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The charge transfer and ion formation in liquid Li-Tl alloys

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Abstract

The ^{7}Li NMR Knight shift, K, and the spin-lattice relaxation time, T_1, were measured for liquid Li-Tl alloys. The K decreases rapidly with the addition of Tl up to 20 at.% Tl. In the concentration from 20 to 50 at.% Tl, the K decreases only slightly and the K of 50 at.% Tl is 60% of K for the pure liquid Li. Such a decrease of K is considered as an indication for the strong charge transfer from Li to Tl. These tendencies are similar to those from previous studies for liquid Li-Ga and Li-In alloys. However, beyond 50 at% Tl, the K increases and reaches to an almost constant value (70% of K for the pure liquid Li). Such a back donation of charge is absent for liquid Li-Ga and Li-In alloys. It is considered that the tendency of the formation of ionic structural unit for liquid Li-Tl alloys is slightly weaker compared with the cases of liquid Li-Ga and Li-In alloys. The T_1 is also discussed with the relation to the Knight shift and the electronic properties.

PACS codes

61.20.-p, 61.25.MV, 72.15.Lh, 76.60.Cq.

1. Introduction

Lithium-based alloys have attracted much attentions recently as materials for lithium batteries. Lithium-group XIII element systems in solid states exist as the intermetallic compounds around some specific composition. For example, the 1:1 intermetallic compounds for lithium-group XIII elements has two kinds of the structures[1]; one is the 'CsCl' structure, which has a body centered cubic lattice; the other is the 'NaTl' structure, which is so-called 'Zintl phase'. According to the concept of Zintl ion[2-4], electrons are transferred from the Li atom to the more electronegative group XIII one. The negatively charged ion of group XIII elements forms a diamond lattice similar to the case of C, Si and Ge. The alkali atoms occupy the empty interstitial sites of this diamond lattice. The transfer of one electron charge in the Zintl phase seems to be rather complete compared with that in CsCl structure case. The Zintl phase is found in Li-Ga and Li-In alloys. The CsCl structure is found in Li-Tl alloys. It is very interesting to investigate whether such an unit of intermetallic compound is also present in the liquid states. However, the Li-alloys in the liquid states are very reactive and difficult to handle because of their high reactivity. Up to this date, the physical properties and the effects of such an intermetallic compound unit on them have not always been clarified sufficiently for the liquid state of Li-polyvalent alloys. The degree of charge transfer is a key to understand the electronic properties of the liquid states. The Knight shift is a good probe for the detection of charge transfer. The purpose of this paper is to discuss the electronic

properties of liquid Li-Tl alloys from the ^{7}Li Knight shift, K, and the nuclear spin-lattice relaxation time, T_1.

2. Experimental

Prior to NMR measurements, the phase diagram of Li-Tl system was investigated by a thermal analysis method using a DSC 200(Seiko Instrument Inc.) to determine the experimental temperature range precisely. The sample preparation was performed inside the Ar-circulating glove box with less than 1 ppm of oxygen, nitrogen and water content respectively.

All of the samples for NMR measurements was prepared inside the glove box descried above. The nominal purity of the metals used was 99.9% for both Li (with 92.5 at.% ^{7}Li) and Tl metals. Sample alloys were prepared by keeping the components together in a Mo crucible at about 100K higher temperature than the presumed melting temperature. The melted samples were quenched on a Cu plate. The NMR samples were prepared by mixing the quenched alloys with the LiF powder in the Mo crucible at 50~100K higher temperature than the liquidus temperature. This LiF powder provided the reference peak for the NMR measurements. The solubility of LiF in these samples is negligibly small at the relevant temperatures[5)].

The NMR measurements of the ^{7}Li Knight shift and the spin-lattice relaxation time were

performed using a Bruker CXP40 spectrometer. The resonance frequency was 14.87MHz. The spin-lattice relaxation time was measured by using the inversion recovery method. The NMR measurements in the liquid state were performed during the cooling process from 833K to 10K higher temperature than the liquidus temperature.

