A Calorimetric Study on the Interaction of Phenol Derivatives with Phospholipid Liposomes as a Model for Biological Membranes

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Received on December 23, 1985

The interaction of eighteen phenol derivatives such as cresols, eugenols, phenols etc. with dipalmitoyl phosphatidylcholine (DPPC) liposomes was investigated by the application of differential scanning calorimetry (DSC), to clarify their activity in the biological system at the membrane level. Exogenous phenol partition into DPPC liposomes caused changes in the phase transition properties of the liposomes which were characterized by both a shift of the phase transition temperature (T) to a lower temperature and a decrease in the enthalpy (\(\Delta H\)). T and \(\Delta H\) were dependent on either the concentration or the hydrophobicity (\(\pi\)). When the concentrations or \(\pi\) increased, the T decreased linearly. A parabolic curve in the alkylphenols was exhibited.

The maximum change in the T and \(\Delta H\) was obtained when \(\pi\) was approx. 1. Of the alkylphenols having a \(\pi\) of approx. 1 ethylphenols showed the largest changes in the T and \(\Delta H\), and eugenols showed smaller changes. Changes in the T and \(\Delta H\) were governed by the interaction between phenol derivatives and acyl chains of liposomes.

Key words: Phenol derivatives, Phospholipid liposomes, Phase transition properties

INTRODUCTION

Phenol derivatives are used in dentistry for a variety of purposes; phenols, guaiacols, p-chlorophenols, cresols, thymols, cresatins, etc. as root canal disinfectants. Very small amounts of hydroquinones are used as polymerization inhibitors in resin systems. The eugenols which are combined with zinc oxide, in clinical use, are widely used for cement bases, indirect cappings, temporary fillings and root canal sealers. While phenol derivatives are disinfectants, they may also produce pulpal or periodontal inflammation. However, the biological behavior of phenol derivatives has not been fully studied at the membrane level.

Liposomes have been employed in model systems at the membrane level, to study the interaction of lipid soluble drugs and monomers which are used in dentistry, with biological membranes. Liposomes consist of lipid bilayers and they closely resemble the structure of biological membranes due to the lipid bilayers.

Depending on the hydrophobicity, an exogenous compound will reside predominantly in liposomes or in the aqueous core of liposomes. Drug partitioning into the lipid bilayers of liposomes causes changes in the endothermic phase transition temperature (T) and the enthalpy (\(\Delta H\)) of synthetic phospholipid liposomes. The lowering of T and a decrease in \(\Delta H\) and H/HHW (height/half-height width) of cooperativity in an endothermic peak have been highly related to the biological activities. Differential scanning calorimetry (DSC) has been used as a powerful, yet relatively rapid and inexpensive thermodynamic technique for...
In the present study, we investigated the changes in the T, $\Delta$H and H/HHW of DPPC liposomes induced by phenols using DSC. The correlation between the biological activity and the phase transition properties has been discussed.

**MATERIALS AND METHODS**

The test compound used were phenol, resorcin, guaiacol, hydroquinone monomethyl ether, eugenol, isoeugenol, o-, m- and p-cresol, p-ethylphenol, p-hexylphenol, thymol, m- and p-chlorophenol, 2, 4-dichlorophenol, m-nitrophenol, 2, 4-dinitrophenol, picric acid, o-ethoxybenzoic acid and m-cresylacetate. L-$\alpha$-dipalmitoyl phosphatidyl choline (DPPC Sigma Co.) was used as the lipid in the preparation of liposomes.

The liposomes + additive samples for DSC were prepared by one of the following methods.

(i) If the additive was soluble in a 70mM sodium phosphate buffer solution, then its saturated solution was diluted and mixed with liposome dispersion.

(ii) If the additive was insoluble in buffer solution (0.5% $>\Delta$), then a known amount of the additive was sonicated in buffer solution and the dispersion was mixed with liposomes directly.

Liposome preparation: An appropriate amount of DPPC mixed in chloroform solution was subjected to vacuum and formed a dry film in a glass tube under a nitrogen atmosphere at room temperature and then was dispersed in a 70 m M sodium phosphate buffer at pH 6.8 with a Vortex shaker at 45°C for about 2-3 min. DPPC liposomes were sonicated further under a nitrogen atmosphere at 45°C for 30 min using a bath-type sonicator (200 w, 45 kHz).

