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# Electrical Conductivity, Phase Diagram, and Infrared Study of Tetra-*n*-Pentylammonium Thiocyanate and Benzoic Acid

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Electrical conductivities were measured for the binary system tetra-*n*-pentylammonium thiocyanate + benzoic acid in the range of temperatures from 30 to 180 °C, and theoretical glass transition temperatures were derived using the Vogel–Tammann–Fulcher equation. Electrical conductivities decrease as the acid content increases in the mixtures, and theoretical and experimental glass transition temperatures increase with the acid content. A partial phase diagram of the system is presented, revealing an incongruent melting point compound. An infrared study, particularly in the range 1025–1150 cm$^{-1}$, gives support to the formation of an organic complex.

## Introduction

There are several reasons for an interest in glass-forming molten organic salts, such as (a) they can be used for technological applications (polymers, batteries, and energy transfer and energy conversion systems), (b) they can provide a new tool for organic physical chemistry investigations of less stable organic complex ions, (c) they are capable of nearly continuous structure variation, (d) their low freezing points bring fused salt chemistry into the temperature range of standard equipment and instrumentation, and (e) in general, they are good glass-forming materials and synthetic organic media and allow crystal growth. The differentiation of organic as compared to inorganic glasses is wholly artificial. Both ionically or covalently (including metallically) bonded glasses and molecular glasses are of great interest in that context. The differences are reflected in all properties that depend on the strength and directions of the bonds responsible for the cohesion of a glass (*1*, *2*). The molecules in molecular glasses are composed of atoms held together in at least one dimension—by any of the three types of chemical bonds or their hybrids. But the intermolecular forces, responsible for the fact that the particular assembly of molecules is in the liquid or solid state at the temperature of observation, are commonly much weaker, often by an order of magnitude, than the chemical bonding forces.

Tetra-*n*-pentylammonium thiocyanate ($(C_5H_{11})_4NSCN$) + benzoic acid ($C_6H_5COOH$) has been selected for this study. This choice was dictated by the desirability of a variable organic cation in the study of donor properties of a nucleophilic anion in the glass-forming melt. Consideration has