3. Results

The phase diagram of Li-Tl system determined in this study is essentially the same as the previous one[6]. The explicit values of determined liquidus temperatures are given as follows: (0,451); (5,518); (10,555); (15,635); (20,674); (25,724); (28.6,722); (33,704); (40,746); (50,781); (52,773); (60,712); (75,579); (85,488). In the notation of (A,B), A indicates the concentration of Tl and B the liquidus (absolute) temperature. The liquidus temperature at 65 at.% Tl, which was estimated by the interpolation procedure, is 671 K. All experimental concentrations are described above.

The obtained ^{7}Li Knight shift for pure liquid Li are in good agreement with the previous value[7]. The *K* decreases rapidly with the addition of Tl to liquid Li. At about 20at.% Tl it is reduced to 60% of the *K* for the pure liquid Li. In the concentration range from 20 to 50 at.% Tl, the *K* decreases only slightly. Beyond 50 at.% Tl, the *K* increases and reaches to the value which is 70% of the *K* for pure liquid Li. Fig. 2 shows the concentration dependence of the

temperature coefficient of the ^{7}Li Knight shift, dK/dT, for Li-Tl alloys. The large value of the dK/dT is observed in the concentration range from 20 to 50 at% Tl. Fig. 3 shows the concentration dependence of the spin-lattice relaxation time, T_1, at 793K. The T_1 increases rapidly up to 20 at.% Tl. From 20 to 50 at.% Tl, the T_1 keeps an almost constant value, which is nearly the twice of T_1 for pure liquid Li. The T_1 decreases slightly beyond 50 at.% Tl. This behavior of T_1 corresponds to the inverse tendency of the Knight shift, K. The reproducibility of K and T_1 is within 3 ppm and 3msec respectively, judging from the data scattering of experiments. The error bar of the dK/dT was dependent on the temperature range measured and the Li concentration. In the Li rich region, it was 0.006 ppmK^{-1}. In the Tl rich region, it was within 0.015 ppmK^{-1}. In the intermediate concentration range, it was within 0.02 ppmK^{-1}.

4. Discussion

Fig.1 reveals that the particular feature of present data for ^{7}Li Knight shift, K; the rapid decrease on Tl addition followed by the constant value from 20 to 50 at.% Tl and the increase beyond 50 at.% Tl. The rapid decrease of K itself has been reported in previous studies for liquid Li-group XIII element[8,9] and Li–group XIV element alloys[10,11]. For the latter alloys a monotonous increase of K beyond a stoichiometric concentration(20 at.% Pb or Sn) has been also reported[10]. In other words, in liquid Li-Pb and Li-Sn alloys, single minimum of K can be seen on the isotherm of K. In liquid Li-Ge alloys[11], there is another smaller minimum of K at

50 at.% Ge in addition to that at 20 at.% Ge. However, for the former alloys[8,9], the K was almost constant beyond 20 at.% In[8] and Ga[9]. In addition, the increase of *K* beyond 50 at.% group XIII element can be found only for present liquid Li-Tl alloys among the former alloys.

It is very important to analyze the complicated behavior of Knight shift in Fig. 1. The conduction electrons cause the shift of nuclear magnetic resonant frequency, namely the Knight shift, due to the change of the average static magnetic field at the nucleus. Under the assumption of contact interaction between conduction s-electrons and the nuclei[12], this Knight shift can be written as

$$K = \frac{8\pi}{3}\Omega\chi_{\mathrm{P}}P_{\mathrm{F}}(C). \qquad (1)$$

In this equation, Ω denotes the atomic volume, χ_{P} the Pauli spin susceptibility and $P_{\mathrm{F}}(C)$ the Fermi surface average of the contact density of s-electrons at the nucleus for the alloy with concentration *C*.

If the Ω and the χ_{P} are given for liquid Li-Tl alloys, the $P_{\mathrm{F}}(C)$ can be evaluated as a function of Tl concentration, *C*. This $P_F(C)$ for alloy states is conventionally discussed in terms of the relative contact density. The explicit form of relative contact density is

$$\delta(C) = P_{\mathrm{F}}(C) / P_{\mathrm{F}}(0), \qquad (2)$$

in which the $P_F(0)$ is the Fermi qverage contact density for pure Li.

