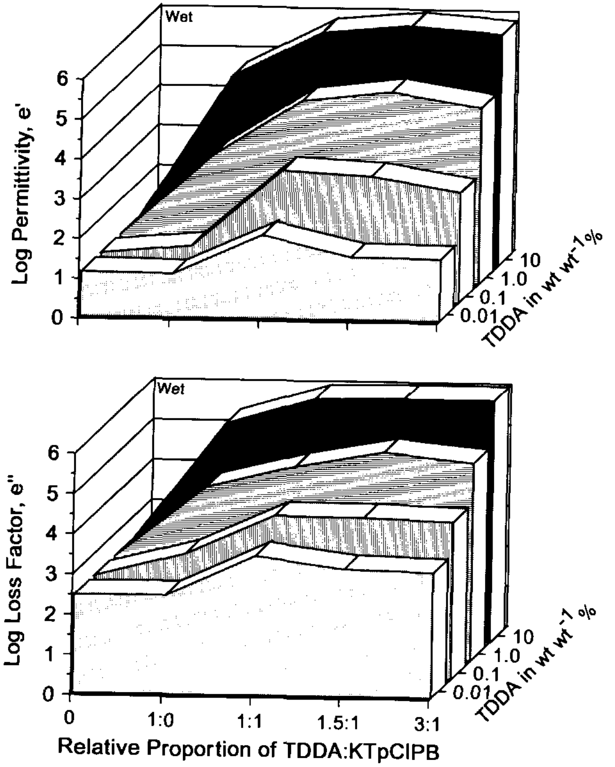

Fig. 4. Influence of TDDA loading in wt wt^{-1}% and the relative proportion of TDDA/KTpClPB on e' and e'' for o-NPOE plasticized PVC membranes in the dry condition at 37°C and at 10 Hz. The solid circles indicate the results for pure, unplasticized PVC, that is, 0_{NP}.

Fig. 5. Influence of TDDA loading in wt wt^{-1}% and the relative proportion of TDDA/KTpClPB on e' and e'' for o-NPOE plasticized PVC membranes in the wet condition after hydration in a pH 7 buffer at 37°C and at 10 Hz.

Table 3

Selected dielectric properties of *o*-NPOE plasticized PVC membranes loaded with TDDA and KTpClPB in the fixed proportion of 1:0

TDDA in wtwt^{-1}%	Frequency in Hz	Temperature in °C	Dry		Wet	
			log e'	log e''	log e'	log e''
0.01	10	0	0.979	1.917	0.981	1.394
0.01	10	37	1.408	3.002	1.098	2.466
0.01	10	100	2.767	4.159	2.525	3.911
0.01	1	0	1.529	2.893	1.260	2.365
0.01	1	37	2.906	3.975	2.135	3.443
0.01	1	100	3.959	5.196	4.132	4.851
0.01	0.1	0	2.922	3.849	2.163	3.320
0.01	0.1	37	4.342	4.839	3.857	4.453
0.01	0.1	100	5.148	6.084	5.150	5.593
0.1	10	0	0.887	2.126	1.123	2.054
0.1	10	37	1.651	3.135	1.335	3.031
0.1	10	100	2.814	4.251	3.249	4.345
0.1	1	0	1.673	3.105	1.588	3.037
0.1	1	37	3.265	4.092	2.857	4.008
0.1	1	100	3.902	5.216	4.715	5.219
0.1	0.1	0	3.344	4.049	2.994	3.973
0.1	0.1	37	4.369	4.919	4.239	4.890
0.1	0.1	100	5.195	6.107	5.498	5.931
1	10	0	1.721	3.437	1.411	3.022
1	10	37	3.333	4.435	3.138	4.222
1	10	100	4.932	5.337	5.007	5.235
1	1	0	3.238	4.407	2.969	3.990
1	1	37	4.647	5.351	4.723	5.079
1	1	100	5.781	6.012	5.632	5.918
1	0.1	0	4.654	5.308	4.507	4.798
1	0.1	37	5.769	6.187	5.409	5.693
1	0.1	100	6.372	6.693	6.172	6.601
10	10	0	3.017	4.207	2.850	3.974
10	10	37	4.619	5.327	4.680	5.331
10	10	100	5.654	6.022	5.772	6.117
10	1	0	4.592	5.110	4.219	4.897
10	1	37	5.666	6.210	5.698	6.115
10	1	100	6.435	6.774	6.665	6.870
10	0.1	0	5.535	5.777	5.475	5.744
10	0.1	37	6.720	6.731	6.625	6.860
10	0.1	100	7.021	7.500	7.112	7.530