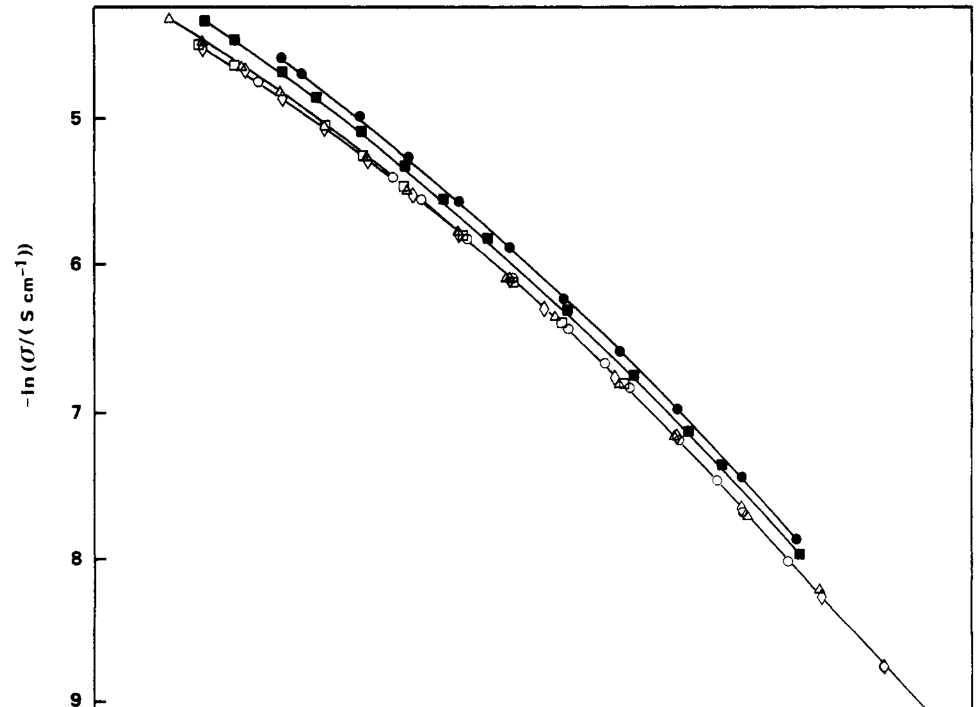

**Figure 1.** Electrical conductivity Arrhenius plots for the system $X$ $C_6H_5COOH$ + $(1 - X)$ $(C_5H_{11})_4NSCN$. Key: (●) $X = 0$, (■) $X = 0.10$, (△) $X = 0.20$, (□) $X = 0.30$, (◇) $X = 0.40$, and (○) $X = 0.50$.

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**Table I. Experimental Electrical Conductivities for $C_6H_5COOH + (C_5H_{11})_4SCN$ as a Function of Temperature and Composition[a]**

| $t$/°C | $\sigma \times 10^2$/(S cm$^{-1}$) | $t$/°C | $\sigma \times 10^2$/(S cm$^{-1}$) | $t$/°C | $\sigma \times 10^2$/(S cm$^{-1}$) |
|---|---|---|---|---|---|
| $X = 0$ | | $X = 0.10$ | | $X = 0.20$ | |
| 52.31 | 0.0365 | 50.20 | 0.0342 | 49.58 | 0.0240 |
| 60.33 | 0.0570 | 63.21 | 0.0620 | 59.26 | 0.0437 |
| 70.88 | 0.0903 | 68.49 | 0.0789 | 71.35 | 0.0743 |
| 80.61 | 0.1330 | 77.62 | 0.1141 | 80.36 | 0.1080 |
| 90.90 | 0.1911 | 89.31 | 0.1761 | 91.96 | 0.1649 |
| 100.69 | 0.2710 | 103.78 | 0.2790 | 100.27 | 0.2241 |
| 110.29 | 0.3639 | 113.09 | 0.3670 | 111.02 | 0.3062 |
| 120.86 | 0.5021 | 121.02 | 0.4749 | 121.32 | 0.4078 |
| 132.19 | 0.6739 | 130.91 | 0.6110 | 130.23 | 0.5140 |
| 145.59 | 0.9050 | 139.37 | 0.6829 | 140.22 | 0.6411 |
| 151.09 | 1.0099 | 150.39 | 0.9281 | 151.45 | 0.7989 |
| | | 162.01 | 1.1500 | 158.03 | 0.9205 |
| | | 170.51 | 1.3102 | 170.66 | 1.1302 |
| | | | | 177.50 | 1.3299 |
| $X = 0.30$ | | $X = 0.40$ | | $X = 0.50$ | |
| 78.96 | 0.1008 | 30.95[b] | 0.0081 | 31.41[b] | 0.0092 |
| 86.56 | 0.1320 | 39.70[b] | 0.0145 | 39.60[b] | 0.0153 |
| 97.22 | 0.1950 | 49.17[b] | 0.0255 | 57.96[b] | 0.0435 |
| 100.13 | 0.2165 | 68.30[b] | 0.0666 | 64.23[b] | 0.0537 |
| 108.68 | 0.2835 | 70.73 | 0.0754 | 70.73[b] | 0.0725 |
| 113.85 | 0.3280 | 80.98 | 0.1128 | 78.47 | 0.1023 |
| 123.36 | 0.4516 | 90.49 | 0.1549 | 82.24 | 0.1177 |
| 131.71 | 0.5300 | 99.42 | 0.2176 | 89.17 | 0.1534 |
| 142.48 | 0.6671 | 110.58 | 0.2997 | 99.98 | 0.2187 |
| 163.53 | 1.0049 | 119.62 | 0.3791 | 108.53 | 0.2851 |
| 175.68 | 1.2279 | 129.10 | 0.4844 | 119.01 | 0.3773 |
| | | 139.73 | 0.6097 | 125.25 | 0.4383 |
| | | 149.50 | 0.7447 | 157.88 | 0.8438 |
| | | 158.22 | 0.8804 | | |
| | | 170.46 | 1.085 | | |

[a] $X$ is the mole fraction of benzoic acid. [b] Values taken in the supercooled region.

