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Influence of plasticizer configurational changes on the dielectric characteristics of highly plasticized poly(vinyl chloride)

William S. Gibbons[a] and Robert P. Kusy[a,b,c,*]

[a]*Biomedical Engineering, University of North Carolina, Chapel Hill, NC 27599, USA*
[b]*Dental Research Center, University of North Carolina, Chapel Hill, NC 27599, USA*
[c]*Curriculum in Applied and Material Sciences, University of North Carolina, Chapel Hill, NC 27599, USA*

Three citrate-related compounds [Citroflex A-4 (CFA4), Citroflex A-6 (CFA6), and Citroflex B-6 (CFB6)] and six sebacate-related compounds [dimethyl sebacate (DMS), diethyl sebacate (DES), dibutyl sebacate (DBS), dioctyl sebacate (DOS), dioctyl azelate (DOZ), and dioctyl adipate (DOA)] were used to evaluate the effects of configurational changes in plasticizer on the dielectric properties of ion-selective poly(vinyl chloride) membranes. Tridodecylamine (TDDA) and potassium tetrakis-4-chlorophenyl borate (KTpClPB) were used as neutral charge carriers and negative sites, respectively. Using parallel plate sensors, the dielectric properties [ionic conductivity (σ) and tan δ] of the plasticized PVC membranes were determined at temperatures from -100 to $+100°C$ and seven log frequencies ($-1, 0, 1, 2, 3, 4,$ and 5 Hz). Generally, increasing the amount of plasticizer in the membrane improved the σ and lowered the temperature of the tan δ peak. A positive linear correlation existed between the log σ and the log phr ratio for a given temperature and frequency, when no data was included for membranes below the melting temperature of the plasticizer. When plotted *versus* temperature, the slopes of all these lines passed through a maximum between 0 and 60°C. The intercepts of all these lines increased monotonically with increasing temperature. These intercepts were highly dependent on the frequency at low temperatures, becoming less frequency dependent as the temperature increased. Having established that configurational changes of the plasticizers had no effect above the melting point of each plasticizer, global nomograms were only required for the citrate- and sebacate-related plasticizers, respectively. Using the appropriate nomogram for a selected plasticizer, the σ could be predicted at a given phr ratio, temperature, and frequency. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

In 1970 Frant and Ross introduced the ion-selective electrode (ISE) for measurement of potassium ions[1]. By 1978 Hill *et al.* established the biosensor using the ISE for *in vivo* applications[2]. The key operating component of ISEs was the ion-selective membrane, which was composed of poly(vinyl chloride) (PVC), a plasticizer, an ionophore, and a salt. For the early investigations of ISEs the ratio of plasticizer to PVC was two to one, which was five to 10 times more plasticizer than conventional applications[3]. This high amount of plasticizer formed liquid-phase membranes that were capable of ionic transport. Unfortunately, the high level of plasticization also resulted in plasticizer leaching from the membrane. This excess plasticizer formed a resistive film on the electrode surface and caused the electrode to fail over time[4]. The excess plasticizer could also be harmful during *in vivo* applications, since the traditional plasticizers were non-biocompatible synthetic organic chemicals.

In previous work[5,6] three traditional plasticizers and four natural derivatives were investigated at different levels of plasticization. Dielectric analysis determined the ionic conductivity (σ, the capacity of a membrane to transfer ions) and the tan δ. The dielectric properties were examined over temperatures ranging from -100 to $100°C$ and frequencies from 10^{-1} to 10^5 Hz at decade increments. Based upon these measurements, the log σ increased substantially as the phr ratio was increased from 0 to about 0.75 or 1.0, dependent on the plasticizer species. Above these phr ratios less substantial increases were observed. As such, the amount of plasticizer could be reduced, which produced stronger and tougher membranes[6]. These increases in strength and toughness decreased the likelihood of ISE and biosensor damage during production, insertion, and operation. Furthermore, a reduction in plasticizer deterred the negative biological consequences associated with leaching of the plasticizer.

The present study examined the effects of configurational changes in the molecular structure of the plasticizers. Like Heijboer's study of configurational changes in the structure of poly(methacrylate) using dynamic mechanical analysis[7], nine plasticizers from two homologous series were evaluated using dielectric analysis. Four of these plasticizers were related to dibutyl sebacate and dioctyl sebacate, both of which were traditionally used in biosensors[2,8]. The other three plasticizers were biocompatible derivatives of citrate[9], which included a compound (Citroflex B-6) used in previous studies[5,6]. Each plasticizer was chosen so that a distinct configurational change in its molecular structure was discernible. By understanding the effects of these changes on the bulk membrane properties, future choices of

* To whom correspondence should be addressed

plasticizer could be made on a more informed basis via nomograms. Thereby plasticizers might be tailored to produce optimal results based on the particular application.

MATERIALS AND METHODS

Membrane preparation

Membranes were prepared by dissolving 1.1 wt% PVC in tetrahydrofuran (THF, Mallinckrodt). A 50/50 blend of low and high molecular weight (MW) PVCs (MW 77 300 and 193 600, Scientific Polymer) provided a good combination of strength and processability[10]. One of nine plasticizers was added in the appropriate amount. In addition, 2.5 wt% of a proton-selective ionophore, tridodecylamine (TDDA, Fluka), and 1.7 wt% of a salt, potassium tetrakis-4-chlorophenyl borate (KTpClPB, Lancaster), were added as neutral charge carriers and negative sites, respectively. This ratio of 1.5:1 of TDDA:KTpClPB was previously established as optimal for ion-conductive membranes[11]. 10 ml of the mixture was evaporated in a hood for at least five days, so that clear, non-turbid membranes were produced. The evaporation was performed in a 2.5 cm diameter glass ring under weighted filter papers, producing membranes that were at least 125 μm thick.

As a minimum five levels of plasticization were examined for each plasticizer. Tests were performed on membranes for each of the nine plasticizers to evaluate the effects of molecular structure and amount of plasticizer.

Three plasticizers were citrate-related compounds: Citroflex A-4 (CFA4), Citroflex A-6 (CFA6), and Citroflex B-6 (CFB6) (*Table 1*). In their lowest energy configurations these citrate compounds formed a tetrahedron (*Figure 1*), with three identical groups at the base (designated R") and a different group at the top (designated R'). The CFB6, which was studied in the previous work[5], had three saturated six-carbon chains as the R" groups and a saturated three-carbon chain at the R' position. The CFA6 had the same base as CFB6 but only a saturated one-carbon chain substituted at R'. The reduction in this chain length from the CFB6 to the CFA6 made the molecule more planar without substantially affecting the hydrodynamic volume or the MW of the molecule (*cf. Table 1*). The CFA4 had the same R' group as the CFA6 but had three saturated four-carbon chains substituted at the R" positions. The deletion of two carbons at each base decreased the hydrodynamic volume of the CFA4 compared to CFA6 but did not drastically change the non-planar conformation of the molecule.