Table 4

Selected dielectric properties of *o*-NPOE plasticized PVC membranes loaded with TDDA and KTpClPB in the fixed proportion of 1:1

TDDA in wtwt^{-1}%	Frequency in Hz	Temperature in °C	Dry		Wet	
			log e'	log e''	log e'	log e''
0.01	10	0	1.039	2.383	1.019	2.135
0.01	10	37	2.130	3.694	2.094	3.462
0.01	10	100	3.471	5.006	4.050	4.741
0.01	1	0	1.949	3.519	1.922	3.265
0.01	1	37	3.736	4.646	3.774	4.399
0.01	1	100	4.814	5.968	5.225	5.451
0.01	0.1	0	3.650	4.467	3.524	4.182
0.01	0.1	37	4.731	5.547	4.858	5.042
0.01	0.1	100	6.131	6.812	5.823	6.064
0.1	10	0	1.902	3.420	1.426	2.845
0.1	10	37	3.666	4.525	3.270	4.014
0.1	10	100	4.952	5.843	5.040	5.256
0.1	1	0	3.539	4.380	3.017	3.790
0.1	1	37	4.865	5.333	4.470	4.747
0.1	1	100	6.077	6.766	5.758	5.894
0.1	0.1	0	4.823	5.137	4.369	4.654
0.1	0.1	37	5.756	6.114	5.267	5.465
0.1	0.1	100	7.161	7.339	6.269	6.376
1	10	0	3.319	4.333	2.951	3.686
1	10	37	4.662	5.323	4.543	4.766
1	10	100	5.534	6.490	6.027	6.345
1	1	0	4.596	5.221	4.177	4.410
1	1	37	5.741	6.156	5.185	5.446
1	1	100	6.952	7.379	6.797	6.937
1	0.1	0	5.705	5.950	4.902	5.162
1	0.1	37	6.593	6.588	5.941	6.093
1	0.1	100	7.717	7.674	7.186	7.201
10	10	0	4.758	5.278	4.838	5.146
10	10	37	6.015	6.281	5.805	5.970
10	10	100	6.775	6.920	6.833	7.017
10	1	0	5.811	5.979	5.618	5.752
10	1	37	6.755	6.936	6.454	6.650
10	1	100	7.418	7.532	7.508	7.627
10	0.1	0	6.407	6.441	6.183	6.358
10	0.1	37	7.207	7.390	6.999	7.098
10	0.1	100	7.833	7.929	7.731	7.882

Table 5

Selected dielectric properties of *o*-NPOE plasticized PVC membranes loaded with TDDA and KTpClPB in the fixed proportion of 1.5:1

TDDA in wtwt^{-1}%	Frequency in Hz	Temperature in °C	Dry		Wet	
			log e'	log e''	log e'	log e''
0.01	10	0	0.949	2.087	0.957	2.019
0.01	10	37	1.646	3.212	1.575	3.165
0.01	10	100	3.185	4.695	3.592	4.596
0.01	1	0	1.568	3.064	1.483	2.997
0.01	1	37	3.362	4.274	3.157	4.128
0.01	1	100	4.373	5.664	4.755	5.492
0.01	0.1	0	3.324	4.166	2.969	3.955
0.01	0.1	37	4.372	5.153	4.348	4.993
0.01	0.1	100	5.824	6.522	5.899	6.355
0.1	10	0	1.564	3.137	1.369	2.753
0.1	10	37	3.219	4.204	3.152	3.989
0.1	10	100	4.302	5.481	4.669	5.215
0.1	1	0	3.118	4.101	2.858	3.705
0.1	1	37	4.623	5.031	4.374	4.788
0.1	1	100	5.623	6.523	5.651	6.047
0.1	0.1	0	4.577	4.905	4.063	4.504
0.1	0.1	37	5.448	5.913	5.145	5.560
0.1	0.1	100	6.943	7.132	6.394	6.492
1	10	0	3.250	4.081	3.065	4.006
1	10	37	4.714	4.968	4.801	5.142
1	10	100	5.534	6.292	6.094	6.501
1	1	0	4.631	4.814	4.457	4.832
1	1	37	5.323	5.716	5.532	5.867
1	1	100	6.814	7.071	6.972	7.195
1	0.1	0	5.197	5.331	5.304	5.673
1	0.1	37	6.088	6.216	6.371	6.525
1	0.1	100	7.283	7.193	7.441	7.492
10	10	0	4.864	5.286	5.091	5.368
10	10	37	5.970	6.190	6.068	6.316
10	10	100	6.784	6.957	6.795	7.044
10	1	0	5.799	5.966	5.809	5.916
10	1	37	6.694	6.816	6.766	6.909
10	1	100	7.556	7.536	7.487	7.677
10	0.1	0	6.440	6.529	6.320	6.492
10	0.1	37	7.137	7.367	7.188	7.280
10	0.1	100	7.797	7.814	7.799	8.060