**Table II. Parameters of the Equation $\ln(\sigma/(\mathrm{S\ cm^{-1}})) = a + b(T/\mathrm{K})^{-1} + c(T/\mathrm{K})^{-2} + d(T/\mathrm{K})^{-3}$**

| $X$[a] | $a$ | $b$ | $c$/10 | $d \times 10^{-8}$ | SD[b] |
|---|---|---|---|---|---|
| 0.00 | 3.945 41 | −5 136.33 | 139 221 | −3.170 992 | 0.01 |
| 0.10 | 11.848 48 | −14 176.44 | 470 280 | −7.088 849 | 0.1 |
| 0.20 | −9.639 90 | 7 883.98 | −266 795 | 0.840 658 | 0.1 |
| 0.30 | −13.566 94 | 13 312.62 | −510 427 | 4.371 570 | 0.02 |
| 0.40 | −0.708 30 | −1 497.39 | 486 718 | −2.546 770 | 0.01 |
| 0.50 | −9.722 88 | 8 596.49 | −328 207 | 2.145 488 | 0.02 |

[a] X is the mole fraction of benzoic acid. [b] SD is standard deviation.

been limited to a quaternary salt since for many uses the pressure of acidic $NH^+$ protons is undesirable (*3*). The information of the theoretical (or ideal) glass transition temperature, $T_o$, and the experimental glass transition temperature, $T_g$, is related to the composition of both systems and shows evidence of organic complex formation.

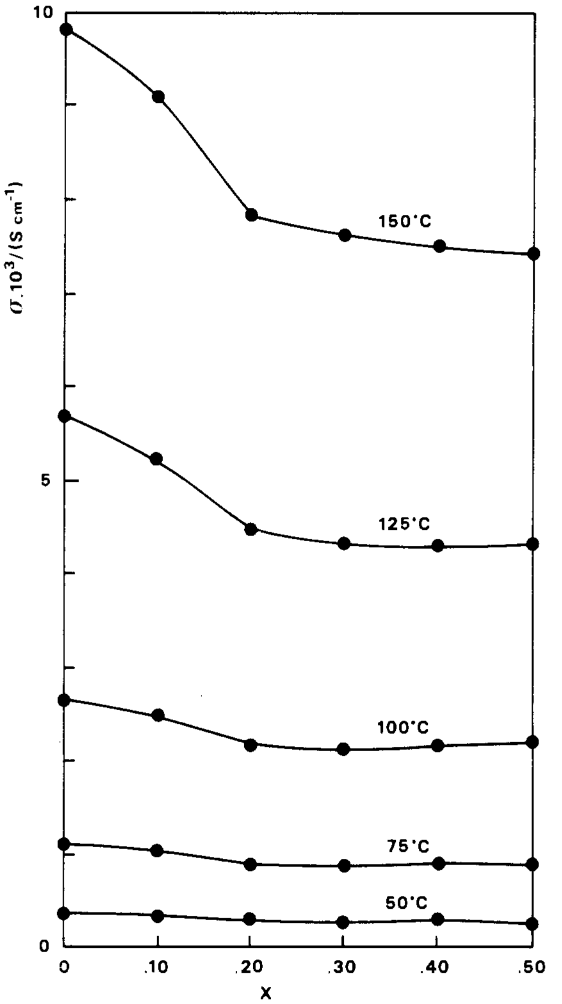


**Figure 2.** Electrical conductivity as a function of temperature for the system $X\ C_6H_5COOH + (1 - X)\ (C_5H_{11})_4NSCN$.

## Experimental Section

The general procedures are described elsewhere (*3*, *4*). Tetra-*n*-pentylammonium thiocyanate was synthesized according to the techniques previously presented (*5*), showing a melting point of 50.5 ± 0.1 °C; benzoic acid was recrystallized twice and sublimed (*6*), and its melting point was 122.1 ± 0.1 °C. The samples were prepared in a drybox filled with $N_2$, by the mixing of preweighed components followed by melting.

