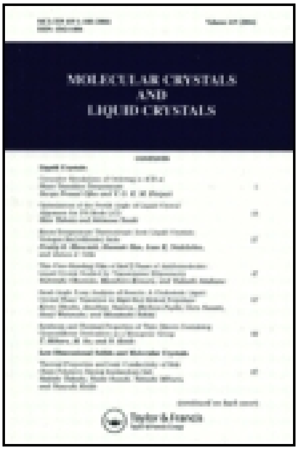


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Electron Donor-Acceptor Aspect of Superconductivity in Metal-$C_{60}$ Complexes

Reiko Notoya [a]
[a] Catalysis Research Center, Hokkaido University, Sapporo, Japan

To cite this article: Reiko Notoya (1996): Electron Donor-Acceptor Aspect of Superconductivity in Metal-$C_{60}$ Complexes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 285:1, 193-198

To link to this article: http://dx.doi.org/10.1080/10587259608030800

*Mol. Cryst. Liq. Cryst.*, 1996, Vol. 285, pp. 193–198
Reprints available directly from the publisher
Photocopying permitted by license only

# ELECTRON DONOR-ACCEPTOR ASPECT OF SUPERCONDUCTIVITY IN METAL-$C_{60}$ COMPLEXES

REIKO NOTOYA
Catalysis Research Center,Hokkaido University,Sapporo,Japan

Abstract The electron donor-acceptor aspect applies to the bonds in metal-doped fullerene $M_3C_{60}$. The superconductivity in $M_3C_{60}$ may be assumed to be related to the electron accepting property $\varepsilon_i$ of alkali-metal ion M.The value of transition temperature Tc in $M_3C_{60}$ quoted from the literature showed a good linear relation with the sum of $\varepsilon_i$ for $M_3$.

## INTRODUCTION

The superconductivity in potassium-doped fullerene had been found by Hebard et al at 1991[1] and that in the other metal-doped fullerene was also published within one year by some groups. But,after that there was no novelty concerning the superconductivity in the fullerene complex and the highest transition temperature Tc still remained about 33 K for $RbCs_2C_{60}$ which was quoted from a series of works done at 1991-1992, except for 48 K for $RbTl_2C_{60}$.

On the other hand, the electron accepting property $\varepsilon_i$ of a mono-atomic cation i could be determined on the basis of an empirical rule concerning the solvation energies in various solvents.[2] It has been known that this property was very useful for estimating quantitatively the bond energies of various dative bonds in metal-organic complexes, metal-halides in a gas phase, and the catalytic activities of metal-cations in homogeneous and heterogeneous systems and so forth.[3]

In this paper the electron donor-acceptor aspect applies to the bonds in the complex $M_3C_{60}$ of alkali-metals and fullerene. The superconductivity may be assumed to be related to the electron accepting property of the alkali-metal ions $M_3$. A good linear relationship is shown between Tc in $M_3C_{60}$ and the sum of $\varepsilon_i$ for $M_3$, with a few exceptions. The former values used in this work have been determined by Tanigaki et al[4] and Fleming et al.[5] The linear relationship will be useful for obtaining some information on the further findings of new superconductors of metal-fullerene complexes.

First, this paper describes the electron donor-acceptor concept briefly and then the relation of the sum of $\varepsilon_i$ for $M_3$ on the basis of this concept with Tc in $M_3C_{60}$.

## ELECTRON DONOR ACCEPTOR CONCEPT

The absolute values of the donating and accepting properties of monoatomic ions were determined by Notoya et al.[1] on the basis of an empirical rule concerning the solvation energy of a monoatomic ion and the dissociation energy of halides.Then we found also that the electron donor acceptor aspect could be applicable to the interactions between solute-solvent,in concentrated solution[3] and in fused salts[6] and interactions between cation-substrate in organometallic compounds[3] and in biologically important substances[7] and to various types of catalysis[3] in the last decade.

The solvation of an ion is one of the most difficult problems remained unsolved still now, because the electrostatic energy involved in the real free energy of solvation of an ion can not be determined as the concrete quantity even for some of the most popular solvents,which Schwabe et al. mentioned[8] Strictly speaking at a thermodynamic point of view,we can not split the real free energy of solvation of an individual ion into the chemical and the electrostatic terms,as pointed out by Guggenheim at 1929. However, we found out that the difference in the standard chemical or real free energy of solvation between two different ions in the same solvent, with each divided by the valence,is a quantity calculable by a thermodynamic cycle.