Table 6

Selected dielectric properties of *o*-NPOE plasticized PVC membranes loaded with TDDA and KTpClPB in the fixed proportion of 3:1

TDDA in wtwt^{-1}%	Frequency in Hz	Temperature in °C	Dry		Wet	
			log e'	log e''	log e'	log e''
0.01	10	0	0.940	2.177	1.030	1.945
0.01	10	37	1.676	3.286	1.555	3.108
0.01	10	100	3.374	4.554	3.395	4.481
0.01	1	0	1.702	3.153	1.678	2.918
0.01	1	37	3.095	4.256	3.125	4.076
0.01	1	100	4.704	5.481	4.695	5.380
0.01	0.1	0	3.408	4.317	3.076	3.858
0.01	0.1	37	4.562	5.167	4.489	4.896
0.01	0.1	100	5.908	6.300	5.836	6.252
0.1	10	0	1.201	2.856	1.295	2.756
0.1	10	37	2.718	3.908	2.790	3.917
0.1	10	100	4.247	5.083	4.444	5.156
0.1	1	0	2.626	3.829	2.614	3.723
0.1	1	37	4.291	4.811	4.302	4.799
0.1	1	100	5.161	6.000	5.468	6.039
0.1	0.1	0	4.253	4.716	4.129	4.595
0.1	0.1	37	5.279	5.463	5.098	5.585
0.1	0.1	100	6.357	6.609	6.474	6.628
1	10	0	2.542	3.741	2.574	3.761
1	10	37	4.371	4.777	4.437	4.911
1	10	100	5.094	5.986	5.666	6.176
1	1	0	4.208	4.638	4.161	4.664
1	1	37	5.272	5.201	5.296	5.660
1	1	100	6.244	6.928	6.679	6.992
1	0.1	0	5.147	5.022	5.022	5.386
1	0.1	37	5.615	5.731	6.195	6.406
1	0.1	100	7.403	7.521	7.245	7.360
10	10	0	4.405	4.943	3.921	4.533
10	10	37	5.593	5.736	5.835	6.188
10	10	100	6.411	6.911	6.722	6.931
10	1	0	5.457	5.482	4.999	5.308
10	1	37	6.170	6.495	6.645	6.809
10	1	100	7.549	7.763	7.407	7.470
10	0.1	0	5.882	6.003	5.768	5.933
10	0.1	37	6.807	7.188	7.012	7.193
10	0.1	100	8.096	8.069	7.733	7.831

Selected dielectric properties of pure, unplasticized PVC membranes (0_{NP}) and o-NPOE plasticized PVC membranes without TDDA or KTpClPB (0_P) were summarized for three frequencies (10, 1 and 0.1 Hz) and three temperatures (0, 37 and 100°C) (Table 2). The results for both dry and wet conditions are shown for the plasticized membranes. This table supports the observation that e' and e'' increase with increasing temperature and decreasing frequency. Similar outcomes were observed for membranes using the four loadings of TDDA and the four relative proportions of TDDA/KTpClPB at the same temperatures and frequencies (Tables 3–6). Using Eqs. (3) and (4), σ and $\tan\delta$ can be derived from these results.