The conductivity cell was a U-cell with deep bright platinum electrodes. The calibration was performed with aqueous solutions of recrystallized potassium chloride (1.0 D), and the cell constant has a value of $a = 1439.2\ \mathrm{cm^{-1}}$. The temperature control was $2 \times 10^{-2}$ °C. The values of electrical conductivity were measured in the range $X = 0.0$–$0.50$ mole fraction of benzoic acid using a Wayne Kerr B641 Autobalance Universal Bridge, over a range of temperatures of 30–80 °C. Glass transition temperatures, $T_g$, were measured using a DTA analyzer (*3*, *4*). The heating rate from the liquid nitrogen temperature was 10 °C/min. Analysis was performed on heating to measure the experimental glass transition temperature, $T_g$, melting temperature, $T_m$, and transition temperature, $T_{trans}$. Also, melting points and solid–solid transition temperatures were determined on heating using a Perkin-Elmer DSC. IR spectra were obtained in the solid-state samples, dispersed in KBr pellets, using a Perkin-Elmer 598. Above $X = 0.50$ mole fraction of benzoic acid the system shows instability according to

$$n(C_5H_{11})_4NSCN \rightarrow n(C_5H_{11})_4NCN + S_n$$

and as is referred to in the Discussion.

## Results

The values of the electrical conductivity, $\sigma$, as a function of temperature for the system $(C_5H_{11})_4NSCN + C_6H_5COOH$ are shown in Table I. In Figure 1 are represented the Arrhenius plots of the conductivity for the same system. The values of ln $\sigma$ were fitted to a third-order polynomial in the $T^{-1}$ equation to derive the conductivity isotherms and Arrhenius coefficient plots. In Table II are presented least-squares parameters for the electrical conductivity. The conductivity isotherms are shown in Figure 2 for the different systems. The partial phase diagram is shown in Figure 3. At 44 °C a eutectic appears at $X = 0.16$ mole fraction of benzoic acid, and the system $(C_5H_{11})_4NSCN + C_6H_5COOH$ presents an incongruent melting point of 55.5 °C, corresponding to