The standard real or chemical free energy of solvation of ion i for solvent s may be defined by the free energy change for a transfer to the gas phase g from solution, $\Delta\overline{G}^{\circ}_{i,g\leftarrow s}$ or $\Delta G^{\circ}_{i,g\leftarrow s}$, which may be given by the difference in the electrochemical or chemical potential of the ion between the two phases,

$$\Delta\overline{G}^{\circ}_{i,g\leftarrow s} = \overline{\mu}^{\circ}_{i,g} - \overline{\mu}^{\circ}_{i,s} \tag{1}$$

$$\Delta G^{\circ}_{i,g\leftarrow s} = \mu^{\circ}_{i,g} - \mu^{\circ}_{i,s} \tag{2}$$

where the superscript $^{\circ}$ denotes the standard state.The surface potential $\chi_s$ of the solvent may be given by

$$\Delta\overline{G}^{\circ}_{i,g\leftarrow s} = \Delta G^{\circ}_{i,g\leftarrow s} - z_i F\chi_s \tag{3}$$

where $z_i$ is the valence of ion i and F the Faraday.

The relative standard free energy of solvation of ion i in solvent s, ${}^{i}\Delta^{j}\{\Delta G^{\circ}_{g\leftarrow s}/z\}$ can be defined as following, at a given temperature as referred to a definite reference ion j in the same solvent

$${}^{i}\Delta^{j}\{\Delta G^{\circ}_{g\leftarrow s}/z\}=\{\Delta\overline{G}^{\circ}_{i,g\leftarrow s}/z_i\}-\{\Delta\overline{G}^{\circ}_{j,g\leftarrow s}/z_j\}$$

$$=\{\Delta G^{\circ}{}_{i,g\leftarrow s}/z_i\}-\{\Delta G^{\circ}{}_{j,g\leftarrow s}/z_j\} \qquad (4)$$

with each divided by the valence of the ion.

The standard real free energy of formation of ion i and the electron in the gas phase from its pure substance $\Delta\overline{G}^{\circ}{}_i$ can be expressed by use of $\Delta\overline{G}^{\circ}{}_{i,g\leftarrow s}$ and the absolute standard electromotive force $\Phi^{\circ}{}_{i,s}$ of the ion/pure substance of electrode in solvent s,

$$\Delta\overline{G}^{\circ}{}_i = \Delta\overline{G}^{\circ}{}_{i,g\leftarrow s} + z_i F\Phi^{\circ}{}_{i,s} \qquad (5)$$

where $\Phi^{\circ}{}_{i,s}$ is given by the difference in electrochemical potential of the electron in the gas phase and in the electrode m as

$$F\Phi^{\circ}{}_{i,s} = \overline{\mu}^{\circ}{}_{e,g} - \overline{\mu}^{\circ}{}_{e,m} \qquad (6)$$

Using Equations(5) and (6) for ions i and j,we obtain

$${}^{i}\Delta^{j}\{\Delta G^{\circ}{}_{g\leftarrow s}/z\}=\{\Delta\overline{G}^{\circ}{}_i/z_i\}-\{\Delta\overline{G}^{\circ}{}_j/z_j\} - FE^{\circ}{}_{ij,s} \qquad (7)$$

where $FE^{\circ}{}_{ij,s}=\Phi^{\circ}{}_{i,s}-\Phi^{\circ}{}_{j,s}$. In this way ${}^{i}\Delta^{j}\{\Delta G^{\circ}{}_{g\leftarrow s}/z\}$ can be expressed in terms of the well-defined measurable thermodynamic quantities $\Delta\overline{G}^{\circ}{}_i$, $\Delta\overline{G}^{\circ}{}_j$, and $FE^{\circ}{}_{ij,s}$. The numerical values for $\Delta\overline{G}^{\circ}{}_i$ and $\Delta\overline{G}^{\circ}{}_j$ can be calculated by use of the free energy of atomization of the pure substance and the ionization potential for the cations or the electron affinity for the anions,and $FE^{\circ}{}_{ij,s}$ obtained from the literatures, for example, the thermodynamic tables compiled by National Bureau of Standard[9] and Samsonov[10] etc. and the electrochemical data books compiled by Bard[11] and Dobos[12] etc,for a variety of ionic species and solvents.