4. Discussion

Recent measurements via DSC [20] and DMA [2] of unmodified PVC have indicated T_g values of 78 and 77°C, respectively, that decrease with the addition of *o*-NPOE to −78 and −50°C, respectively. Given these results for the dummy membrane, one would conclude that the present membranes would also have subambient T_g values. Fig. 1 shows that e' and e'' collapse to different magnitudes at the same temperature, ca. −75°C. Below this common temperature the plasticizer is in a glassy state so that any carriers, which may have been present and mobile at higher temperatures, are now frozen-in. Dulic et al. reported similar results for a *o*-NPOE plasticized PVC [16]. In their work the dielectric properties (e' and e'') of pure *o*-NPOE were found to have sharp maximums at −62 and −67°C, respectively.

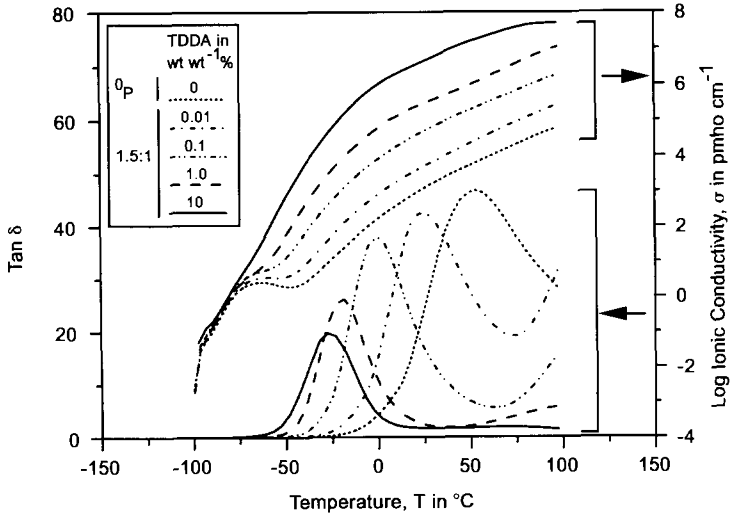

Fig. 6. Influence of TDDA loading in wtwt.$^{-1}$% on the temperature dependence of $\tan\delta$ and σ for *o*-NPOE plasticized PVC membranes in the dry condition at the relative proportion of TDDA/KTpClPB equal to 1.5:1 at 10 Hz.

As seen by the solid dots on Figs. 2 and 4 and the data in Tables 2–6 in the dry condition, the pure PVC (0_{NP}) has minimal influence on the overall dielectric properties of these highly plasticized membranes until the *o*-NPOE, the TDDA, and the KTpClPB are incorporated. By adding the *o*-NPOE to the pure PVC (0_P), e' increased by a factor ranging from 3 to 1500 times, and e'' increased up to 120 000 times (Table 2). When TDDA is included in the plasticized PVC membrane (1:0), e' and e'' increase up to 4000 and 500 times, respectively (on average, e' and e'' increase by factors of 400 and 80 times, respectively; cf. Table 3), relative to the plasticized membrane, 0_P. Finally, by including KTpClPB in relative proportions of TDDA/KTpClPB equal to 1:1, 1.5:1, and 3:1 to the TDDA-enriched and plasticized membranes, e' and e'' are enhanced by as much as 90 000 and 6000 times, respectively (on average, e' and e'' increase by factors of 5000 and 500, respectively; cf. Tables 4–6), relative to the plasticized membrane, 0_P.