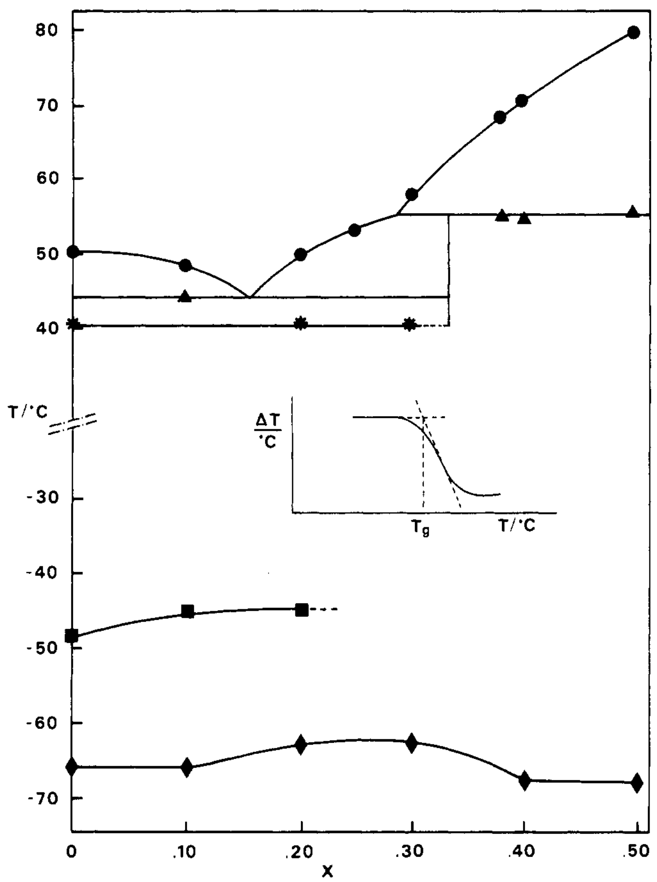


**Figure 3.** Partial phase diagram (upper part) experimental glass transition temperature, $T_g$, and theoretical glass transition temperature, $T_0$, for the system $X$ $C_6H_5COOH$ + (1 − $X$) $(C_5H_{11})_4NSCN$, at $B$ = 860 K (lower part), and an illustration of the method used to derive the glass transition temperature, $T_g$ (inset). Key: (●) melting temperature, $T_m$, (■) $T_g$, (♦) $T_0$, (▲) eutectic temperature, $T'$, and (*) solid transition, $T''$.

the formation of a 2:1 compound. The Vogel–Tammann–Fulcher equation (*7–9*) was used to derive the values of the theoretical glass transition temperature, $T_0$:

$$\ln \sigma = A - [B/(T - T_0)]$$

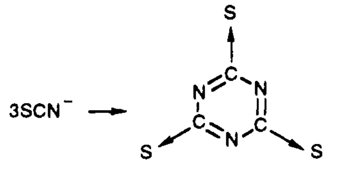
where $T$ is the absolute temperature and $A$ and $B$ are constants.

A fitting was performed for the three-parameter equation, from which $T_0$ values were found for several representative compositions. Again, in Figure 3, $T_0$ (constant $B$) and $T_g$ values are presented at constant $B$ = 860 K. In Figures 4 and 5 are also shown the values of parameters found at monotonic $B$ and $A$ parameters for $B$ = 860 K for the system under study and for $(C_5H_{11})_4NSCN$ + $C_6H_5NO_2$ (*5*) which was studied earlier. IR spectra of representative compositions of the system, taken at 20 °C, are shown in Figure 6.

## Discussion

As expected electrical conductivity presents a non-Arrhenius behavior. $\partial \ln \sigma/\partial T^{-1}$ shows a marked dependence of temperature, and Arrhenius plots are well described by the Vogel–Tammann–Fulcher equation.

In pure liquid thiocyanate a ring structure was found (*10*):



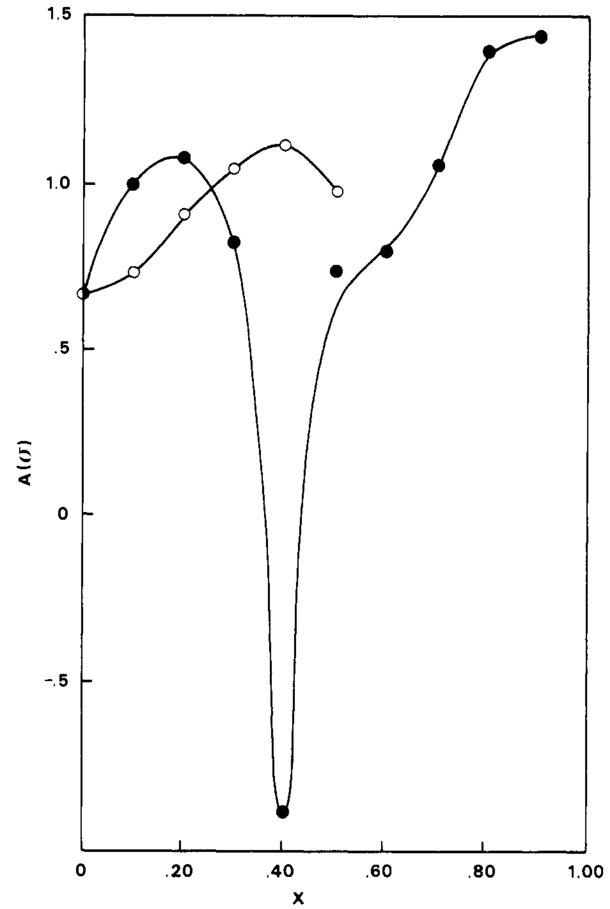


**Figure 4.** Vogel–Tammann–Fulcher equation $A$ parameter, at $B$ = 860 K, for the systems (○) $X$ $C_6H_5COOH$ + (1 − $X$) $(C_5H_{11})_4NSCN$ and (●) $X$ $C_6H_5NO_2$ + (1 − $X$) $(C_5H_{11})_4NSCN$ (ref 5).