On the basis of Equation(7), we found the very good linear relations between ${}^{i}\Delta^{j}\{\Delta G^{\circ}{}_{g\leftarrow w}/z\}$ in water and $I_i/z_i$ for the cations of each group which is given by the regression line as shown in FIGURE 1

$${}^{i}\Delta^{j}\{\Delta G^{\circ}{}_{g\leftarrow w}/z\}= \rho_w(I_i/z_i) - A_{jw} \qquad (8)$$

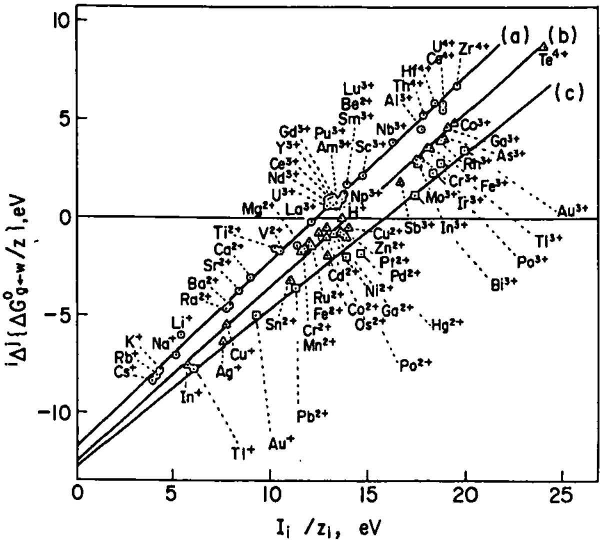
where $\rho_w$ for each straight line is a constant characteristic of water and $-A_{jw}$ equals ${}^{i}\Delta^{j}\{\Delta G^{\circ}{}_{g\leftarrow w}/z\}$ for an ideal ion whose ionization energy equals zero.

In this way for any solvent available the same type of linear relation as Equation(8) is obtained for the cations of each group,which is given by the regression line

$$ {}^{i}\Delta^{j}\{\Delta G^{\circ}_{g\leftarrow s}/z\} = \rho_{s}(I_{i}/z_{i}) - A_{js} \qquad (9) $$

where $\rho_s$ is a constant characteristic of solvent s and $-A_{js}$ equals ${}^{i}\Delta^{j}\{\Delta G^{\circ}_{g\leftarrow s}/z\}$ for an ideal ion of $I_i = 0$. Equation (9) will be called hereafter rule II for the solvation of mono-atomic cations, because another linear relation had been found by us and called as rule I.

The cations of the three groups can be classified by four criteria$^2$, one of which is concerning the periodic table of the elements represented in FIGURE 2.



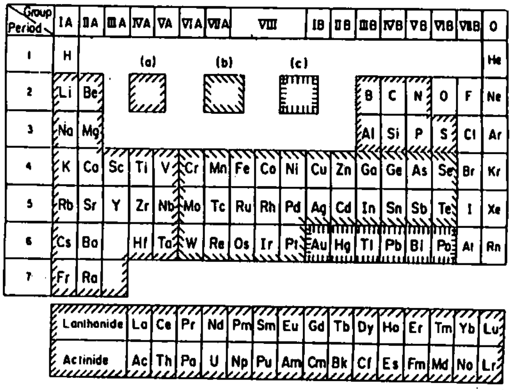


FIGURE 1 Relation between ${}^{i}\Delta^{j}\{\Delta G^{\circ}_{g\leftarrow w}/z\}$ and $I_i/z_i$ at 25°C for (a,b or c)group cations with j=H$^+$; ○,△or□.

FIGURE 2 Classification of monoatomic cations into (a),(b) and (c)groups in the periodic table.

In order to estimate the value of $\Delta G^{\circ}_{i,g\leftarrow s}$ for an individual ion, we introduced an extrathermodynamic assumption that the ideal ion of the rare gas type, (a) group, has no chemical interaction with any solvent, i.e.

$$(\Delta G^{\circ}_{i,g\leftarrow s}/z_i)_{Ii=0} = 0 \tag{10}$$

Then we obtain from Equation(8)

$$\Delta G^{\circ}_{i,g\leftarrow s}/z_i = \varepsilon_i \rho_s^a \tag{11}$$

for an individual ion in any group, where

$$\varepsilon_i = I_i^a/z_i \tag{12a}$$

$$\varepsilon_i = (\rho_w^b/\rho_w^a)[(I_i^b/z_i)+\{(A_{jw}^a-A_{jw}^b)/\rho_w^b\}]$$

$$= 0.936\{(I_i^b/z_i)-0.94\}, \text{eV} \tag{12b}$$

$$\varepsilon_i = (\rho_w^c/\rho_w^a)[(I_i^c/z_i)+\{(A_{jw}^a-A_{jw}^c)/\rho_w^c\}]$$

$$=0.862\{(I_i^c/z_i)-1.43\}, \text{ eV} \tag{12c}$$

for the ions of the respective group.