These e' and e'' measurements should be contrasted with the values of tan δ; and like their DMA counterparts [21], these measurements should not be construed to represent the T_g of the unplasticized or plasticized polymer. Indeed, the absolute magnitude and

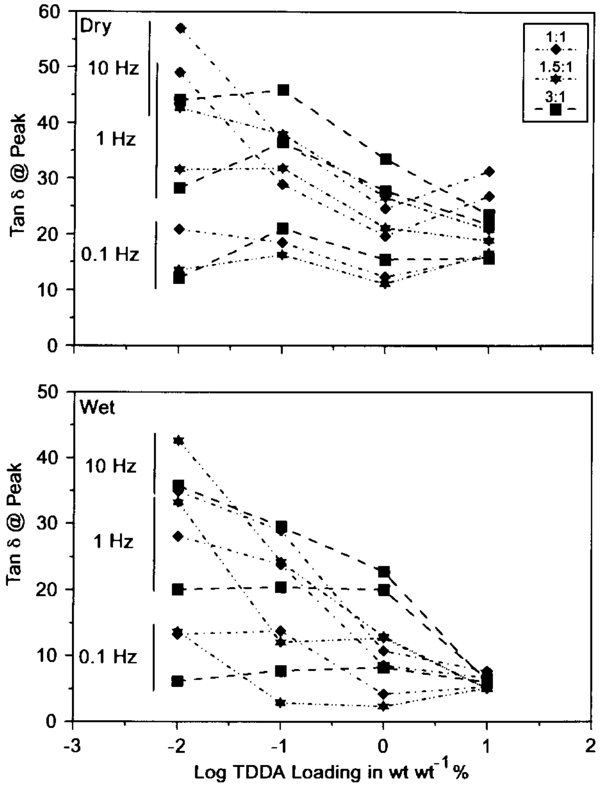

Fig. 7. Influence of TDDA loading in wtwt^{-1}% and frequency in Hz on the magnitude of tan δ at the peak for *o*-NPOE plasticized PVC membranes in the dry (top frame) and wet (bottom frame) conditions as a function of three relative proportions of TDDA/KTpClPB (1:1, 1.5:1 and 3:1). The results for the 1:0 proportion are not shown, because they did not follow a consistent trend.

Table 7

Summary of tan δ peaks of TDDA loaded, *o*-NPOE plasticized PVC membranes in the dry condition

Proportion of TDDA/ KTpClPB	TDDA in wt wt^{-1}%	Frequency in Hz								
		10			1.0			0.1		
		Log σ in pmho cm^{-1}	Tan δ	*T* at tan δ in °C	Log σ in pmho cm^{-1}	Tan δ	*T* at tan δ in °C	Log σ in pmho cm^{-1}	Tan δ	*T* at tan δ in °C
0p[a]	0	3.700	46.54	49.1	2.783	36.62	16.2	2.715	12.03	3.7
1:0	0.01	3.842	39.56	40.1	3.166	25.97	7.1	2.286	9.77	–9.2
	0.1	3.485	28.35	–3.9	3.028	21.54	–9.7	2.148	11.83	–16.3
	1	4.034	43.68	–2.4	2.702	44.47	–23.4	2.160	43.97	–36.6
	10	4.230	33.76	–14.4	2.907	29.72	–31.6	2.100	28.53	–45.2
1:1	0.01	3.848	57.03	18.7	2.936	49.08	–6.1	2.328	20.83	–18.5
	0.1	3.813	36.77	–8.0	2.955	28.89	–24.4	2.061	18.53	–33.2
	1	3.923	24.55	–23.9	2.550	19.67	–36.8	2.308	12.34	–45.9
	10	4.220	31.31	–31.8	3.092	26.77	–45.5	2.550	16.05	–50.9
1.5:1	0.01	3.625	42.68	22.4	2.961	31.56	2.1	2.246	13.59	–14.4
	0.1	3.697	37.96	–4.9	2.906	31.81	–21.2	2.087	16.26	–34.6
	1	3.704	26.56	–22.7	2.855	21.12	–35.5	2.115	11.12	–44.7
	10	4.326	20.84	–31.2	3.264	18.89	–44.3	2.349	16.59	–53.6
3:1	0.01	3.689	44.09	23.3	2.898	28.25	–3.0	2.240	12.10	–19.4
	0.1	3.767	45.89	5.4	2.687	36.45	–19.3	2.167	21.01	–33.0
	1	3.983	33.48	–16.6	2.740	27.71	–33.5	2.043	15.46	–42.6
	10	4.180	23.46	–29.2	3.190	21.75	–42.2	2.351	15.67	–51.4

[a] Contains *o*-NPOE plasticizer but no TDDA or KTpClPB.