The presence of benzoic acid modifies this structure, and conductivity decreases in the range $X$ = 0.00–0.20 in $C_6H_5COOH$. The glass transition temperature, $T_0$, at constant $B$, increases in the same range of compositions. These facts are due to the change in configurational entropy, $S_c$, to lower values, which means the break of the ring structure. On the other hand, benzoic acid has a lower conductivity than thiocyanate species, and its presence forces a melt rearrangement. A similar situation was found in other systems, α-picolinium chloride and α-picolinium fluoride + α-picolinium chloride (*3, 11*).

The slight decrease in conductivity from $X$ = 0.20 to $X$ = 0.40 in $C_6H_5COOH$ and the maximum in the range 0.30–0.40 in $T_0$ (constant $B$) and less clear in $T_0$ (monotonic $B$) as shown in Figure 5 give evidence of formation of a complex species with a stoichiometry of 0.33:0.66 for $C_6H_5COOH/(C_5H_{11})_4NSCN$ or a 1:2 compound. This is consistent with the partial phase diagram, in which an incongruent melting point compound is found at that composition and is explained by the decrease in $S_c$. Indeed, the formation of complex species in glass-forming systems modifies the configurational entropy and consequently glass transition temperature (*3, 4*). So, the addition of benzoic acid causes the breakup of the thiocyanate ring structure with a change in conductivity, but it is not so marked for $X \geq 0.20$.

A kink block model (*12, 13, 19*) applied to carbon–carbon bonds in the pentyl chains gives an explanation to the solid–solid transition found in the tetra-*n*-pentylammonium thiocyanate + benzoic acid, up to $X$ = 0.30.

One of the ionic complex species present in these systems after the first addition of benzoic acid seems to be $SCN\text{-}H\text{-}NCS^-$; the structure $SCN\text{-}H\text{-}SCN^-$ is unlikely.

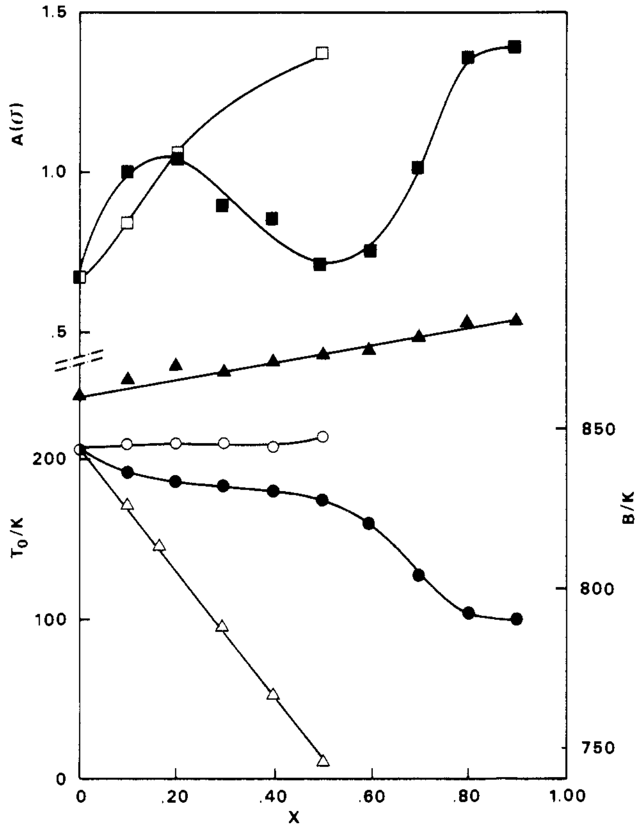


**Figure 5.** Theoretical glass transition temperature, $T_o$, and Vogel–Tammann–Fulcher equation $A$ parameter, at monotonic $B$, for the system $X$ $C_6H_5COOH$ + (1 − $X$) $(C_5H_{11})_4NSC$. Key: (○) $T_o$, (□) $A$, and (△) $B$. Theoretical glass transition temperature, $T_o$, and Vogel–Tammann–Fulcher equation $A$ parameter, at monotonic $B$, for the system $X$ $C_6H_5NO_2$ + (1 − $X$) $(C_5H_{11})_4NSCN$ (ref 5). Key: (●) $T_o$, (■) $A$, and (▲) $B$.