Table 1 List of nine plasticizers, molecular weights (MWs), phr ratios at the traditional plasticization level of 200 phr, and melting points (MPs). The bars indicate homologous compounds

Plasticizer	Symbol	MW	phr Ratio at 200 phr	MP (°C)
Citroflex A-4[a]	CFA4	402	4.4	− 59
Citroflex A-6[a]	CFA6	486	3.6	− 57
Citroflex B-6[a]	CFB6	514	3.4	− 55
Dimethyl sebacate[b]	DMS	230	7.6	30
Diethyl sebacate[b]	DES	260	6.7	2
Dibutyl sebacate[c]	DBS	314	5.6	− 11
Dioctyl sebacate[b]	DOS	427	4.1	− 65
Dioctyl azelate[d]	DOZ	412	4.3	− 60
Dioctyl adipate[d]	DOA	373	4.7	− 65

[a] Morflex, Inc. (Greensboro, NC)
[b] Aldrich Chemical Co. (Milwaukee, WI)
[c] Eastman Kodak Co. (Rochester, NY)
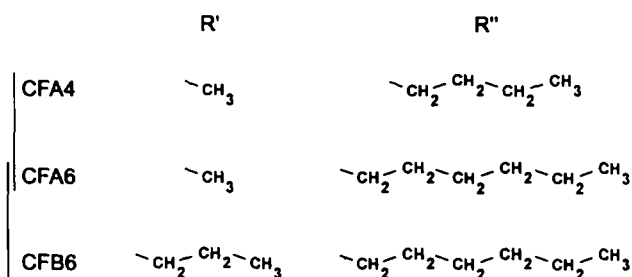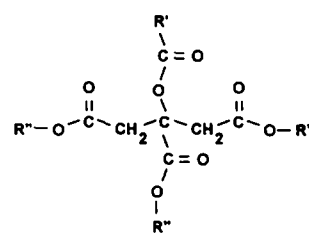[d] C.P. Hall Co. (Memphis, TN)

Figure 1 Configurations of the citrate-related plasticizers. The bars to the left highlight the homologous compounds
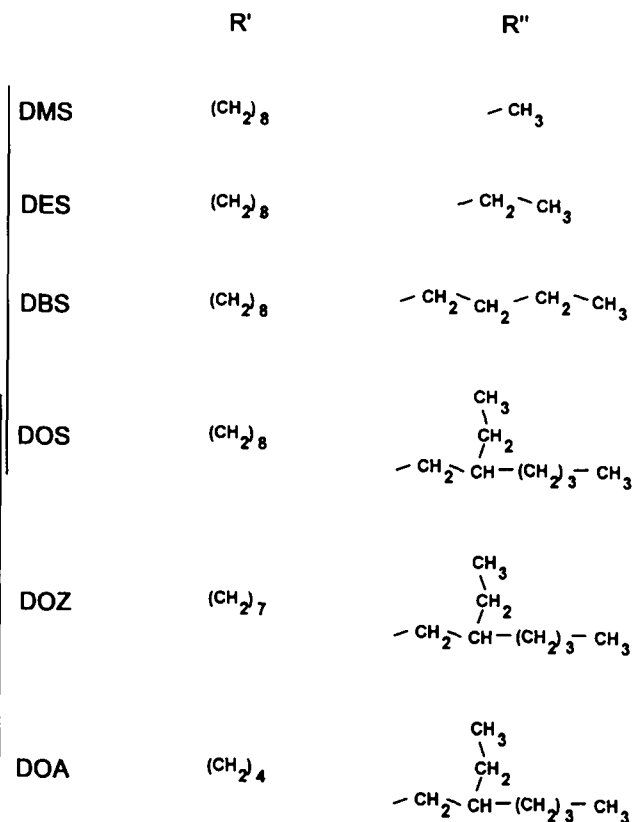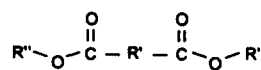
Figure 2 Configurations of the sebacate-related plasticizers. The bars to the left highlight the homologous compounds

The sebacate-related compounds were based on a binary ester molecule (*Table 1*). A set of four sebacate materials evaluated the effects of changes in the outer chain (R") length and structure: dimethyl sebacate (DMS), diethyl sebacate (DES), dibutyl sebacate (DBS), and dioctyl sebacate (DOS) (*Figure 2*). The first three members of this group were a simple homologous series of one-, two-, and four-carbon chains, respectively. The fourth member

changed the linear end group to an eight-carbon, branched 2-ethylhexyl end group. The final three structures of *Figure 2* evaluated the effects of inner chain (R') length and structure: DOS, dioctyl azelate (DOZ), and dioctyl adipate (DOA). These three structures varied in a homologous manner at R' using eight-, seven-, and four-carbon chains, respectively.

'phr' Ratio

The amount of plasticizer in a membrane can be described in terms of the phr ratio, which accounts for the MW of the plasticizer. The per cent mass ratio of the plasticizer to the PVC (phr_{exp}) is defined as:

$$phr_{exp} = \frac{mass\ of\ plasticizer}{mass\ of\ PVC} \times 100 \qquad (1)$$

Based on the MW of the plasticizer and the MW of one helical unit of PVC (MW 875), the minimum plasticizer ratio necessary for complete plasticization (phr_{min}) can be determined as follows:

$$phr_{min} = \frac{MW\ of\ plasticizer}{875} \times 100 \qquad (2)$$

This phr_{min} occurred when all polar groups on the PVC backbone were shielded from each other by a monolayer of plasticizer[12]. Finally, the phr ratio is defined as:

$$phr\ ratio = \frac{phr_{exp}}{phr_{min}} \qquad (3)$$

Test apparatus

Dielectric measurements were made on a TA Instruments Dielectric Analyser 2970 (DEA) using parallel plate sensors. A ram pressure of 200 N and nitrogen gas purge at 1.0 l/min ensured uniformity of the test conditions. As the temperature was ramped from -100 to $100°C$ at a rate of $3°C/min$, an alternating electric field was applied to the membranes at frequencies (*f*) ranging from 10^{-1} to 10^5 Hz at decade increments. The effects of the configuration of the plasticizer were analysed on the basis of four principle dielectric quantities: permittivity (ε'), loss factor (ε''), tan δ, and ionic conductivity (σ). The tan δ peak was representative of the glass transition temperature (T_g). The σ of the material was indicative of the molecular mobility and thereby of the ease of ion transmission across the

Table 2 Measured values of log σ (pmho/cm) and tan δ peak for six plasticizer levels of PVC membranes plasticized with Citroflex A-4 (CFA4); all temperatures are within $\pm 2°C$

phr Ratio	Dielectric measurement		log *f* (Hz)						
			-1	0	1	2	3	4	5
0.5	log σ	-60°C	-2.93	-2.13	-1.28	0.36	0.57	1.48	2.44
		37°C	0.01	0.30	0.94	1.81	2.41	3.17	3.97
		90°C	4.40	4.47	4.32	4.36	4.43	4.81	5.25
	tan δ	max.	1.9	—[b]	—[b]	—[b]	—[b]	—[b]	—[b]
		T (°C)	45	—[b]	—[b]	—[b]	—[b]	—[b]	—[b]
1.0	log σ	-60°C	-2.94	-2.15	-1.37	-0.51	0.43	1.30	2.25
		37°C	0.60	0.95	1.15	1.64	2.62	3.38	4.16
		90°C	3.89	4.65	4.69	4.71	4.73	4.65	5.12
	tan δ	max.	1.5	1.9	50.1	—[b]	—[b]	—[b]	—[b]
		T (°C)	23	40	85	—[b]	—[b]	—[b]	—[b]
1.5	log σ	-60°C	—[a]	-1.75	-0.82	0.01	0.89	1.70	2.75
		37°C	—[a]	3.33	3.45	3.50	3.72	4.19	4.73
		90°C	5.40	5.65	5.75	5.68	5.69	5.70	5.82
	tan δ	max.	2.0	4.2	30.2	86.1	—[b]	—[b]	—[b]
		T (°C)	-9	30	66	80	—[b]	—[b]	—[b]
2.0	log σ	-60°C	-1.98	-1.19	-0.41	0.35	1.17	1.92	2.89
		37°C	4.14	4.19	4.01	4.04	4.12	4.50	4.98
		90°C	5.94	6.06	6.10	6.12	6.13	6.14	6.21
	tan δ	max.	6.1	—[a]	61.8	132.1	—[b]	—[b]	—[b]
		T (°C)	-7	—[a]	45	75	—[b]	—[b]	—[b]
3.0	log σ	-60°C	-1.63	-0.83	-0.03	0.73	1.50	2.28	3.15
		37°C	4.90	4.98	5.00	5.02	5.04	5.03	5.30
		90°C	6.19	6.39	6.44	6.39	6.40	6.41	6.43
	tan δ	max.	—[a]	105.7	112.6	150.2	—[b]	—[b]	—[b]
		T (°C)	—[a]	6	28	62	—[b]	—[b]	—[b]
4.4	log σ	-60°C	-0.52	0.00	0.68	1.37	2.18	2.93	3.67
		37°C	5.64	5.65	5.67	5.68	5.69	5.71	5.79
		90°C	6.60	6.74	6.79	6.81	6.81	6.82	6.82
	tan δ	max.	154.2	195.7	296.0	535.0	—[b]	—[b]	—[b]
		T (°C)	-11	10	44	88	—[b]	—[b]	—[b]