Table 8

Summary of tan δ peaks of TDDA loaded, *o*-NPOE plasticized PVC membranes in the wet condition after hydration in pH 7 buffer

Proportion of TDDA/ KTpClPB	TDDA in wt wt^{-1}%	Frequency in Hz								
		10			1.0			0.1		
		Log σ in pmho cm^{-1}	Tan δ	*T* at tan δ in °C	Log σ in pmho cm^{-1}	Tan δ	*T* at tan δ in °C	Log σ in pmho cm^{-1}	Tan δ	*T* at tan δ in °C
0p*	0	4.088	56.21	78.9	2.960	36.08	30.0	2.075	17.46	1.7
1:0	0.01	3.934	38.46	64.0	2.775	29.72	19.1	2.065	14.31	−1.5
	0.1	3.776	49.65	38.4	2.917	37.17	5.4	2.866	11.24	4.5
	1	3.768	40.90	0.8	2.765	31.23	−20.0	1.919	17.18	−33.5
	10	4.173	16.38	−13.1	3.141	19.35	−30.5	2.482	21.29	−39.5
1:1	0.01	3.596	34.90	17.9	2.692	28.12	−6.1	2.042	13.24	−19.6
	0.1	3.418	28.88	−5.1	2.394	23.84	−25.4	1.739	13.73	−35.4
	1	3.686	10.70	−17.4	2.574	8.50	−35.3	0.6370	4.18	−56.0
	10	3.517	7.64	−45.0	2.552	6.66	−54.2	1.855	5.30	−59.1
1.5:1	0.01	3.676	42.66	28.3	2.889	33.22	3.8	2.217	13.63	−12.4
	0.1	3.498	24.22	0.9	2.959	12.01	−11.3	3.872	2.86	20.5
	1	4.024	12.90	−17.4	2.913	12.69	−35.2	4.418	2.33	1.8
	10	4.131	4.95	−36.9	3.040	5.05	−49.6	2.402	5.13	−55.2
3:1	0.01	3.853	35.75	36.5	2.944	20.06	7.5	0.8916	6.12	−34.1
	0.1	3.656	29.50	5.0	2.963	20.40	−11.2	2.512	7.70	−19.8
	1	3.983	22.75	−12.9	3.000	20.00	−30.4	2.329	8.17	−39.7
	10	4.257	5.93	−25.3	3.428	6.38	−38.7	2.355	5.98	−51.9

[a] Contains *o*-NPOE plasticizer but no TDDA or KTpClPB.

location of tan δ may be influenced by the ionic conductivity of the plasticized PVC, that is, in part, a consequence of the intrinsic impurities, the TDDA, and/or the KTpClPB. When the tan δ data at one relative proportion of TDDA/KTpClPB (1.5:1) and at 10 Hz was plotted as a function of the temperature (Fig. 6), the tan δ peaks shifted from 53°C for the dummy membrane (0 wtwt^{-1}% TDDA) to −27°C for the proton-selective membrane (10 wtwt^{-1}% TDDA). Simultaneously, the magnitude of tan δ at the peak decreased from 47 to 20. Since the absolute amount of TDDA is being varied, perhaps this is an ionic transition associated with the ionophore which, in addition to being a neutral carrier, acts as a secondary plasticizer and further increases the conformational mobility. In any event, the depression of the tan δ peak decreases rapidly at first with decade increases in TDDA loading but appears to be approaching a limiting value (ca. −30°C) by 10 wtwt^{-1}% loading. When the σ data was plotted at the same test conditions as a function of the temperature, as expected σ followed the same trends as e'', including the collapse to a single line at the T_g (cf. Figs. 1 and 6 and Eqs. (2) and (3)).