The χ_{P} in Eqn.(1) was estimated from the assumption of the linear law, $\chi_{\mathrm{P}} = (1\text{-}C)\chi_{\mathrm{P}}^{\mathrm{Li}} + C\chi_{\mathrm{P}}^{\mathrm{Tl}}$: $\chi_{\mathrm{P}}^{\mathrm{Li}}$ and $\chi_{\mathrm{P}}^{\mathrm{Tl}}$ are respectively the Pauli spin susceptibility of liquid Li and that of liquid Tl[13].

The Ω was estimated by the assumption, $\Omega = \Omega^{L} + \Delta\Omega$; Ω^{L} is the volume of linear approximation and $\Delta\Omega$ is the deviation of volume from the linear law. The Ω^{L} is given as (1-C)Ω_0^{Li} + CΩ_0^{Tl}: Ω_0^{Li} and Ω_0^{Tl} are the atomic volumes of liquid Li and that of liquid Tl respectively[14]. The $\Delta\Omega$ for liquid Li-Tl alloys was assumed to be same as that for liquid Li-In alloys[15]. The former assumption for χ_P was done simply by the lack of literature values. The latter assumption for the Ω was performed based on the similarity of physical properties between Li-Tl system and Li-In one; the large volume contraction of 20% was reported at 25 at.% In[15] in liquid Li-In. In the present study, rather crude assumptions described above were adopted because of the lack of data for the χ_P and the Ω. The present analysis is rather qualitative and the precise estimation must be performed in further.

The evaluated result for the $\delta(C)$ is shown in Fig. 4. The concentration dependence of $\delta(C)$ decreases rapidly with the addition of Tl up to 20 at.% Tl. The decrease of $\delta(C)$ indicates the charge transfer from less electropositive Li atoms to more electronegative Tl ones. From 20 to 50 at.% Tl, the $\delta(C)$ decreases only slightly and the $\delta(C)$ at 50 at.% Tl is 70% of $\delta(0)$. In this concentration range (20~50 at.% Tl), the various intermetallic compounds appear in the solid state[6]. Particularly, the intermetallic compound at 50 at.% Tl , which shows the maximum melting temperature, is known to have the 'CsCl' structure with ionic character. The behavior of $\delta(C)$ in this concentration range indicates the formation of such an ionic structural unit. However, the $\delta(C)$ increases slightly beyond 50 at.% Tl. This increasing tendency indicates

the back donation of the charge from Tl atoms to Li ones. Therefore, this ionic structural unit may be not so rigid in liquid Li-Tl alloys compared with that in liquid Li-In and Li-Ga alloys, for which no increase of the K was found beyond 50 at.% In[10] and 50 at% Ga[11] respectively. This weaker ionic structural unit in liquid Li-Tl may be supported also from the concentration dependence of dK/dT, the temperature coefficient of Knight shift, shown in Fig.2. The large value of dK/dT in the concentration range from 20 to 50 at.% Tl may also indicate the dissociation of this ionic structural unit with the increase of the temperature. The reproducibility of this evaluation of $\delta(C)$ is within 2 %.

As shown in Fig.3, the T_1 also increases rapidly in the concentration range up to 20 at.% Tl, where the rapid decrease of the K in Fig.1 indicates the progress of charge transfer from Li atom to Tl one. This means that the relaxation of ^{7}Li nuclear spin takes longer time with the progress of the charge transfer. In the range from 20 to 50 at.% the T_1 shows a larger constant value, which may indicate the almost accomplishment of charge transfer, as shown in Fig.1.