[a] Testing error
[b] Values were outside the test range

Table 3 Measured values of log σ (pmho/cm) and tan δ peak for six plasticizer levels of PVC membranes plasticized with Citroflex A-6 (CFA6); all temperatures are within $\pm$ 2°C

phr Ratio	Dielectric measurement		$\log f$ (Hz)						
			− 1	0	1	2	3	4	5
0.5	log σ	− 60°C	− 2.70	− 1.84	− 1.00	− 0.12	0.83	1.85	2.89
		37°C	1.75	1.92	2.06	2.38	2.97	3.60	4.30
		90°C	5.17	5.22	5.27	5.30	5.32	5.36	5.49
	tan δ	max.	2.7	23.9	37.3	−[b]	−[b]	−[b]	−[b]
		T (°C)	24	59	72	−[b]	−[b]	−[b]	−[b]
1.0	log σ	− 60°C	− 2.54	− 1.75	− 0.94	− 0.10	0.71	1.64	2.78
		37°C	1.31	2.39	2.54	2.65	3.22	3.92	4.56
		90°C	5.38	5.46	5.48	5.50	5.51	5.43	5.68
	tan δ	max.	2.0	2.9	−[a]	−[b]	−[b]	−[b]	−[b]
		T (°C)	12	25	−[a]	−[b]	−[b]	−[b]	−[b]
1.5	log σ	− 60°C	− 2.20	− 1.40	− 0.60	0.17	0.98	1.81	2.74
		37°C	−[a]	2.87	3.17	3.22	3.42	4.14	4.73
		90°C	5.51	5.66	5.69	5.72	5.73	5.75	5.88
	tan δ	max.	3.1	3.5	−[a]	−[b]	−[b]	−[b]	−[b]
		T (°C)	− 4	10	−[a]	−[b]	−[b]	−[b]	−[b]
2.0	log σ	− 60°C	− 1.79	− 1.00	− 0.20	0.57	1.18	2.02	2.99
		37°C	4.61	4.64	4.67	4.69	4.74	4.92	5.21
		90°C	6.18	6.27	6.29	6.31	6.31	6.32	6.34
	tan δ	max.	−[a]	90.7	123.9	268.9	−[b]	−[b]	−[b]
		T (°C)	−[a]	20	54	83	−[b]	−[b]	−[b]
3.0	log σ	− 60°C	− 1.36	− 0.62	0.18	0.98	1.76	2.49	3.30
		37°C	5.16	5.19	5.21	5.23	5.24	5.27	5.42
		90°C	6.29	6.40	6.42	6.43	6.44	6.45	6.45
	tan δ	max.	−[a]	195.1	221.6	338.0	−[b]	−[b]	−[b]
		T (°C)	−[a]	3	25	60	−[b]	−[b]	−[b]
3.6	log σ	− 60°C	− 1.19	− 0.48	0.31	1.13	1.92	2.48	3.37
		37°C	5.34	5.36	5.38	5.39	5.40	5.42	5.52
		90°C	6.28	6.49	6.51	6.52	6.53	6.53	6.54
	tan δ	max.	−[a]	278.4	321.5	402.6	−[b]	−[b]	−[b]
		T (°C)	−[a]	− 3	20	56	−[b]	−[b]	−[b]

[a] Testing error
[b] Values were outside the test range

membrane. Since the TDDA-H$^+$ complex is an ionic molecule, the capability to increase ionic transmission, or σ, was the key parameter to validate biosensors.

Statistics

Linear regressions of log σ versus log phr ratio plots were made at eight temperatures (− 90, − 60, − 30, 0, 23, 37, 60, and 90°C) and seven frequencies (10^{-1}, 10^0, 10^1, 10^2, 10^3, 10^4, and 10^5 Hz). The probabilities were determined from the correlation coefficients, using the plasticizers individually and in homologous groups. The data would be grouped in the nomograms according to whether the individual plasticizers or the homologous groups were significant and different from one another.

RESULTS

General trends

Throughout the range of temperatures the σ increased as the frequency increased, where the amount of increase was dependent on the temperature and plasticization (*Table 2–7*). (The data for CFB6, DBS, and DOS can be found in

tables 3–5 of ref.[5] and are not repeated here.) Note that the 0.1 Hz data were inconsistent and not considered representative of the general trends. At all frequencies the σ increased as the temperature increased, as can be observed from the three temperatures selected: − 60, 37, and 90°C. The temperature of the tan δ peak was representative of the T_g of the membrane, and the magnitude of this peak indicated the number of active dipoles within the membrane. Both the T_g and the number of active dipoles increased as the test frequency increased (*cf. Tables 2–7*). These results were consistent with those previously measured for CFB6, DBS, and DOS[5].

Dependence on frequency

Three regions of activity were distinguishable in the log σ versus temperature plots (*Figures 3 and 4*). The CFA4-, CFA6-, CFB6-, DBS-, DOS-, DOZ-, and DOA-plasticized membranes behaved similarly, as represented by CFA4 in *Figure 3*. The DMS- and DES-plasticized membranes had different characteristics, as represented by DMS in *Figure 4*. The boundaries of these regions were somewhat arbitrary, since the transition between regions occurred over a range

Table 4 Measured values of log σ (pmho/cm) and tan δ peak for five plasticizer levels of PVC membranes plasticized with dimethyl sebacate (DMS); all temperatures are within ± 2°C

phr Ratio	Dielectric measurement		log f (Hz)						
			− 1	0	1	2	3	4	5
0.6	log σ	− 60°C	− 3.76	− 2.41	− 1.58	− 0.53	0.52	1.48	2.88
		37°C	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]
		90°C	0.89	3.71	3.75	3.66	3.69	3.9	4.49
	tan δ	max.	8.8	15.9	30.8	—[b]	—[b]	—[b]	—[b]
		T (°C)	31	52	88	—[b]	—[b]	—[b]	—[b]
1.0	log σ	− 60°C	− 2.77	− 1.88	− 0.99	− 0.04	0.92	1.86	3.06
		37°C	0.63	1.99	2.19	2.63	3.23	3.72	4.36
		90°C	4.90	5.02	5.06	5.09	5.11	5.16	5.45
	tan δ	max.	1.6	1.7	—[a]	—[b]	—[b]	—[b]	—[b]
		T (°C)	19	37	—[a]	—[b]	—[b]	—[b]	—[b]
3.1	log σ	− 60°C	− 1.27	− 0.64	0.11	0.95	1.84	2.75	3.68
		37°C	5.42	5.50	5.58	5.61	5.63	5.65	5.81
		90°C	6.64	6.82	6.82	6.84	6.85	6.85	6.85
	tan δ	max.	3.0	2.4	2.1	2.6	—[b]	—[b]	—[b]
		T (°C)	− 17	− 12	− 6	3	—[b]	—[b]	—[b]
5.0	log σ	− 60°C	− 2.52	− 1.60	− 0.74	0.17	1.10	2.01	2.95
		37°C	6.15	6.29	6.34	6.36	6.37	6.38	6.40
		90°C	6.74	7.08	7.17	7.20	7.21	7.22	7.21
	tan δ	max.	13.8	15.1	26.7	104.9	265.4	—[b]	—[b]
		T (°C)	18	21	36	37	56	—[b]	—[b]
7.6	log σ	− 60°C	− 2.85	− 1.87	− 0.97	− 0.02	0.96	1.91	2.81
		37°C	6.39	6.57	6.64	6.67	6.49	6.60	6.62
		90°C	6.77	7.19	7.29	7.32	7.33	7.33	7.33
	tan δ	max.	33.3	16.3	23.3	99.0	377.1	—[b]	—[b]
		T (°C)	18	21	41	38	43	—[b]	—[b]

[a] Testing error
[b] Values were outside the test range

of temperatures. Region I occurred at relatively low temperatures and was only marked by a strong dependence of log σ on the frequency. In this region, an order of magnitude increase in the frequency produced an order of magnitude increase in the σ. At all frequencies the log σ was relatively independent of temperature. In Region II, the log σ increased as the temperature increased. Over a given temperature range within Region II, the log σ increased at a greater rate, when low frequencies were compared to high frequencies. The log σ became less dependent on frequency as the temperature increased. The transition into Region III was marked by the frequency independence of the log σ, which was increasingly maintained throughout Region III. The log σ increased gradually as the temperature increased in Region III. These three regions could be distinguished for all types and amounts of plasticizer, although the temperatures at which the regions occurred did differ as discussed in the next section. The tan δ peak occurred at higher temperatures as the frequency increased. Increasing the frequency also generally increased the magnitude of the tan δ peak.

