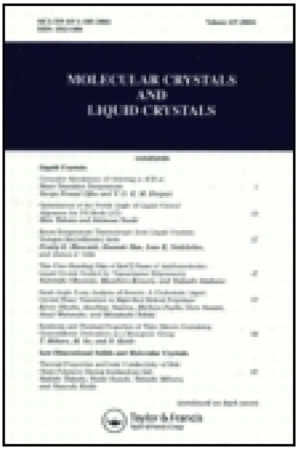

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

A New Relation Between the Melting Points of Organic Solids and Their Reactivity

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Version of record first published: 13 Dec 2006.

To cite this article: Mohsin Qureshi , S. Ashfaq Nabi , Ali Mohammad & Pushkin M. Qureshi (1982): A New Relation Between the Melting Points of Organic Solids and Their Reactivity, Molecular Crystals and Liquid Crystals, 88:1-4, 13-18

To link to this article: http://dx.doi.org/10.1080/00268948208072580

Mol. Cryst. Liq. Cryst., 1982, Vol. 88, pp. 13–18
0026-8941/82/8801-0013/$06.50/0

A New Relation Between the Melting Points of Organic Solids and Their Reactivity

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(*Received March 25, 1982*)

A new relation between the melting points of organic solids and their reactivity has been established. The relation follows $\sqrt{\xi} = -k \log Mp + C$ where ξ is the thickness of the colored boundary Mp is the melting point of the organic solid and k and C are constants.

The Rastogi technique[1] offers a simple and fast method to study the reactivity of organic solids. The solid substance is introduced into a glass capillary of uniform bore. Care is taken that the particle size is uniform and packing is done in a reproducible manner. After the first substance A has been introduced a second substance B is also introduced through the other end. At the junction of A and B the chemical reaction starts and if the product is colored the length of the colored boundary ξ is the measure of the rate of reaction. The chemical reaction between A and B is fast and therefore reaction rate is controlled by the diffusion of A or B across the product layer AB. According to Rastogi the rate of diffusion is a function of the particle size, the packing and the temperature. But he has not mentioned the effect of the melting point of the reactant on the rate of diffusion and hence on the diffusion controlled rate of solid state chemical reactions.

While making a systematic study of the rate of reaction of organic solids using the Rastogi technique we noticed that if organic substances B, C, D, E etc. with melting points m_B, m_C, m_D, m_E etc. were allowed to

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react with *A* having a melting point m_A then the reactivity of *B*, *C*, *D*, *E* etc. depended considerably, if not entirely, on their melting points. A plot of melting points m_B, m_C, m_D, m_E versus their reactivities as determined by the Rastogi technique gave curves similar to Figure 1A. At first the reactivity decreases rapidly as the melting point increases and later on it decreases slowly. Thus we obtain two intersecting straight lines. What is surprising is that the point of intersection nearly corresponds to m_A. We have repeated these experiments with numerous compounds (Table I) and in all cases we noticed similar trends (Figures 1A–5A). A plot of $\sqrt{\xi}$ vs. log m_B, log m_C, log m_D . . . etc. gives a straight line (Figures 1B–5B) and the following equation is followed.

$$\sqrt{\xi} = -k \log Mp + C \tag{1}$$

where *K* and *C* are constants and *Mp* is the melting point of the substrate. This is a novel and interesting relation which emphasizes, for the first time, the effect of melting point on the reactivity of organic solids.