The density functional theory developed by Parr etal[13] gives us the expression of the chemical potential of electron in a particle. By use of this theory, the extrathermodynamic assumption that the ionization energy of an ideal ion equals zero, was verified by Matsuda et al.[14]

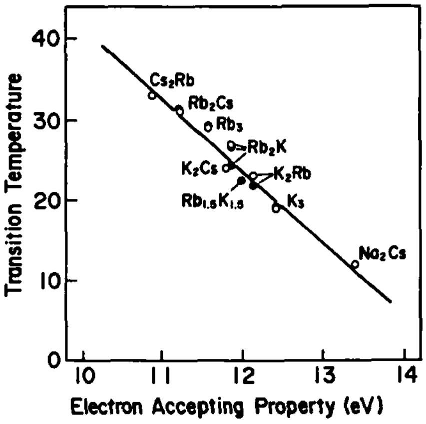


FIGURE 3 Relation between sum of $\varepsilon_i$ for $M_3$ and Tc in $M_3C_{60}$ quoted from refs.4 and 5;○ and ●.

## LINEAR RELATION BETWEEN $\varepsilon_i$ AND Tc

FIGURE 3 shows a good linear relation between the totals of $\varepsilon_i$ for $M_3$ and Tc values in $M_3C_{60}$, which were reported by Tanigaki et al.[4] Excepting the three cases of $Li_2CsC_{60}$, $Na_2RbC_{60}$ and $Na_2KC_{60}$, the linear relation can be expressed with the regression coeffisient ≧ 0.982 as follows,

$$Tc = 137 - 9.45\,\varepsilon_i \qquad (13)$$

The above three compounds have only less than 2% of face-centred cubic phases according to the result showned by Tanigaki et al.[4] The linearity was almost unchanged by exchanging the Tc values for those determined by Fleming et al.[5] in some compounds. It is remarkable that the line includes eventhe point for $Na_2Cs_{60}$ having only 8% f.c.c. structure.

Conclusively, $\varepsilon_i$ proved to be very useful parameter for obtaining information on superconductivity in metal-$C_{60}$ complexes.

## REFERENCES

1. A.F.Hebard, M.J.Rosseinsky, R.C.Haddon, D.W.Murphy, S.H. Glarum, T.T.M.Paltra, A.P.Ramirez & A.R.Kortan, Nature, 350, 18 Apr., 600(1991).
2. R.Notoya and A.Matsuda, J.Phys.Chem., 89, 3922(1985).
3. R.Notoya, Trends in Phys.Chem., 4, 219(1994).
4. K.Tanigaki, I.Hirosawa, T.W.Ebbesen, J.Mizuki, Y.Shimakawa, Y.Kubo, J.S.Tsai&S.Kuroshima, Nature, 356, 2 Ap., 419(1992).
5. R.Fleming, A.Ramirez, M.Rosseinsky, D.Murphy, R.Haddon, S.M. Zahurak&A.Makhija, Nature, 352, 29 Au., 787(1991).
6. R.Notoya and A.Matsuda, Nippon Kagaku Kaishi, 990(1982).
7. R.Notoya and A.Matsuda, Denki Kagaku, 56, 1096(1989).
8. K.Schwabe, C.Queck, Abh.Saechs.Akad.Wiss.Leipzig, Math.-Naturwiss.Kl.53, 104(1979).
9. Natl.Inst.Stand, Selected Values of Chemical and Thermodynamic Properties, No.500, (1952).
10. G.V.Samsonov, Svoistva Elementov(Metallurgia, Moscow, Part I, 1976)p.14.
11. A.J.Bard, Encyclopedia of the Elements, 1-9&11-15(Marcel Dekker, New York1973-).
12. D.Dobos, Electrochem.Data Book(Elsevier, Amsterdam1975).
13. R.G.Parr, Electron Distributions and the Chemical Bonds, (Plenum Press, New York, 1982)p.95.
14. Fundamental Problems of Interface Structure & Electrochem.Kinetics, (Hokkaido Univ.Press., Sapporo, 1988)p.32.