Dependence on phr ratio

Below the melting point (MP) of the plasticizer (*Table 1*), the log σ increased up to phr ratios of 3.0 for both citrate-related and sebacate-related compounds (*cf. Tables 2–7* and tables 3–5 of ref. [5]). Above phr ratios of 3.0, the log σ generally decreased as more plasticizer was added. For DMS (MP 30°C) and DES (MP 2°C) this trend was

exhibited by the − 60°C data in *Tables 4 and 5*. In contrast, above the MP of the plasticizer, the log σ increased as the phr ratio increased throughout the range of plasticization tested.

The tan δ peak generally occurred at lower temperatures as the phr ratio increased (*cf. Tables 2–7* and tables 3–5 of ref. [5]). However, for membranes plasticized with DMS or DES to phr ratios above 3.0, the temperature of the tan δ peak reversed and increased at low frequencies (*cf. Tables 4 and 5*). The magnitudes of the tan δ peaks generally increased as the amount of plasticizer increased (*cf. Tables 2–7* and tables 3–5 of ref. [5]).

The transition from Region I to Region II generally occurred at lower temperatures as the amount of plasticizer was increased (compare upper and lower graphs of *Figure 3*, which are representative of CFA4-, CFA6-, CFB6-, DBS-, DOS-, DOZ-, and DOA-plasticized membranes). In contrast, when phr ratios were increased to 3.0 or more for DMS- and DES-plasticized membranes, the transition from Region I to Region II occurred at higher temperatures (compare upper and lower graphs of *Figure 4*). Like the Region I–II transition, the transition from Region II to Region III generally occurred at lower temperatures as the amount of plasticizer was increased (*cf. Figure 3*). For DMS- and DES-plasticized membranes the Region II–III transitions decreased using low phr ratios but could not be lowered beyond the MP of these plasticizers, when high phr ratios were employed (*cf. Figure 4* and MPs in *Table 1*). Consequently, when DMS and DES were used at high phr
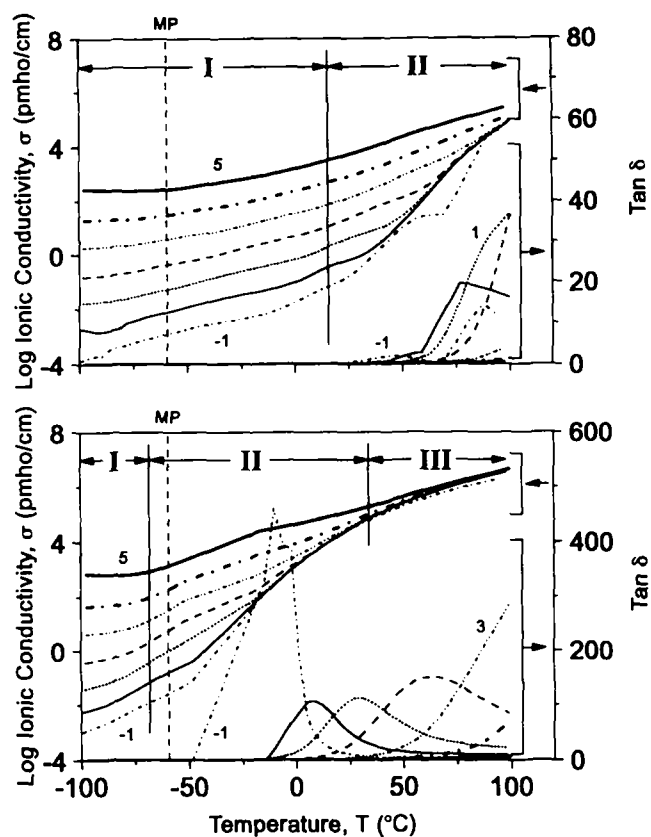
Figure 3 Representative plots showing the effects of frequency (*f*) on the log σ and tan δ *versus* temperature (*T*) for CFA4-plasticized membranes. The upper and lower graphs contrast the dependency of dielectric properties on phr ratio at 0.5 and 3.0, respectively. Both graphs represent seven frequencies: 10^5 Hz (——————), 10^4 Hz (-·-·), 10^3 Hz (- - - - ·), 10^2 Hz (- - -), 10^1 Hz (· · ·), 10^0 Hz (——————), and 10^{-1} Hz (-·-·). Note the three regions that are delineated, the labels of log frequencies, and the location of the melting point (MP) of this plasticizer
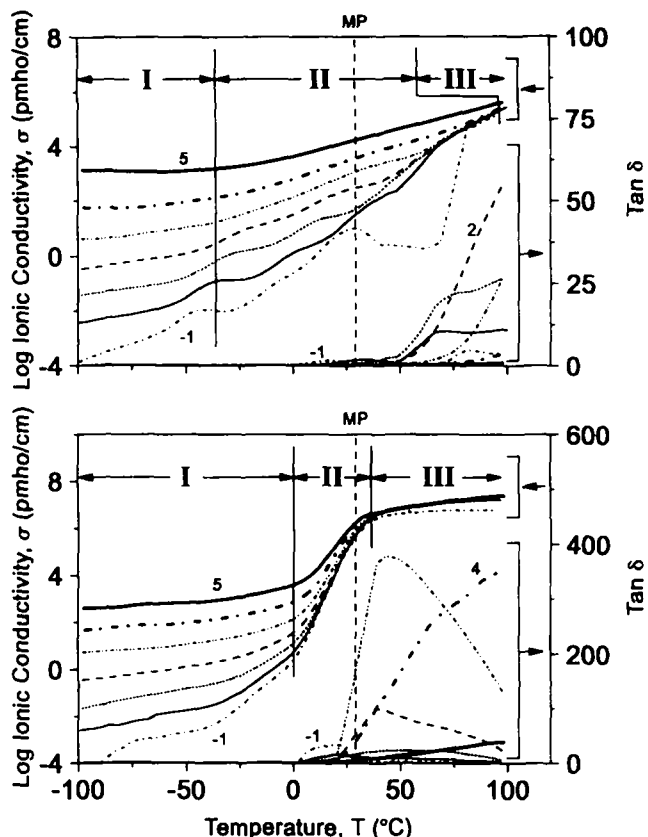
Figure 4 Representative plots showing the effects of frequency (*f*) on the log σ and tan δ *versus* temperature (*T*) for DMS-plasticized membranes. The upper and lower graphs contrast the dependency of dielectric properties on phr ratio at 1.1 and 7.6, respectively. Both graphs represent seven frequencies: 10^5 Hz (——————), 10^4 Hz (-·-·), 10^3 Hz (- - - - ·), 10^2 Hz (- - -), 10^1 Hz (· · ·), 10^0 Hz (——————), and 10^{-1} Hz (-·-·). Note the three regions that are delineated, the labels of log frequencies, and the location of the melting point (MP) of this plasticizer
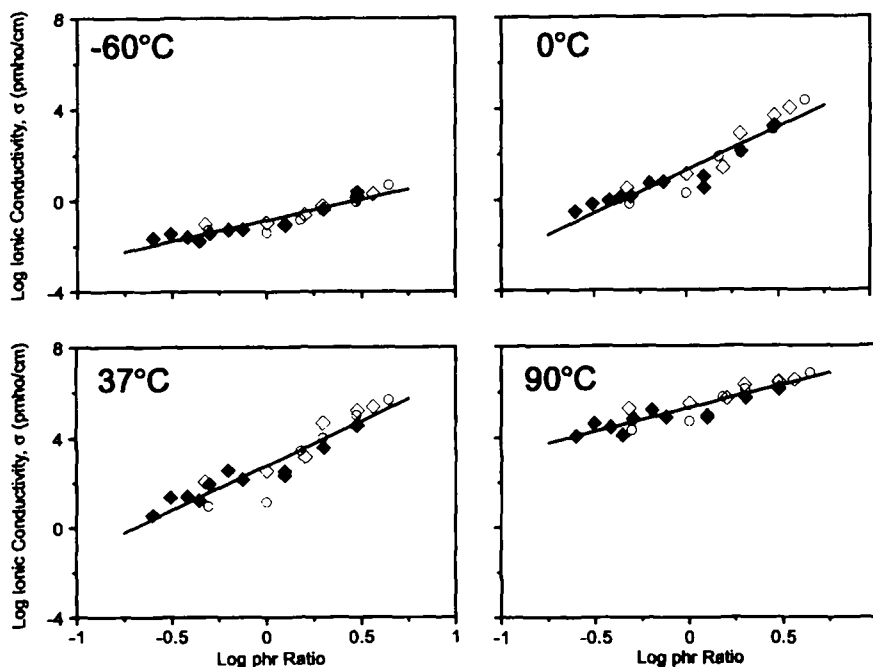