Calorimetric Studies: All samples for DSC were 70 mM DPPC, 70 mM sodium phosphate and the appropriate concentration of lipid-soluble compounds. Each 10 $\mu$l sample of both DPPC liposomes and a test compound was put in a DSC container which was then sealed. The sample was then allowed to equilibrate for 20 or 48 hrs at 25°C and finally shaken again for one minute by hand at 25°C. The sample (20 $\mu$l) was scanned in a sealed calorimetric container on a DSC-Rigaku calorimeter operating at a heating rate of 5°C/min with a range setting of 0.5 kcal/sec.

While interpreting the phase transition data, we derived the following parameters from each of the thermotropic profiles: T (°C), H (height)/HHW (half-height width) and $\Delta$H (Kcal/mol). Phase transition temperature (T) did not represent the beginning of the transition (Ts) for each peak but a temperature on the cross point between an access line of the DSC peak (running from Ts to a temperature (Tc) at which the specific heat reaches a maximum) and the baseline. The transition enthalpy ($\Delta$H) was calculated by weighing the area under the curve. The reproducibility in this experiment (2 to 3 samples) was as follows: T, ±0.5°C and $\Delta$H, ±0.2 Kcal/Mol. Since the change in free energy ($\Delta$G) is zero at the T, the entropy change ($\Delta$S) associated with the transition can be calculated from the equation $\Delta$S = $\Delta$H/T where $\Delta$S is normally expressed in cal/K•Mol.
RESULTS

Changes in the T, ΔH and H/HHW of the DPPC liposomes induced by phenols are shown in Table 1. The DSC curves between 20–50°C for DPPC liposomes induced by exogenous phenols were characterized in two groups as shown in Fig. 1. The type was dependent on the concentration.

At 20–40 mM, cresols, chlorophenols and ethylphenols were type A 1 whereas eugenols were type A 2.

In the series of the methoxy group OCH₃ (guaiacol, hydroquinone monomethyl ether and eugenol) at 20 mM, eugenol had the largest decrease in ΔH, 2.5 Kcal/Mol and H/HHW, 5 at

Table 1 Changes in phase transition temperature(T) and enthalpy(ΔH) and transition profile value(H/HHW) of dipalmitoyl phosphatidylcholine(DPPC) liposomes induced by phenols

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Compound</th>
<th>Conc.# mM</th>
<th>T °C</th>
<th>ΔH Kcal/Mol</th>
<th>(H/HHW)§</th>
<th>pKa##</th>
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<tr>
<td>H</td>
<td>Control§</td>
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<td>100</td>
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<tr>
<td></td>
<td>Phenol</td>
<td>40</td>
<td>40*</td>
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<td>74</td>
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<tr>
<td></td>
<td></td>
<td>20</td>
<td>40*</td>
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<td>92</td>
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<td></td>
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<td>2.5</td>
<td>41*</td>
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<td>100</td>
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<tr>
<td>3-OH</td>
<td>Resorcin</td>
<td>500</td>
<td>39</td>
<td>5.9</td>
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<td>2.5</td>
<td>41*</td>
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<tr>
<td>2-OCH₃</td>
<td>Guaiacol</td>
<td>20</td>
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<td>8.1</td>
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<td>Hydroquinone monomethyl ether</td>
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<td>32</td>
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<td>Eugenol</td>
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<td>4-CH=CH CH₃</td>
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<td>6.1</td>
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<td>28</td>
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<td>3-CH₃, 6-CH(CH₃)₂</td>
<td>Thymol</td>
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<td>p-Chlorophenol</td>
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<td>30</td>
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<td>3-NO₂</td>
<td>m-Nitrophenol</td>
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<td>32</td>
<td>7.9</td>
<td>76</td>
<td>0.34</td>
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<tr>
<td>2,4-Di-NO₂</td>
<td>2,4-Dinitrophenol</td>
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<td>41.5</td>
<td>6.8</td>
<td>100</td>
<td>0.04</td>
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<tr>
<td>2,4,6-Tri-NO₂</td>
<td>Picric acid</td>
<td>40</td>
<td>35</td>
<td>5.4</td>
<td>24</td>
<td>-0.11</td>
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</tbody>
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# sodium phosphate buffer solution at pH 6.8 for 20 hrs at 25°C
§ transition profile value of main peak [Height (H)/Half-Height Width (HHW)]
## from reference (Hansch and Fujita, 1964)
§§ DPPC liposomes without phenol (70mM)
* pretransition, ΔH 0.6–1.8 Kcal/Mol at 33.5°C
† 1 hr
Fig. 1 Typical DSC transition profiles for DPPC liposomes doped with phenols. Two types of profiles (A1 and A2) have been observed for compounds shown in Tables 1 and 2. 1. DPPC liposomes without the addition of additives (Control: pretransition peak, $\Delta H \approx 1.8$ Kcal/Mol at 33.5°C; main transition peak, $\Delta H \approx 8.6$ Kcal/Mol at 41.5°C; Height/Half-Height Width = H/HHW = 100). 2. Pretransition was abolished by phenols, and the main transition temperature ($T$) shifted to a lower temperature (38°C). 3. Type A1: The $T$ further shifted to a lower temperature (27-30°C) with a decrease in $\Delta H$ and H/HHW. 4. Type A2: An broadening of the main peak at approx. 35°C was accompanied by a decrease in $\Delta H$ and H/HHW.