The Korringa enhancement factor, η, combines the spin-lattice relaxation time, T_1, (Fig. 3) with the Knight shift, K, (Fig. 1). The η is defined by[16]

$$\eta = \frac{(K^2 T_1 T)_{Korr}}{(K^2 T_1 T)_{Exp}} = \left(\frac{\gamma_e}{\gamma_n}\right)^2 \frac{\hbar}{4\pi k_B} \frac{1}{(K^2 T_1 T)_{Exp}}. \qquad (3)$$

In this equation, γ_e and γ_n denote respectively the electronic gyromagnetic ratio and the nuclear one respectively; $\hbar$ and k_B are respectively the Planck's constant divided by 2π and the Boltsmann's constant; T is the absolute temperature.

Fig.5 shows the concentration dependence of η at 793K, which was calculated by the experimental values of K and T_1. The region of larger η(~0.95) (from 20 to 50 at.% Tl) is surrounded by that of smaller η (~0.75) (up to 20 at.% Tl and beyond 50 at.% Tl). The reproducibility of η is within 5%. It is well known that the smaller value of η for typical metals is derived from the effects of electron-electron interactions and core polarization[17]. The small value of η for pure liquid Li itself may be derived from such effects. However, comparing the η in Fig.5 with the K in Fig.1 and the T_1 in Fig.3, at least up to 50 at.% Tl, the behavior of η seems to be dominated by that of K which indicates the large charge transfer from Li atom to Tl one. The mechanism of electron conduction was discussed with the relation to the value of η[16]. According to this analysis, the localization of electrons starts when η >5. The present value of η is far smaller than this critical value. Therefore, in spite of the progress of charge transfer, conduction electrons in liquid Li-Tl alloys do not show so significant localized character. This is supported also from the fact that the electrical resistivity of liquid Li-Tl alloys shows the maximum value of only 175 μΩcm[18], which is a far smaller value than the onset value of electron localization[11]. Probably the decrease of K and the increase of η from 20 to 50 at.% Tl may be interpreted as the loss of s-electron density at Li nucleus and the increase of the p-electrons at Tl atoms which seem to form anions and contributes to the electron conduction. It is a future problem to solve the relation

among such a charge transfer, electron conduction and the structure and the life time of ionic structural unit.

5. Conclusion

The Knight shift, K, and the relaxation time, T_1, measured in the present study, reveals that the ionic structural unit is present in liquid Li-Tl alloys due to the charge transfer effect. On the other hand, the Korringa enhancement factor, η, indicates that the conduction electrons are not Brownian particles like but rather free electron like. Therefore, it can be considered that the life time of the ionic unit is not so long though it exists surely. The strength of ionic unit in liquid Li-Tl alloys seems to be weaker compared with that in liquid Li-In and Li-Ga alloys judging from the existence of the back donation of electronic charge beyond 50 at.% Tl and the large temperature dependence of the Knight shift from 20 to 50 at.% Tl.

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Captions for figures

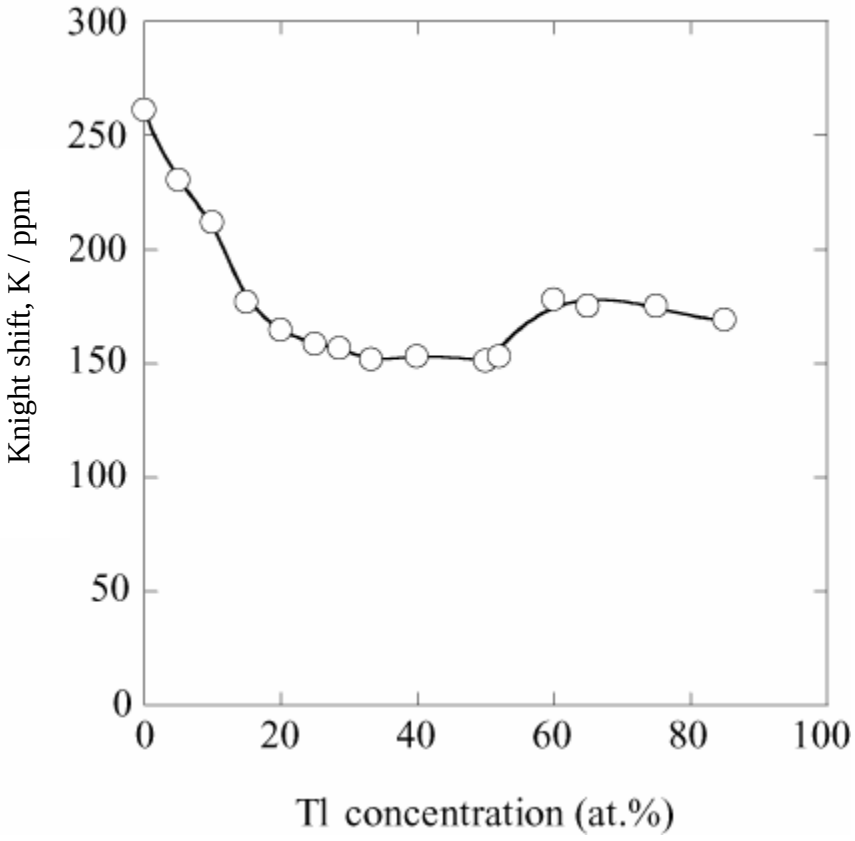
Fig. 1 The concentration dependence of the ^{7}Li Knight shift, K, for liquid Li-Tl alloys at the temperature 10K higher than the liquidus temperature. The line is the fitted curve. The error is within the size of data points.