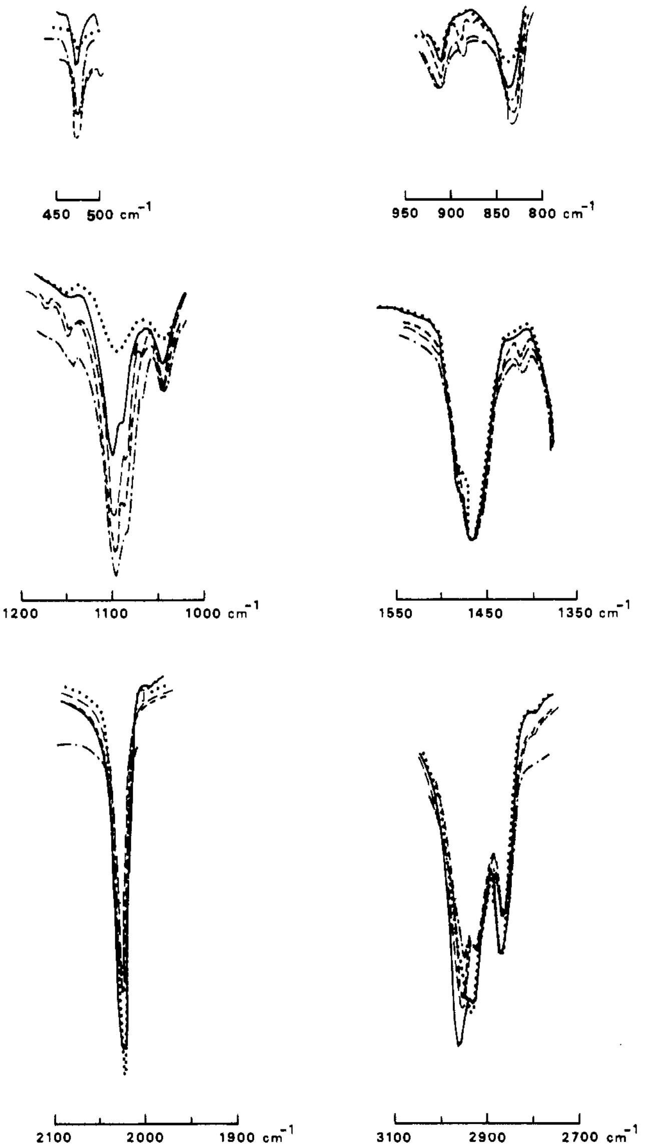


**Figure 6.** Infrared absorption spectral bands, in the solid phase, for the system $X$ $C_6H_5COOH$ + (1 − $X$) $(C_5H_{11})_4NSCN$, at 20 °C. Key: (···) $X$ = 0.10, (—) X = 0.20, (– – –) $X$ = 0.30, (- - -) $X$ = 0.40, and (-·-) $X$ = 0.50.

Indeed, in a work with a 3:1 mixture of KSCN/NaSCN and benzoic acid, in the molten state, some decomposition of the thiocyanate was found because of the formation of HSCN (*14*). Also, in a methyl and ethyl 3,5-dihydroxybenzoate with potassium/sodium thiocyanate eutectic mixture the product compositions in 96% $CH_3SCN$, 4% $CH_3NCS$ (w/w), and 54% $C_6H_5SCN$, 46% $C_2H_5NCS$ (w/w) were found (*15*). Investigations with an MNCS (M = Li, Na, and K) system in tetrahydrofuran and 1,3-dioxolane have characterized triple ions $Li_2NCS^+$ and $Na_2NCS^+$ by IR (*16*), and the ionic species $SCN^-M^{+-}NCS$ have been reported (*17*).