$35^\circ$C. Hydroquinone had a larger effect on the $T$, $\Delta H$ and H/HHW than guaiacol (Table 1). The effect of alkyl phenols on the $T$ at 2.5 mM was as follows: Phenol (41) > p-Hexylphenol (40.5) > p-Butylphenol (40) > Thymol (39) > p-Cresol (37) > p-Ethylphenol (35). The $\Delta H$ and H/HHW were 6–8 Kcal/Mol and 13–40, respectively, except for phenol.

Parachlorophenol markedly lowered the $T$ (approx. 30°C) at 40 mM without a large decrease in $\Delta H$ 7 Kcal/Mol and H/HHW 80. This was similar to the effect of the cresols. In the series of phenol derivatives having a pKa of 0.38–9.98 (phenol, chlorophenol, mono-, di-, and tri-nitrophenol), dinitrophenol had the smallest change in $T$, $\Delta H$ and H/HHW, which were similar to the control values. Phase transition properties of these compounds were not dependent on pKa.

Figure 2 shows the plots of $T$ vs. logarithm of the concentration of phenol, p-cresol and p-ethylphenol. As the concentration increased, T shifted to a lower temperature. Phenol had
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Fig. 2 Plots of T vs. concentration.
PH phenol; CR p-cresol; EP p-ethylphenol; C control.

Table 2 Changes in phase transition temperature (T) and enthalpy (ΔH) and transition profile value (H/HHW) of dipalmitoyl phosphatidylcholine (DPPC) liposomes induced by phenols

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conc./# mM</th>
<th>Phase transition property</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>T</td>
</tr>
<tr>
<td>Control</td>
<td></td>
<td>41.5*</td>
</tr>
<tr>
<td>Phenol</td>
<td>40</td>
<td>34</td>
</tr>
<tr>
<td>Resorcin</td>
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<td>37</td>
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<tr>
<td>Guaiacol</td>
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<td>34</td>
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<tr>
<td>Hydroquinone monomethyl ether</td>
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<td>31.5</td>
</tr>
<tr>
<td>p-Cresol</td>
<td>40</td>
<td>30.5</td>
</tr>
<tr>
<td>p-Chlorophenol</td>
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<tr>
<td>2,4-Dichlorophenol</td>
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<td>33</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>32</td>
</tr>
</tbody>
</table>

# 48 hrs at 25°C; * pretransition, ΔH 1.8 Kcal/Mol at 33.5°C

a small change whereas p-cresol and p-ethylphenol decreased linearly. Thus T is dependent on the concentration.

Transition properties of the DPPC liposomes caused by the phenols after 48 hrs are shown in Table 2. The samples were allowed to equilibrate for 48 hrs, because the highly
hydrophobic phenols (40 mM) do not saturated in the aqueous solution. The T of phenol (20 hrs) decreased after 48 hrs without a large decrease in ΔH and H/HHW at 40 mM, whereas p-cresol had a large decrease in ΔH and H/HHW without a decrease in the T at both 5 and 40 mM (Tables 1 and 2).