Fig. 2 The concentration dependence of the temperature coefficient of the Knight shift, dK/dT, for liquid Li-Tl alloys at 793K. The line is the aide for the eye. The line is the fitted curve. The error is attached to the data points.

Fig. 3 The concentration dependence of the spin-lattice relaxation time, T_1, for liquid Li-Tl alloys at 793K. The line is the fitted curve. The line is the fitted curve. The error is within the size of data points.

Fig. 4 The concentration dependence of the relative contact density at ^{7}Li nucleus, $\delta(C)$, for liquid Li-Tl alloys at the temperature 10K higher than the liquidus temperature. The line is the fitted curve. The line is the fitted curve. The error is within the size of data points.

Fig. 5 The concentration dependence of the Korringa enhancement factor for liquid Li-Tl alloys at 793K. The line is the aide for the eye. The line is the fitted curve. The error is within the size of data points.



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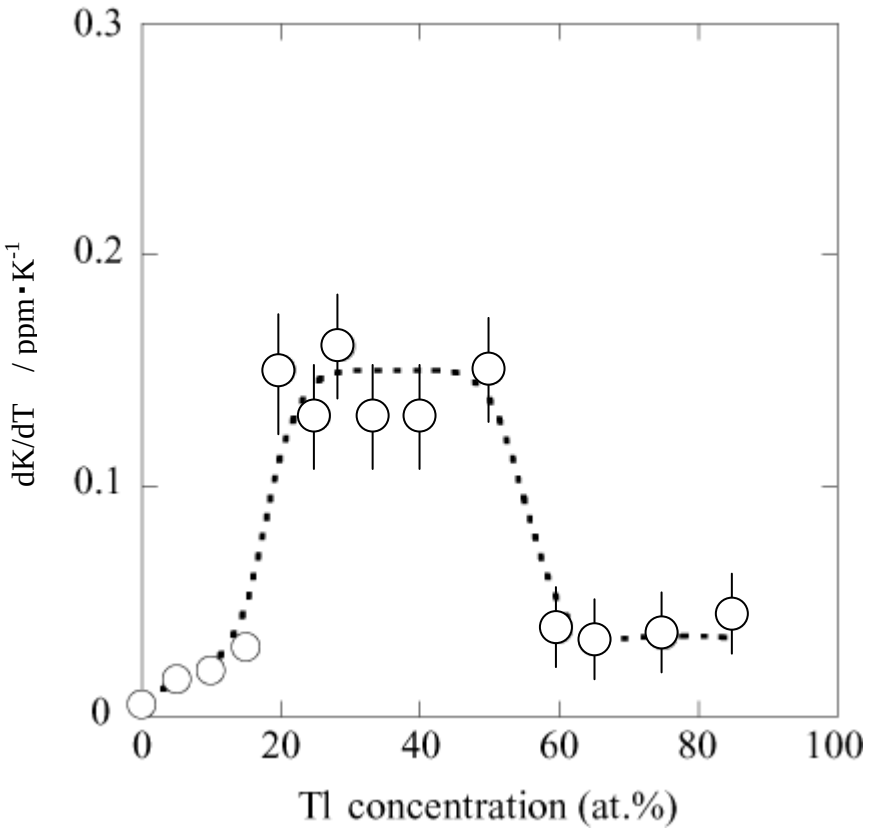
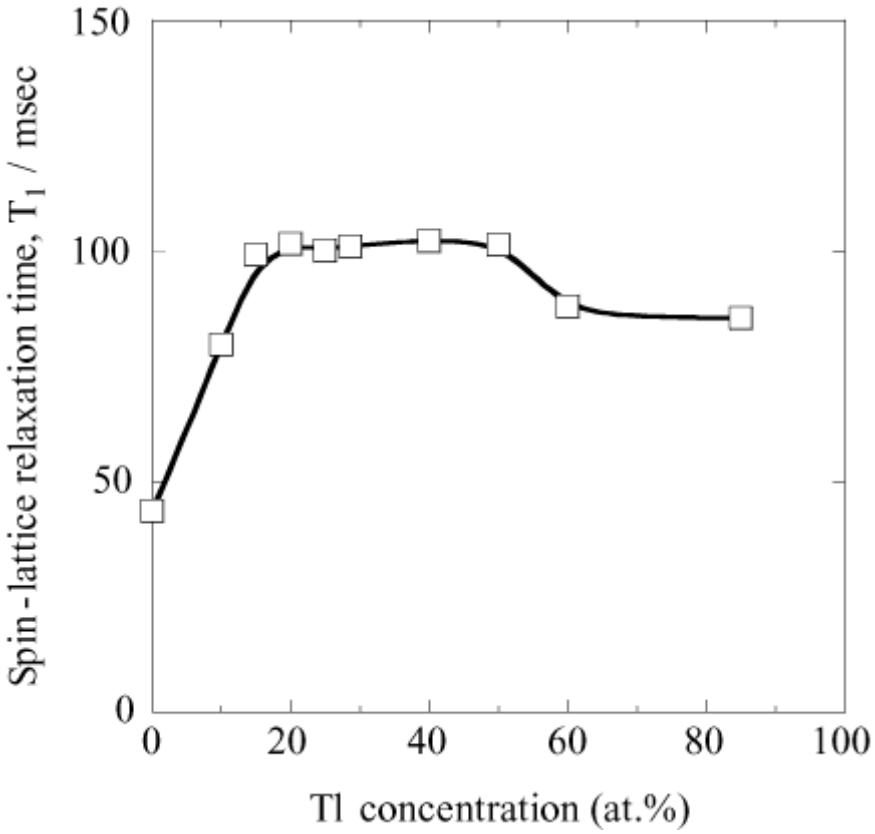


Fig. 2 The concentration dependence of the temperature coefficient of the Knight shift, d*K*/d*T*, for liquid Li-Tl alloys at 793K. The line is the aide for the eye. The error is attached to the data points.



