Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Phase Transition and Phase Diagram of Anion Radical Salts of $[(C_6H_5)_3PCH_3]^+$ $[(C_6H_5)_3AsCH_3]^+$ $_x(TCNQ)^-{}_2$ $(0 \leq x \leq 1)$

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To cite this article: Yôichi Iida (1977): Phase Transition and Phase Diagram of Anion Radical Salts of $[(C_6H_5)_3PCH_3]^+$ $[(C_6H_5)_3AsCH_3]^+$ $_x(TCNQ)^-{}_2$ $(0 \leq x \leq 1)$, Molecular Crystals and Liquid Crystals, 39:3-4, 195-198

To link to this article: http://dx.doi.org/10.1080/00268947708084401

Mol. Cryst. Liq. Cryst., 1977, Vol. 39, pp. 195–198

Printed in Holland

Phase Transition and Phase Diagram of Anion Radical Salts of $[(C_6H_5)_3PCH_3]^+_{1-x}$ $[(C_6H_5)_3AsCH_3]^+_x$ $(TCNQ)_2^-$, $(0 \leq x \leq 1)$

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(*Received November 18, 1976*)

Much attention has been paid to the solid anion radical salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ), because of their prominent electronic properties.[1–4] In particular, the salts containing mixed cations represented by $[(C_6H_5)_3PCH_3]^+_{1-x}$ $[(C_6H_5)_3AsCH_3]^+_x$ $(TCNQ)_2^-$, $(0 \leq x \leq 1)$, are known to undergo phase transitions at 1 atm pressure in the solid state.[1–4] The phase transition of pure methyltriphenylphosphonium salt, $(x = 0.00)$, takes place at 315.7 K. Heat-capacity measurements of this phase transition have been made by Kosaki *et al.*[3] The transition has thus been found to be of the first order. The enthalpy and the total entropy change associated with the phase transition were experimentally determined to be 485.18 cal/mol and 1.7206 cal/deg.mol, respectively. For the solid solutions, it was found that the transition temperature (T_c) is increased, while the magnitude of the heat of transition (ΔH) is decreased, progressively with an increase in the composition parameter (x) and that pure methyltriphenylarsonium salt, $(x = 1.00)$, has no such phase transition up to the decomposition temperature of about 480 K at 1 atm pressure.[1–3] Figure 1 shows the experimental relation between T_c and x, together with the relation between ΔH and x.[4] In the present paper, we attempted to explain thermodynamically the phase diagram of Figure 1 for the solid solutions of those TCNQ anion radical salts.

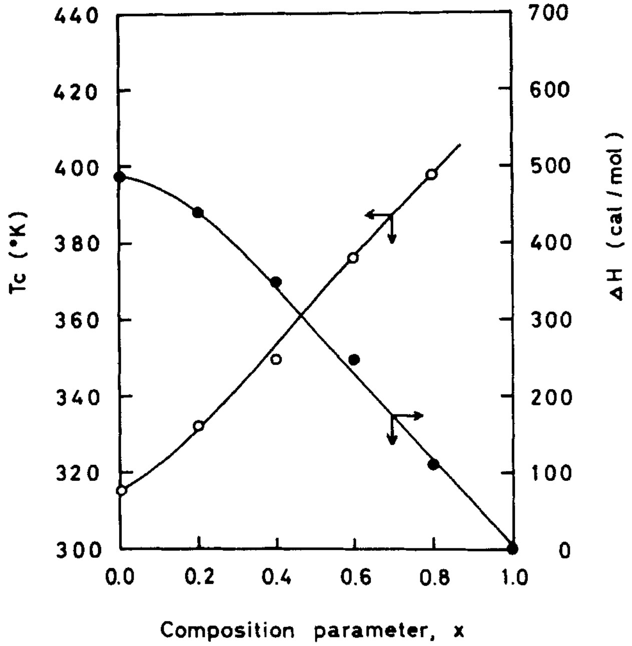

FIGURE 1 The experimental relations of the transition temperature (T_c) and of the magnitude of the heat of the phase transition (ΔH) to the composition parameter (x) in $[(C_6H_5)_3PCH_3]^+_{1-x}[(C_6H_5)_3AsCH_3]^+_x\ (TCNQ)_2^-$, $(0 \leq x \leq 1)$, at 1 atm pressure.

In a previous paper,[4] we proposed a thermodynamical theory of ideal solid solution model for $[(C_6H_5)_3PCH_3]^+_{1-x}[(C_6H_5)_3AsCH_3]^+_x\ (TCNQ)_2^-$, $(0 \leq x \leq 1)$, in order to understand the mechanism of the phase transition. This model assumes that the phase transition does not change the manner of ideal mixing of the two components, because the methyltriphenylphosphonium and methyltriphenylarsonium cations are so bulky that we cannot expect the cation exchange in the phase transition. In this respect, we have to note that the phase transition of our system is not the usual order–disorder type with respect to the mixing of the two components. Moreover, we could well assign the low- and high-temperature phases of the solid solutions at 1 atm pressure as $\alpha\gamma$ and $\beta\gamma$ phases, respectively.[4] Their Gibbs free energies per mol can be well expressed by

$$G^{i\gamma}(T, p, x) = (1 - x)G^{i}_{1}(T, p) + xG^{\gamma}_{2}(T, p) + RT\{(1 - x)\ln(1 - x) + x \ln x\},$$
$$(i = \alpha, \beta), \quad (1)$$

where $(1 - x)$ and x are the mole fractions of the component $[(C_6H_5)_3PCH_3]^+\ (TCNQ)_2^-$ and $[(C_6H_5)_3AsCH_3]^+\ (TCNQ)_2^-$, respectively. $G^{\alpha}_{1}(T, p)$

and $G_1^\beta(T, p)$ are the Gibbs free energies per mol for the low-temperature (α) and high-temperature (β) phases of pure phosphonium salt, respectively, while $G_2^\gamma(T, p)$ is that for the (γ) phase of pure arsonium salt at 1 atm pressure.