Figure 5 Dependence of the log σ *versus* the log phr ratio at four temperatures and 10 Hz using the three citrate-related plasticizers: CFA4 (O), CFA6 (◇), and CFB6 (♦). Each data point represents one plasticized PVC membrane. All data were included, since the test temperatures were above the MP of the plasticizer

Table 5 Measured values of log σ (pmho/cm) and tan δ peak for five plasticizer levels of PVC membranes plasticized with diethyl sebacate (DES); all temperatures are within ± 2°C

| phr Ratio	Dielectric measurement		log f (Hz)						
			− 1	0	1	2	3	4	5
0.5	log σ	− 60°C	− 3.46	− 2.38	− 1.47	− 0.42	0.60	1.49	2.30
		37°C	0.47	0.73	1.21	1.69	2.21	2.87	3.56
		90°C	1.49	3.28	3.33	3.36	3.41	3.80	4.52
	tan δ	max.	4.3	6.0	9.4	—[b]	—[b]	—[b]	—[b]
		T (°C)	46	61	76	—[b]	—[b]	—[b]	—[b]
1.1	log σ	− 60°C	− 1.86	− 0.96	− 0.15	0.70	1.57	2.47	3.46
		37°C	—[a]	4.32	4.35	4.37	4.40	4.63	5.03
		90°C	6.18	6.12	6.19	6.24	6.25	6.26	6.29
	tan δ	max.	2.8	31.0	49.3	72.4	—[b]	—[b]	—[b]
		T (°C)	− 18	16	35	63	—[b]	—[b]	—[b]
3.1	log σ	− 60°C	− 0.91	− 0.34	0.40	1.27	2.19	3.08	3.98
		37°C	5.87	6.12	6.17	6.18	6.11	6.12	6.17
		90°C	6.98	7.02	7.15	7.19	7.20	7.14	7.14
	tan δ	max.	45.6	42.8	75.6	168.7	293.4	—[b]	—[b]
		T (°C)	− 24	− 19	4	23	69	—[b]	—[b]
5.0	log σ	− 60°C	− 1.97	− 1.11	− 0.19	0.74	1.71	2.64	3.56
		37°C	6.04	6.28	6.33	6.35	6.36	6.37	6.39
		90°C	6.44	7.01	7.13	7.15	7.16	7.16	7.16
	tan δ	max.	7.5	40.2	60.1	168.1	311.3	—[b]	—[b]
		T (°C)	− 9	− 15	− 9	10	66	—[b]	—[b]
6.7	log σ	− 60°C	− 2.13	− 1.23	− 0.31	0.65	1.62	2.55	3.44
		37°C	6.19	6.48	6.54	6.56	6.50	6.50	6.51
		90°C	6.43	7.04	7.20	7.22	7.23	7.23	7.23
	tan δ	max.	4.1	43.3	46.6	247.6	388.2	—[b]	—[b]
		T (°C)	− 5	− 12	− 8	9	49	—[b]	—[b]

[a] Testing error
[b] Values were outside the test range
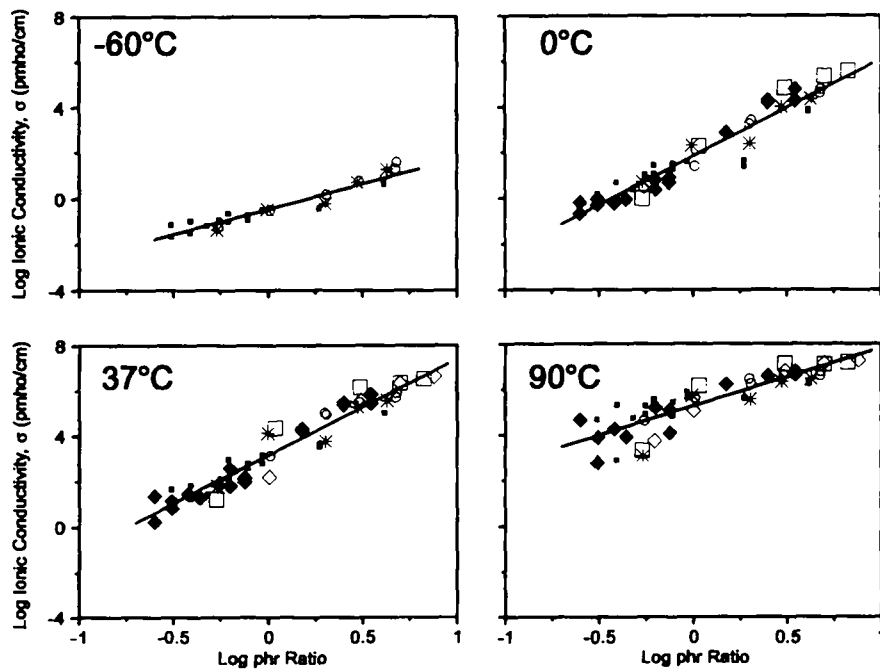
Figure 6 Dependence of the log σ versus the log phr ratio at four temperatures and 10 Hz using the six sebacate-related plasticizers: DMS (◇), DES (□), DBS (◆), DOS (■), DOZ (*), and DOA (○). Each data point represents one plasticized PVC membrane. Some data were excluded, when the test temperatures were below the MP of the plasticizer