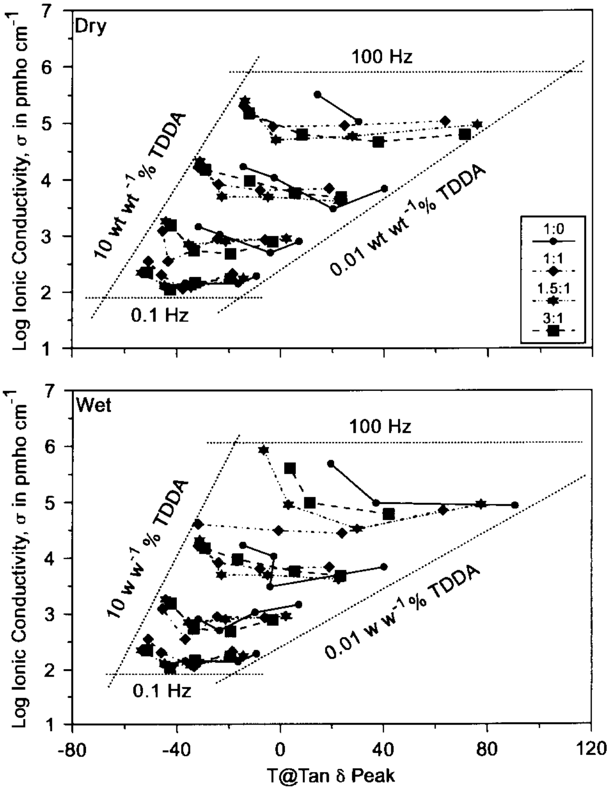

Fig. 8. Influence of TDDA loading in wtwt^{-1}% and frequency in Hz on σ for o-NPOE plasticized PVC membranes in the dry (top frame) and wet (bottom frame) conditions as a function of the temperature at which the peak of tan δ occurs for four relative proportions of TDDA/KTpClPB (1:0, 1:1, 1.5:1, and 3:1). From top to bottom the four bands of lines represent the results at 100, 10, 1, and 0.1 Hz, and from left to right the data represents the results for the 10, 1, 0.1, and 0.01 wtwt^{-1}% loading of TDDA.

After expanding the analysis of o-NPOE plasticized PVC membranes to three frequencies (10, 1, and 0.1 Hz) having four loadings of TDDA and four relative proportions of ionophore/negative sites, the tan δ peaks continued to reach a maximum at lower temperatures for the higher TDDA loadings, whether in the dry (Table 7) or the wet (Table 8) conditions. At the lower frequencies a general decrease was observed in the temperature at which the peak of tan δ occurred (Fig. 7). At these lower frequencies the magnitude of the tan δ at its peak was independent of TDDA loading. As seen in Fig. 6 for one relative proportion of TDDA/KTpClPB, the expanded analysis of Fig. 7 shows that there was a decrease in each magnitude of tan δ at its peak with higher TDDA loadings in both dry and wet conditions. In the wet condition, the results converged to a single value of $\tan\delta = 6$ at 10 wtwt^{-1}% TDDA loading regardless of the relative proportion of TDDA/KTpClPB or test frequency. The data for the 1:0 proportion is not shown because the results did not follow a consistent trend.

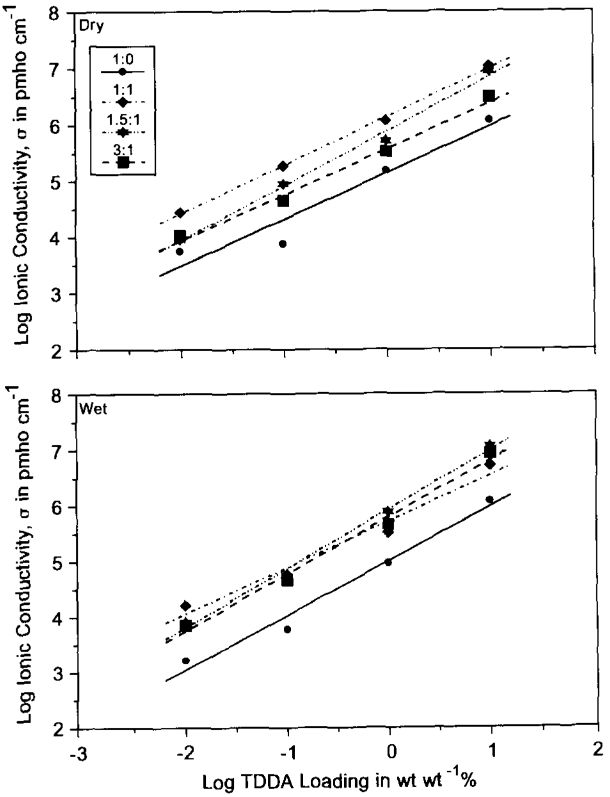

Fig. 9. Influence of the relative proportion of TDDA/KTpClPB (1:0, 1:1, 1.5:1, and 3:1) on σ for o-NPOE plasticized PVC membranes in the dry (top frame) and wet (bottom frame) conditions as a function of TDDA loading in wtwt^{-1}% at 37°C and 10 Hz. The shaded area in the top plot indicates the area covered by the lines drawn from the wet results (bottom frame), and the shaded area in the bottom plot corresponds to the area covered by the lines drawn from the dry results (top frame).