DISCUSSION

Partition coefficient data are commonly used to determine the substituent or hydrophobic bonding constant, π, of the functional group. Hansch and Fujita\textsuperscript{17} and Tute\textsuperscript{18} showed that the partition coefficient (log P) of various drugs between 1-octanol and water could be correlated with biological activity. π shown in Table 1 is defined as: π = log (Pₐ / Pₜₚ) where Pₐ is the log P value of phenol and Pₚ is the value for a derivative. The effect of π on the phase transition properties (T, ΔH, H/HHW and ΔS) has provided some interesting findings, for the interpretation of the biological activity caused by phenols. Figure 3 showed the plots of T vs. π. The T of resorcin, phenol and p-cresol (40 mM, 48 hrs) in the hydrophobic range (−0.70 ≤ π < 0.5) is linear (Fig. 3, I), but that of hydroquinone monomethyl ether appears to fall off because it is easily oxidized. Linearity (Fig. 3, II) is obtained with various series of phenols (40 mM, 20 hrs, 0 ≤ π < 1). As π increases, T decreases, but with picric acid it may fall off due to its strong acidity (pKa 0.38). A parabolic curve seems to be obtained in the series of resorcin, phenol, and p-alkylphenol having a wide hydrophobic range (−0.70 ≤ π ≤ 2.64) at 2.5 mM for 20 hrs (Fig. 3, III).

Fig. 3 Plots of T vs. π.
I 40 mM, 48 hrs; II 40 mM, 20 hrs; III 2.5 mM, 20 hrs.
C control; 1 resorcin; 2 phenol; 3 p-cresol;
4 p-ethylphenol; 5 p-butylphenol; 6 p-hexylphenol;
7 dinitrophenol; 8 m-nitrophenol; 9 p-chlorophenol;
10 picric acid; 11 hydroquinone monomethyl ether;
12 m-cresol.
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Figure 4 shows the $\Delta H$, $H/HHW$ and $\Delta S$ vs. $\pi$ of p-alkylphenols. These plots seem to be a parabolic curve. A minimum point appears to be obtained near 1 $\pi$. The positive entropies were calculated from the equation $\Delta S = \Delta H / T$. A loss of entropy suggests a greater restriction of movement of solute molecules in the ordered acyl chains of DPPC liposomes.

Hansch and Fujita found that the toxicity of phenols (molar phenol coefficient) to gram-positive bacteria shows a linear relationship, and that to gram-negative bacteria shows a parabolic relationship (maximum $\Sigma \pi^2$). The difference in sensibility of the two microorganisms is due to their membrane structure. Despite the large difference in membrane composition between the bacteria and liposomes, the findings of this DSC study seem to be related to the toxicity of the bacteria. Liposomes which consist of the hydrophobic (acyl chain) and hydrophilic (polar head group) portion of the amphiphilic lipid structure are the best model of biological membranes due to the background of lipid bilayers.

A decrease in $H/HHW$ enlarges the temperature range in which two-dimensional domains of fluid gel and gel phase coexist. Below and above this range, the membrane exists in the gel and fluid phases respectively (Fig. 1). Jain et al. found that the hemolytic activity of alkanols, local anesthetics etc. is correlated with the HHW of DPPC liposomes in the DSC peak depending on their concentration, and that an increase in HHW (namely, a decrease in $H/HHW$) is accompanied by an increase in the hemolytic activity. From our experiment, it is clear that the change in $H/HHW$ is dependent on either the concentration or the $\pi$.

The $H/HHW$ of o- and m-cresol was above 100 (Table 1), indicating that cresols may liquefy a portion of the lipid bilayer of the DPPC liposomes at a relatively high concentration.
(40 mM). Compared to the H/HHW of p-cresol for 20 and 48 hrs (Tables 1 and 2), this value decreased with the increase in time and its ΔH also decreased. This indicates that membrane structural changes caused by exogenous compounds are slower. Dental disinfectants are used in high concentrations. Eugenols reach concentrations in excess of 10 mM in dentin just beneath the zinc oxide eugenol cement. Therefore, we used relatively high concentration of phenols in this experiment.

Since a small pretransition peak does not appear in single lamellar liposomes but in multilamellar liposomes, pretransition occurs through the interlamellae. This pretransition is absent when the phenols interact with multilamellar DPPC liposomes (Fig. 1). This seems to be due to the molecular packing of solutes between the lamellae and acyl chains of DPPC liposomes.