Table 6 Measured values of log σ (pmho/cm) and tan δ peak for five plasticizer levels of PVC membranes plasticized with dioctyl azelate (DOZ); all temperatures are within $\pm$ 2°C

phr Ratio	Dielectric measurement		log f (Hz)						
			-1	0	1	2	3	4	5
0.6	log σ	-60°C	-3.06	-2.19	-1.35	-0.53	0.48	1.38	2.43
		37°C	1.56	1.83	1.79	2.10	2.44	3.09	3.85
		90°C	-0.15	1.73	3.08	3.20	3.25	3.59	4.59
	tan δ	max.	3.1	4.6	4.5	$-$[b]	$-$[b]	$-$[b]	$-$[b]
		T (°C)	18	37	52	$-$[b]	$-$[b]	$-$[b]	$-$[b]
1.0	log σ	-60°C	-2.04	-1.24	-0.44	0.38	1.22	2.07	3.01
		37°C	3.98	4.08	4.13	4.16	4.22	4.48	4.83
		90°C	5.60	5.66	5.74	5.77	5.78	5.79	5.84
	tan δ	max.	5.8	11.5	20.1	63.0	$-$[b]	$-$[b]	$-$[b]
		T (°C)	-12	15	37	86	$-$[b]	$-$[b]	$-$[b]
2.0	log σ	-60°C	-1.66	-0.97	-0.21	0.60	1.46	2.24	3.11
		37°C	$-$[a]	3.68	3.76	3.80	3.84	4.03	4.66
		90°C	5.26	5.38	5.57	5.61	5.62	5.53	5.59
	tan δ	max.	3.2	4.0	13.8	39.9	$-$[b]	$-$[b]	$-$[b]
		T (°C)	-28	-14	46	72	$-$[b]	$-$[b]	$-$[b]
3.0	log σ	-60°C	-0.17	0.19	0.72	1.38	2.15	3.01	3.93
		37°C	5.12	5.25	5.28	5.29	5.30	5.34	5.49
		90°C	6.00	6.29	6.35	6.36	6.37	6.37	6.38
	tan δ	max.	44.5	63.6	76.6	162.8	$-$[b]	$-$[b]	$-$[b]
		T (°C)	-20	-12	9	63	$-$[b]	$-$[b]	$-$[b]
4.3	log σ	-60°C	-1.54	-0.76	-0.02	0.83	1.68	2.54	3.52
		37°C	5.40	5.54	5.57	5.58	5.59	5.60	5.68
		90°C	6.12	6.39	6.48	6.49	6.49	6.50	6.50
	tan δ	max.	143.6	142.5	174.9	223.3	$-$[b]	$-$[b]	$-$[b]
		T (°C)	-27	-18	5	40	$-$[b]	$-$[b]	$-$[b]

[a] Testing error
[b] Values were outside the test range

ratios, Region II occupied a more narrow temperature range, as the Region I–II transition shifted to higher temperatures and the Region II–III transition shifted to lower temperatures (*cf.* lower graph of *Figure 4*). As such the rate of increase of log σ *versus* temperature in Region II was much greater for DMS- and DES-plasticized membranes than that which typically occurred using other plasticizers.

DISCUSSION

General observations

Using the plasticizers of this study the membranes generally had properties that were similar to those plasticizers tested previously[5]. The three regions of the log σ *versus* temperature plots (*cf.* *Figures 3 and 4*) were also observed in the previous study (*cf.* figure 2 of ref. [5]). In addition, the characteristics, such as decade changes in the σ with frequency in Region I and frequency independence in Region III, were maintained using the new plasticizers.

At first the DMS and DES appear to be different from all other plasticizers tested. The compression of Region II was not observed as a precipitous decrease in the log σ at low temperatures and high phr ratios using any other plasticizers (*cf.* log σ at -60°C in *Tables 4 and 5*). The higher MPs of these plasticizers *versus* DBS and DOS were accountable for these changes. The DBS and DOS had lower MPs, around -11 and -65°C, respectively, whereas the MPs of

DMS and DES equal 30 and 2°C, respectively (*cf. Table 1*). With the DBS, DOS, DOZ, DOA, and citrate-related plasticizers, the decrease in the log σ at low temperatures and high phr ratios occurred below the T_gs of the membranes (recall that the T_g corresponds to the temperature of the tan δ peak in *Tables 2–7*). Therefore these decreases were unimportant, since σ was not, by definition, a 'real' quantity below the T_g of the membrane. Because the T_gs could be lowered to the MPs of DMS and DES, the limitation of the MPs of these plasticizers became evident.

Importance of the melting point

At phr ratios below 1.0 the addition of plasticizer to the membranes increased the σ for all of the plasticizers. Assuming that the plasticizer was homogeneously distributed within the membrane (as should be the case in these non-turbid membranes), the plasticizer acted as a lubricating tube adjacent to the PVC as described by Kusy *et al.*[13,14]. Since a phr ratio of 1.0 was the minimum necessary for complete isolation of each PVC molecule, all of the plasticizer added below this level contributed to the formation of a monolayer of plasticizer around the PVC molecules. As such all of the membranes have similar dielectric properties, regardless of the plasticizer configuration.

At phr ratios between 1.0 and 3.0 the σ increased as the phr ratio increased for all of the plasticizers, because the

Table 7 Measured values of log σ (pmho/cm) and tan δ peak for five plasticizer levels of PVC membranes plasticized with dioctyl adipate (DOA); all temperatures are within $\pm$ 2°C

phr Ratio	Dielectric measurement		log f (Hz)						
			-1	0	1	2	3	4	5
0.5	log σ	-60°C	-2.88	-2.03	-1.25	-0.35	0.59	1.57	2.72
		37°C	1.71	1.52	1.83	2.25	2.74	3.36	4.09
		90°C	4.64	4.60	4.63	4.65	4.67	4.77	5.25
	tan δ	max.	28.0	—[b]	—[b]	—[b]	—[b]	—[b]	—[b]
		T (°C)	58	—[b]	—[b]	—[b]	—[b]	—[b]	—[b]
1.0	log σ	-60°C	-2.19	-1.35	-0.49	0.25	1.11	1.96	2.94
		37°C	1.13	2.95	3.13	3.21	3.65	4.38	4.90
		90°C	5.38	5.64	5.63	5.66	5.67	5.71	5.97
	tan δ	max.	2.6	2.8	26.3	45.8	—[b]	—[b]	—[b]
		T (°C)	0	17	60	83	—[b]	—[b]	—[b]
2.0	log σ	-60°C	—[a]; -1.23	—[a]; -0.57	—[a]; 0.19	—[a]; 1.00	—[a]; 1.83	—[a]; 2.65	—[a]; 3.53
		37°C	4.74; 4.80	—[a]; 5.00	5.01; 4.95	—[a]; 4.98	5.06; 5.00	—[a]; 5.08	5.43; 5.33
		90°C	6.23; 5.95	—[a]; 6.12	6.47; 6.27	—[a]; 6.29	6.49; 6.30	—[a]; 6.31	6.51; 6.32
	tan δ	max.	11.0; 5.4	—[a]; 10.9	19.8; 16.6	—[a]; 100.9	—[b]	—[b]	—[b]
		T (°C)	-7; -32	—[a]; -2	18; 16.8	—[a]; 65	—[b]	—[b]	—[b]
3.0	log σ	-60°C	-0.15	0.23	0.76	1.42	2.19	3.04	3.95
		37°C	5.26	5.43	5.48	5.39	5.40	5.44	5.62
		90°C	6.41	6.60	6.63	6.65	6.61	6.61	6.62
	tan δ	max.	35.8	56.7	41.1	103.9	—[b]	—[b]	—[b]
		T (°C)	-19	-18	21	44	—[b]	—[b]	—[b]
4.8	log σ	-60°C	0.73; 1.20	0.94; 1.32	1.30; 1.59	1.79; 1.85	2.44; 2.51	3.25; 3.33	4.21; 4.25
		37°C	5.66; 5.72	5.66; 5.87	5.69; 5.90	5.70; 5.91	5.71; 5.84	5.72; 5.85	5.79; 5.91
		90°C	6.51; 6.60	6.63; 6.71	6.62; 6.81	6.64; 6.82	6.64; 6.83	6.64; 6.83	6.64; 6.79
	tan δ	max.	79.8; 247.5	118.4; 121.5	195.0; 137.7	236.4; 199.6	—[b]; 470.0	—[b]	—[b]
		T (°C)	-29; -35	-21; -25	-1; -4	31; 46	—[b]; 83	—[b]	—[b]

[a] Testing error
[b] Values were outside the test range

plasticizer still did not control the bulk membrane properties. While the plasticizer added above a phr ratio of 1.0 did not contribute to the formation of monolayers around the PVCs, this additional quantity of plasticizer was also not sufficient to control the bulk membrane properties. In this range of phr ratios, some occluded regions of plasticizer formed in the membrane, but these regions were not numerous enough or large enough to make substantial contributions to the dielectric properties of the membrane, regardless of the plasticizer configuration.