The formation of complex species in these glass-forming systems modifies the configurational entropy, $S_c$, as we referred to above, and the maximum in the $T_o$ plot is due to the formation of the new complex formed between $(C_5H_{11})_4$-NSCN and benzoic acid. Instead, in the binary system $(C_5H_{11})_4NSCN$ + $C_6H_5NO_2$ no singularities were found in conductivity (*5*), and a quasi-steady decrease is shown for $T_o$ in Figure 5.

The cation formation in the complex species is explained by the change of C=O present in the solid benzoic acid at $\nu_s$(C=O) 1693 cm$^{-1}$ to C—O for both carboxilic groups, where $\nu$(CO) ranges from 1000 to 1200 cm$^{-1}$. On the other hand, the C—O band is strongly increased as the acid content increases. These facts are correlated with the presence of complex bands in the range 1020–1260 cm$^{-1}$ and with the peak at 1410 cm$^{-1}$ whose value increases with benzoic acid content. A band at 1700 cm$^{-1}$ from benzoic acid is not present in any binary system. Those bands are consistent with the cationic structure $(C_5H_{11})_4N^+C_6H_5COO^-(C_5H_{11})_4N^+$. They include maxima at 1040, 1095, and 1145 cm$^{-1}$, corresponding to a substituted benzene ring. It seems likely that the anionic structure unit of the complex shown in the partial phase diagram $[SCN\text{-}H\text{-}NCS]^-$ is present by $\nu_1$ 2025 cm$^{-1}$, $\nu_2$ 467 cm$^{-1}$, and $\nu_3$ 835 cm$^{-1}$. Also, the region from 750 to 900 cm$^{-1}$ confirms the existence of that complex. At 760 cm$^{-1}$ a peak corresponds to the frequency of N–H–N. The NCS bend band is weak and found at 472 cm$^{-1}$. However, it shifts to 467 cm$^{-1}$ for $X$ = 0.50 mole fraction of benzoic acid.

In $(C_5H_{11})_4NSCN$, the S–C band is found at 735 cm$^{-1}$, increases up to $X$ = 0.30–0.40 mole fraction of benzoic acid, and decreases again. At 770 cm$^{-1}$ a new band is found, increasing with $X$, while shifting to 761 cm$^{-1}$ at $X$ = 0.50. At 2500 cm$^{-1}$ a very weak band is probably due to S–H. The band at 2025 cm$^{-1}$ due to thiocyanate shows a reduction in its magnitude as benzoic acid is added.

The partial phase diagram presents a solid–solid transition derived on the heating curves. In fact, $(C_5H_{11})_4NSCN$ was found to be dimorphic. On slow heating, the solid transition II-I (*18*) is observed at 41 °C. Despite in the overall fusion process of the pure salt the greatest structural changes within the cation appear to occur at the solid-state transition, according to Janz (*19*), in the mixtures with the organic acid other complex entities are shown.

In this work, conductivity measurements were taken; however, considering the parallel behavior of electrical conductivity and fluidity, the present system may be considered as fragile (*2, 4, 20*), since the values of that transport property show a highly non-Arrhenius character.

## Conclusions

The electrical conductivities of the binary system tetra-*n*-pentylammonium thiocyanate ($(C_5H_{11})_4NSCN$) with benzoic acid ($C_6H_5COOH$) in the range of temperatures from 30 to 180 °C decrease with acid content, and glass transition temperatures, $T_0$ and $T_g$, increase because of the changes in configurational entropy. An incongruent melting point compound is revealed by the partial phase diagram of the system. The infrared study of the systems gives support to the formation of that 2:1 complex.

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**Registry No.** $(C_5H_{11})_4NSCN$, 3475-60-3; $C_6H_5COOH$, 65-85-0; $C_6H_5COOH{\cdot}2(C_5H_{11})_4NSCN$, 142981-20-2.