Hereafter, we only consider the phase diagram of the solid solutions at 1 atm pressure. The phase equilibrium condition at the transition point is $G^{\alpha\gamma}(T, p, x) = G^{\beta\gamma}(T, p, x)$. If the temperature and the composition parameter vary as $T \to T + dT$ and $x \to x + dx$ under the constant pressure of $p = 1$ atm, then $G^{\alpha\gamma} + dG^{\alpha\gamma} = G^{\beta\gamma} + dG^{\beta\gamma}$. In this case, $dG^{\alpha\gamma}$ and $dG^{\beta\gamma}$ can be expressed by

$$dG^{i\gamma} = -(1 - x)S_1^i dT - G_1^i dx - xS_2^\gamma dT + G_2^\gamma dx$$
$$+ R\{(1 - x)\ln(1 - x) + x \ln x\}dT + RT \ln\left(\frac{x}{1 - x}\right)dx, \tag{2}$$

where $i = \alpha$ or β, and where S_1^i or S_2^γ is the entropy per mol for each phase. Therefore, the condition of $dG^{\alpha\gamma} = dG^{\beta\gamma}$ leads to the theoretical relation expressed by

$$\frac{dT_c}{dx} = \frac{G_1^\alpha - G_1^\beta}{(S_1^\beta - S_1^\alpha)(1 - x)}. \tag{3}$$

For pure phosphonium salt where $x = 0.00$, the experimental values of T_c and $S_1^\beta - S_1^\alpha$ are 315.7 K and 1.7206 cal/deg.mol, respectively, but since $G_1^\alpha - G_1^\beta = 0$, the slope value of Eq. (3) is $(dT_c/dx) = 0$ at $T_c = 315.7$ K. As the value of x increases, the $(S_1^\beta - S_1^\alpha)(1 - x)$ value will decrease progressively, while the $G_1^\alpha - G_1^\beta$ value will be positive and increase, because the α phase of pure phosphonium salt is the unstable phase in the temperature region above 315.7 K. Therefore, the slope value of (dT_c/dx) in Eq. (3) will be positive and increase progressively with the increase of x. At pure arsonium salt where $x = 1.00$, $(S_1^\beta - S_1^\alpha)(1 - x) = 0$ and $(dT_c/dx) = +\infty$ so that the T_c value will diverge to infinity. On the basis of these thermodynamical considerations, the theoretical relation between T_c and x of the solid solutions is schematically demonstrated in Figure 2.

This theoretical prediction can explain pretty well the experimental phase diagram of Figure 1, in which the T_c value is the lowest at the salt of $x = 0.00$ and increases progressively with the increase of x, diverging to very high temperatures at the salt of $x = 1.00$. This agreement, in return, justifies that the phase transition of our system is of the $\alpha\gamma \to \beta\gamma$ process. However, one can find some minor disagreements between Figure 1 and Figure 2; that is, (i) the slope value of (dT_c/dx) in the experimental fact of Figure 1 is positive even at the salt of $x = 0.00$, while the value in Figure 2 is zero at $x = 0.00$, and (ii) in the theoretical relation of Figure 2, there is a drastic increase of the

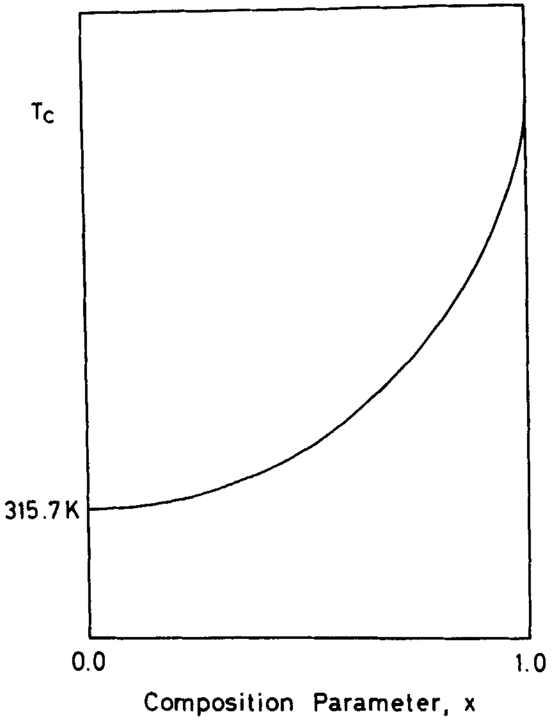

FIGURE 2 The theoretical relation of the transition temperature (T_c) to the composition parameter (x) in the phase transitions of $[(C_6H_5)_3PCH_3]^+_{1-x}[(C_6H_5)_3AsCH_3]^+_x(TCNQ)^-_2$, ($0 \le x \le 1$). See text.

slope value changing from zero to infinity, while it is not so drastic in the experimental relation. However, these discrepancies may be improved by modifying our ideal solid solution model of Eq. (1) to include the effect of heat of mixing.

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