Above phr ratios of 3.0 the plasticizer's MP was critical. At these phr ratios enough plasticizer was occluded so that it dominated the properties of the membrane. Below the MP of the plasticizer, these occluded regions froze within the membrane, which dramatically changed the dielectric properties of the plasticizer. Using DMS and DES at high phr ratios and below their MPs, the σ decreased as the phr ratio of the membrane increased (cf. - 60°C data of *Tables 4 and 5*). In addition, the σ was limited to this inferior value until the plasticizer began to melt (cf. *Figure 4*, lower graph). This limitation of σ at low temperatures using DMS and DES increased the onset temperature of Region II of the log σ versus temperature plot (cf. *Figure 4*, lower graph). As the plasticizer melted, the log σ quickly returned to its 'normal' ranking, based on the phr ratio of the membrane. Since these values were the Region III values for these two plasticizers, Region II of the DMS plot became substantially compressed. The glass transition of the membrane also could not be recognized until the plasticizer melted, due to

the dominance of the dielectric properties by the occluded regions of plasticizer.

Linearity of the log σ versus log phr ratio

The present work was designed to evaluate the plasticizers individually, thereby determining the effect of configurational changes on the dielectric properties. When no data of a membrane was considered below the MP of the plasticizer used, a linear relationship was statistically significant between the log σ and the log phr ratio for citrate- and sebacate-related plasticizers (*Figures 5 and 6* at 10 Hz and four temperatures and *Tables 8-9* at seven frequencies and seven temperatures). The linear relationship between log σ and log phr ratio could not exist below the MP of the plasticizer because the dielectric properties were altered as discussed above. With regard to the dielectric properties, the individual plasticizers were not distinguishable. Using linear fits, the plots of log σ versus log phr ratio were significant at $p < 0.001$ over the entire range of temperatures and frequencies (*Tables 8 and 9*). The slopes of these lines peaked in the range 0 to 60°C, where the peaks generally occurred at higher temperatures for higher frequency trials (*Figures 7 and 8*, upper graphs). As the temperature increased, the so-called 'intercepts' of the lines (i.e. the magnitudes of σ when all polar groups on the PVC backbone were shielded from each other by a monolayer of plasticizer at phr ratio 1 or equivalently at log phr ratio 0) increased and became less frequency dependent (*Figures 7 and 8*, lower graphs). Similar

Table 8 Regression data for selected log σ (pmho/cm) *versus* log phr ratio plots (citrate-related plasticizers); the probability p was $p < 0.001$ for all values, except where noted

Regression quantity	Temperature (°C)	$\log f$ (Hz)						
		− 1	0	1	2	3	4	5
Slope (pmho/cm)	− 60	1.94	1.85	1.82	1.05	1.32	1.06	0.69
	− 30	3.81	2.99	2.47	2.09	1.82	1.69	1.33
	0	5.27	4.55	3.76	2.99	2.31	1.85	1.60
	23	4.62	4.58	4.00	3.36	2.61	1.98	1.52
	37	4.69	4.32	3.96	3.38	2.70	2.06	1.59
	60	3.96	3.37	3.33	3.15	2.62	2.00	1.42
	90	2.10	1.97	2.03	2.02	2.00	1.73	1.32
Intercept (pmho/cm)	− 60	− 2.42	− 1.68	− 0.84	− 0.16	0.90	1.75	2.77
	− 30	− 1.06	− 0.51	0.10	0.80	1.58	2.39	3.22
	0	0.47	0.86	1.28	1.77	2.36	3.03	3.80
	23	1.37	1.88	2.18	2.54	2.99	3.55	4.21
	37	2.31	2.57	2.76	3.01	3.38	3.88	4.49
	60	3.46	3.75	3.91	3.98	4.17	4.50	4.97
	90	5.04	5.25	5.28	5.29	5.31	5.40	5.62
Correlation coefficient r	− 60	0.938	0.938	0.934	0.611[a]	0.889	0.838	0.720
	− 30	0.920	0.918	0.933	0.946	0.951	0.950	0.833
	0	0.956	0.950	0.943	0.942	0.952	0.959	0.960
	23	0.857	0.941	0.939	0.928	0.922	0.935	0.946
	37	0.882	0.928	0.936	0.921	0.904	0.911	0.914
	60	0.849	0.831	0.913	0.912	0.890	0.861	0.881
	90	0.826	0.912	0.918	0.919	0.922	0.898	0.881
Number of samples n	− 60	23	24	24	24	24	24	24
	− 30	22	22	22	22	22	22	22
	0	24	24	24	24	24	24	24
	23	24	24	24	24	24	24	24
	37	20	24	24	24	24	24	24
	60	22	24	24	24	24	24	24
	90	23	24	24	24	24	24	24

[a] $p < 0.01$

trends were observed in the previous work (figures 4–6 of ref. [5]).

Development of nomograms to predict ionic conductivity (σ)

Nomograms are graphical representations of mathematical equations[15]. Using linear correlations of log σ *versus* log phr ratio, the slope and intercept values at discrete temperatures and frequencies (*Tables 8 and 9*) could be used to determine a series of relation points. The relation points of a nomogram were those points through which straight lines could relate the phr ratio to the log σ of a membrane. By placing each of these relation points on a single nomogram, a grid was formed by connecting the relation points along temperature and frequency isograms (*cf. Figures 9 and 10*). For those temperatures and frequencies not discretely determined, interpolation could be used to estimate values. Since the log σ was not influenced by configurational changes in the plasticizer, one nomogram described citrate-related compounds (*Figure 9*), and one nomogram described sebacate-related compounds (*Figure 10*). The nomogram could predict the value of σ for a given phr ratio, temperature, and frequency, or the phr ratio necessary to obtain a σ at a given temperature and frequency. For example, consider a 10 Hz signal measured

at body temperature (37°C), where a log σ of 3 pmho/cm was necessary to accurately measure the signal. For a citrate-related plasticizer, the membrane needed a log phr ratio of 0.07 (i.e. a phr ratio of 1.17) to measure the proper response (*cf. Figure 9*).

The nomogram can only be employed when certain conditions apply. The σ did not exist below the T_g for any membrane (or any polymer), although in principle σ could be calculated at any temperature. Inasmuch, the points were not real at some combinations of temperature, frequency, plasticizer, and phr ratio within the range of plasticization shown. Recall also that the membranes were not considered below the MP of the plasticizer, so that no DMS- or DES-plasticized membrane should be used below 30 and 2°C, respectively.

Implications for electrodes and biosensors

Because the log σ was not influenced by configurational changes in the plasticizer, except its melting point, other properties of the plasticizer must identify the best choice of plasticizer for a particular application. The biocompatibility of the plasticizer is an important consideration for *in vivo* uses of biosensors. The citrate-related plasticizers are approved for use in medical applications and hence are