Despite the fact that the π of p-ethylphenol is almost the same as that of p-chlorophenol, the effect of ethylphenol on liposomes was larger than that of chlorophenol. From this, it is clear that the interaction of the alkyl chain (–CH₂CH₂–) of p-ethylphenol with the acyl chain of DPPC is stronger than that of Cl. Rogers and Davis found that p-alklyphenols have a large effect on dimyristoyl phosphatidylcholine liposomes. These findings suggest that the nature of the interaction of p-alkyl groups and p-halo groups with the phospholipid liposomes is different. The π of eugenol is similar to that of p-ethylphenol, but the changes in the transition properties of the former were smaller than those of the latter (Table 1). This indicates that the hydrogen bonding of the phenolic OH with phospholipids is very important, and that this bonding of eugenol is weaker due to the ortho effect between 1-OH and 2-OCH₃. Eugenol appears to have not a large effect on the T, but on the H/HHW (Fig. 1, Type A 2). The nature of its interaction with biological membranes may be different from that of the type A 1 group. A shift of T caused by eugenol was larger than that caused by isoeugenol, which indicates that this is due to the difference of the substituent between 4-CH₂=CHCH₂, isoeugenol and 4-CH₂CH=CH₂, eugenol. The double bond in the molecular structure has a large effect on the transition properties of DPPC liposomes.

Since biological membranes are a protein-lipid-polysaccharide complex, the findings obtained on the phospholipid liposomes allow only the interpretation of biological activity. However, lipid soluble solutes induce the changes in the phase transition properties of phospholipids which coexist in biomembranes. Consequently, exogenous solutes cause an increase in membrane fluidity resulting from a decrease in the gel phase of the phospholipids. Therefore, a monitor of biological activity would be related to this DSC study.

CONCLUSIONS

Changes in phase transition properties (T, ΔH, ΔS and H/HHW) of DPPC liposomes induced by phenol derivatives were investigated by the application of DSC. When the concentrations or the π of phenol derivatives increased, T decreased linearly. In alkylphenols, a parabolic curve was exhibited between phase transition properties and π. The maximum changes were obtained at a π of near 1. Of the alklyphenols having a π of near 1 (ethylphenol, eugenol and isoeugenol) ethylphenol showed the largest changes, and isoeugenol showed the smallest changes.
This clearly shows that changes in the phase transition properties induced by phenols are not only due to the $\pi$, but also due to the chemical structure.

REFERENCES

生体膜モデルとしてのりん脂質リポソームとフェノール誘導体の相互作用に関する熱量的研究

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フェノール誘導体の生体系に及ぼすメカニズムを分子レベルで明らかにする目的で、クレゾール、ユーティール、フェノールなど18種類のフェノール類とジパルミトイルホスファチジルコリン(DPPC)リポソームとの相互作用を示差走査熱量計で測定した。フェノール類がリポソーム膜に分配されること、リポソームの相転移温度(T)が低温シフトし、エンタルピー(ΔH)が減少した。TおよびΔHは濃度やフェノール類の疎水性(π)に影響される。濃度が増すとTは直線的に減少した。またアルキルフェノール類では、πが1付近でTおよびΔHの最大の変化を示す放物線関係が得られた。πが約1の、エチルフェノールのTおよびΔHは最も大きく変化し、ほぼ同じπ値のユーティールは前者より変化が小さかった。TおよびΔHの変化は、DPPCリポソームのアシル基とフェノール誘導体の相互作用に基づくものであった。

Mn, Si, Alを添加したNi-Cr合金のリン酸塩系埋没材との反応生成物

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*広島大学歯学部歯科補綴学系第一講座  **広島大学歯学部歯科理工学講座

Ni-Cr合金は融解温度が高いため、鍛造時に鍛造体表面で、リン酸塩系埋没材と化学的な反応を生じる欠点を有している。この反応の機序を明らかにし、この反応を防止する目的で、Ni85-Cr15合金にSi, Al, Mnを添加した合金を作製し、鍛造体表面の埋没材との反応物を、X線回折とXMAを用いて検討した。同時に、反応した部分の鍛造体全体に対する比率の測定と、合金組織についても検討した。

その結果, 埋没材と合金との反応物はMgCrO₄であった。また、Ni-Cr合金にMnを添加すると反応は増大し、SiやAlを添加すると反応は減少した。特に、SiとAlがともに2%以上の時には、この反応はほとんど認められなかった。合金組織も、SiとAlが1%以下または4%以上のときは不均一であったが、SiとAlがともに2%のときに均一な組織像を示した。

セメント合着ビン

——保持力と保持面積のin vitroにおける関係——

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6種の直径の異なるビンを、それぞれのビンの直径よりも0.1mm大きい直径のピンホールを持つ。5種の厚みの異なるアクリル板に標準程度で練ったリン酸亜鉛セメントを用いてセメント合着をした。24時間後に引っ張り試験を行い、セメント合着ビンの保持力と保持面積との関係について調べた。さらにピンとピンホールの表面