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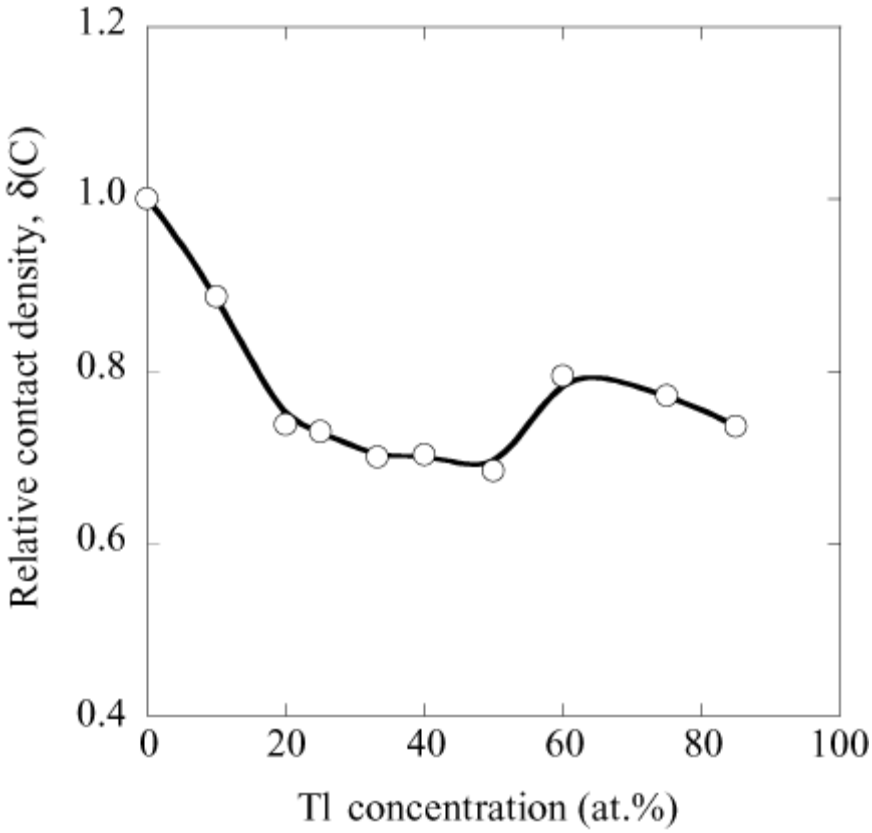

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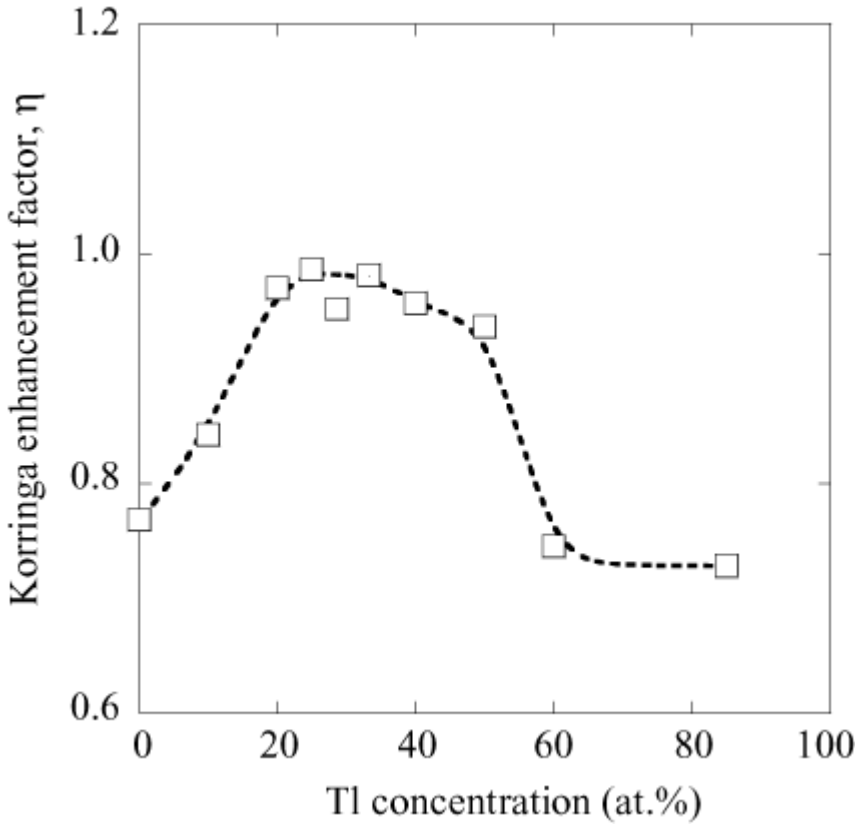

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