When each σ was plotted against its corresponding temperature (T) at which the tan δ peak occurred (cf. Tables 7 and 8 and the results at 100 Hz), the lines collapsed into four bands that could be grouped according to their frequencies (Fig. 8). The value of σ was invariant at each frequency regardless of the TDDA loading and the relative proportion of ionophore/negative sites. Nominal values of σ increased an order of magnitude for each decade increase in frequency from a low of 200 pmho cm^{-1} at 0.1 Hz to a high of 100 000 pmho cm^{-1} at 100 Hz. In contrast, at 25°C the σ of pure PVC (0_{NP}) decreased about four orders of magnitude from a low of 0.02 pmho cm^{-1} at 0.1 Hz (this AC value at 0.1 Hz compares favorably with the DC value of 0.01 pmho cm^{-1} reported in Ref. [22]) to a high of 3 pmho cm^{-1} at 100 Hz; the plasticized PVC (0_P) was substantially better and varied from 980 to 1200 pmho cm^{-1} for the same respective frequency values.

When the influence of hydration and the relative proportions of ionophore/negative sites are considered at a physiologically important temperature (37°C), a statistically significant correlation ($P < 0.05$) is found between σ and TDDA loading for the eight plots at 10 Hz (Fig. 9). The shaded area that is superposed on the dry plot (upper frame); similarly the shaded area that is superposed on the wet plot (bottom frame) corresponds to the lines from the dry results (top frame). Based on these plots, the TDDA loading and the accompanying absolute amount of KTpClPB are the dominant parameters; hydration and the relative proportion of ionophore negative sites are of secondary importance. Specifically, σ increased from 10^3 to 10^7 pmho cm^{-1} as the TDDA loading increased from 0.01 to 10 $wtwt^{-1}$%, whilst the scatter of σ as a function of the relative proportion of sites varied by plus or minus a half-order of magnitude at any TDDA loading. When the plot of the dry condition is scrutinized, the σ is superior under the premise that one negative site potentially exists for every complexed ionophore. This trend is echoed for the wet condition up to a ca. 0.1 $wtwt^{-1}$% TDDA at which point the 1.5:1 proportion becomes superior. If these observations are accurate, performance can be enhanced by as much as a factor of five by adjusting the proportion of ionophore/negative sites to suit the TDDA loading while accommodating the interference that hydration imparts to low loadings of ionophore. Based on the overall analysis, the proportion of 1.5:1 seems best at 10 $wtwt^{-1}$% TDDA loading, although 1 $wtwt^{-1}$% TDDA loading is more practical. These observations are comparable to those seen in both frames of Figs. 4 and 5 in which, at high TDDA loadings, the maximum or plateau is reached at 1:1 in the dry condition, while in the wet condition the maximum or steady state values were reached at 1.5:1.

5. Conclusions

The PVC has minimum influence on the overall dielectric properties of these *o*-NPOE plasticized membranes. In both dry and wet conditions permittivities and loss factors increase with increasing temperature, increasing concentration of TDDA, and decreasing frequency. Above a minimum relative proportion of TDDA/KTpClPB equal to 1:1 for the dry condition and 1.5:1 following hydration in a pH 7 buffer, the relative proportions do not influence the dielectric properties of the membranes as much as the absolute concentrations of TDDA and/or KTpClPB do. The absolute magnitudes of tan δ at its peak decreases with increasing TDDA loading and approaches the values for the tan δ results at the lower frequencies, which are independent of the TDDA loading. The ionic conductivity at the temperature at which the peak of tan δ occurs is independent of both TDDA and/or KTpClPB concentrations but increases with frequency.

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