Table 9 Regression data for selected log σ (pmho/cm) versus log phr ratio plots (sebacate-related plasticizers): the probability p was $p < 0.001$ for all values

| Regression quantity	Temperature (°C)	$\log f$ (Hz)						
		-1	0	1	2	3	4	5
Slope (pmho/cm)	-60	3.17	2.64	2.20	1.89	1.62	1.56	1.46
	-30	4.63	3.96	3.32	2.59	1.95	1.68	1.48
	0	5.48	4.89	4.24	3.58	2.93	2.28	1.81
	23	5.06	4.78	4.37	3.81	3.18	2.52	1.91
	37	4.65	4.38	4.24	3.80	3.20	2.48	2.00
	60	3.96	3.68	3.62	3.49	3.16	2.56	1.92
	90	3.36	2.70	2.55	2.52	2.53	2.26	1.78
Intercept (pmho/cm)	-60	-1.89	-1.17	-0.45	0.32	1.18	2.05	3.02
	-30	-0.33	0.09	0.61	1.20	1.85	2.61	3.42
	0	1.00	1.44	1.83	2.19	2.69	3.27	3.93
	23	1.88	2.36	2.64	2.94	3.31	3.78	4.35
	37	2.40	2.97	3.16	3.38	3.69	4.16	4.62
	60	3.65	4.01	4.13	4.20	4.37	4.67	5.10
	90	4.53	5.11	5.27	5.30	5.32	5.44	5.69
Correlation coefficient r	-60	0.938	0.948	0.951	0.950	0.958	0.956	0.946
	-30	0.965	0.953	0.958	0.961	0.928	0.952	0.949
	0	0.952	0.963	0.960	0.946	0.949	0.946	0.942
	23	0.910	0.953	0.959	0.954	0.940	0.936	0.928
	37	0.889	0.960	0.964	0.963	0.951	0.918	0.936
	60	0.900	0.935	0.940	0.941	0.940	0.936	0.925
	90	0.693	0.819	0.864	0.864	0.868	0.877	0.887
Number of samples n	-60	28	28	28	28	28	28	28
	-30	29	28	29	28	29	28	29
	0	49	47	49	48	49	48	49
	23	47	48	49	48	49	48	49
	37	48	53	54	53	54	53	54
	60	46	54	55	54	55	54	55
	90	52	52	53	52	53	53	54
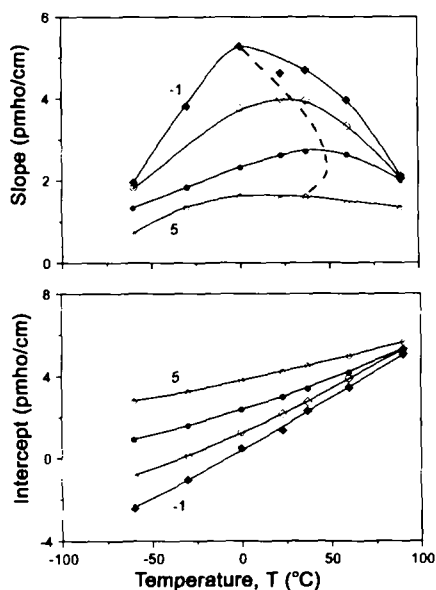
Figure 7 Dependence of the slopes and intercepts versus temperature (T) for the log σ versus log phr ratio plots of *Figure 5* (citrate-related plasticizers), *Tables 2, 3, and 8,* and tables 3 and 10 of ref. [5] at four frequencies (f): 10^5 Hz (O), 10^3 Hz (●), 10^1 Hz (◇), and 10^{-1} Hz (♦). The dashed line represents the positions of the peak slopes, and the numbers represent log frequencies
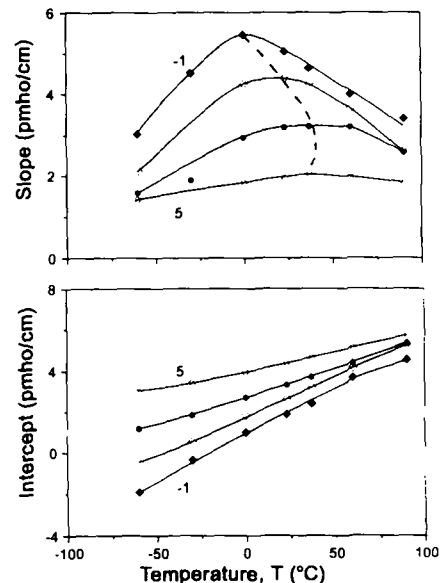
Figure 8 Dependence of the slopes and intercepts versus temperature (T) for the log σ versus log phr ratio plots of *Figure 6* (sebacate-related plasticizers), *Tables 4–7, and 9,* and tables 4, 5 and 10 of ref. [5] at four frequencies (f): 10^5 Hz (O), 10^3 Hz (●), 10^1 Hz (◇), and 10^{-1} Hz (♦). The dashed line represents the positions of the peak slopes, and the numbers represent log frequencies
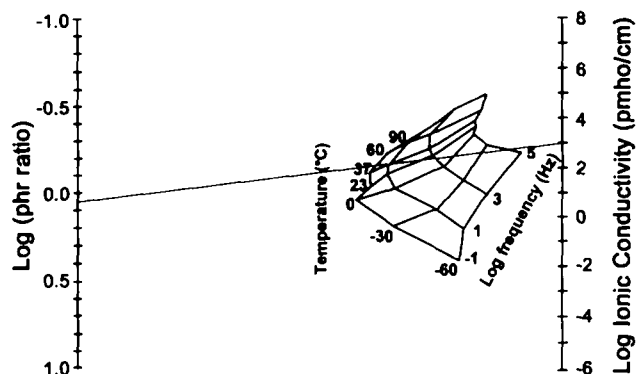
Figure 9 Nomogram to determine the ionic conductivity (σ) of membranes plasticized with citrate-related compounds, when phr ratio, temperature, and frequency are known
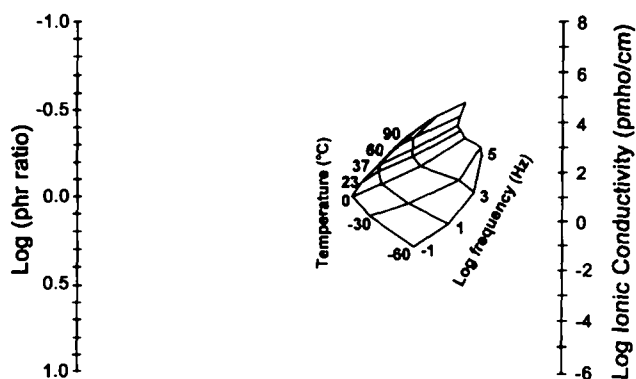

Figure 10 Nomogram to determine the ionic conductivity (σ) of membranes plasticized with sebacate-related compounds, when phr ratio, temperature, and frequency are known

superior to the sebacate-related compounds. Another important consideration in choosing a plasticizer is its leaching characteristics, since any plasticizer that leaches from a membrane forms a highly resistive surface layer[4] and causes the electrode to fail. Branched molecules that have high hydrodynamic volumes are more favourable than linear molecules that have lower hydrodynamic volumes. Also, longer chain compounds are superior to shorter chain molecules. Based on these premises, the citrate-related plasticizers would be selected in this order: CFB6, CFA6, and CFA4. With regard to sebacate-related plasticizers, any of the branched configurations (DOS, DOZ, and DOA) would be generally favoured over the aliphatic configurations (DMS, DES, and DBS). When inner chain length is considered with the branched criterion, the DOS, DOZ, and DOA would be selected in that order. Similarly, when the length of the outer branches is considered for the aliphatic plasticizers, the DBS, DES, and DMS would be selected in that order. Finally, if the mechanical properties of the membranes depend on configurational changes in the plasticizers, these properties must be factored into the selection process. The mechanical properties of strength, stiffness, toughness, and ductility will be considered in a subsequent publication.

CONCLUSIONS

(1) Above the MP of a given plasticizer, the σ of a membrane increases as the amount of plasticizer increases.

(2) No membrane should be used below the MP of its plasticizer.

(3) Increasing the amount of plasticizer in the membrane improved the σ and lowered the temperature of the tan δ peak.

(4) The log σ can be linearly correlated to the log phr ratio for each of the membrane groups evaluated: citrate-related and sebacate-related plasticizers.

(5) Nomograms can be used to predict the value of σ for a given phr ratio, temperature, and frequency. These nomograms can also be used to establish the necessary phr ratio for an application at a specified σ, temperature, and frequency.

(6) The configurational changes of homologous plasticizers cannot be distinguished according to the dielectric properties. As such the biocompatibility, leaching, and mechanical characteristics of the plasticizers must determine the criteria for plasticizer selection.

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