A search of literature shows that no such relation has been reported earlier.[2-5] Some references are available in the literature on the role of the melting point upon the reactivity of a solid. It was noticed[6-8] that as the reaction temperature approached the melting point the reactivity of an inorganic solid increased. Link and Wood[6] studied reactions occurring between the alkali halides in the solid state and noticed that there was no reaction in the solid state if the reaction temperature was more

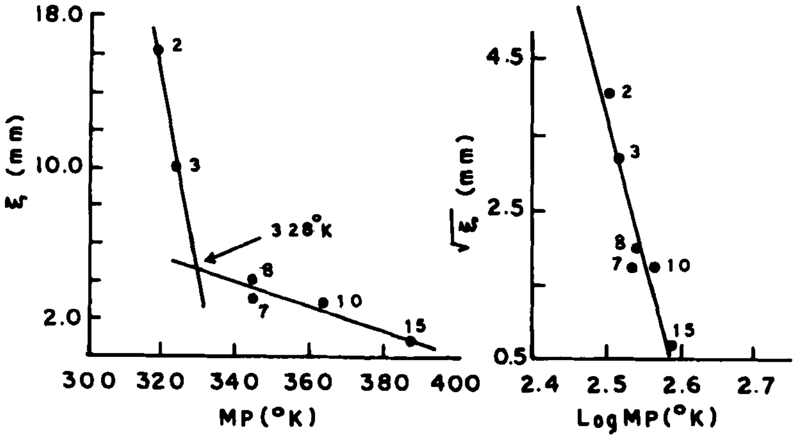

FIGURE 1(a) Plot of ξ vs. melting point (*Mp*) for the reaction of 5 with various organic compounds at 313°K after 3 hours.

FIGURE 1(b) Plot of $\sqrt{\xi}$ vs. log *Mp* for the reaction of Figure 1(a).

TABLE I

Organic compounds used in this study with their serial numbers and melting points

S. No.	Name of the compound	Melting point (°K)
1	*p*-Toluidine	317
2	*o*-Nitrophenol	318
3	1-Chloro-2,4-Dinitrobenzene	323
4	Indole	325
5	Diphenylamine	327
6	*m*-Phenylenediamine	336
7	*o*-Nitroaniline	344
8	2,4-Dinitrotoluene	344
9	*p*-Dimethylaminobenzaldehyde	346
10	*m*-Dinitrobenzene	363
11	Catechol	374
12	*o*-Phenylenediamine	376
13	*N*-Phenyl-2-Naphthylamine	380
14	*β*-Naphthylamine	384
15	*p*-Nitrophenol	387
16	*m*-Nitroaniline	387
17	Benzidine	400
18	*p*-Phenylenediamine	413
19	*m*-Nitrobenzoic acid	417

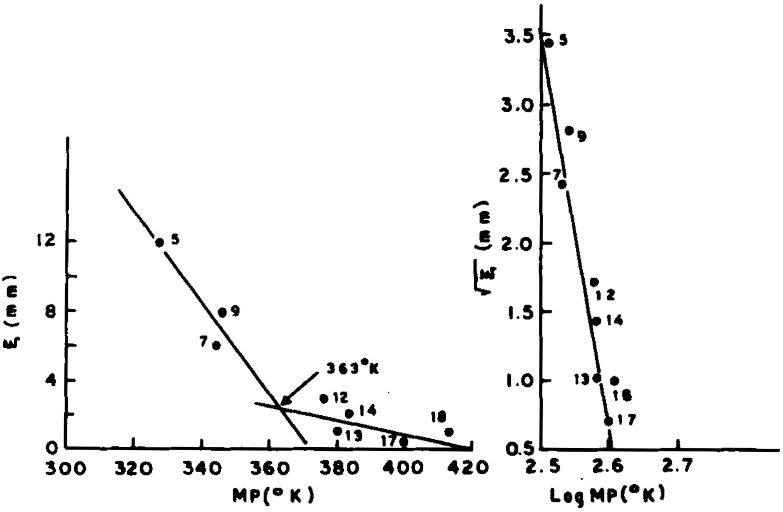

FIGURE 2(a) Plot of ξ vs. melting point (Mp) for the reaction of 10 with various organic compounds at 323°K after 2 hours.

FIGURE 2(b) Plot of $\sqrt{\xi}$ vs. log Mp for the reaction of Figure 2(a).

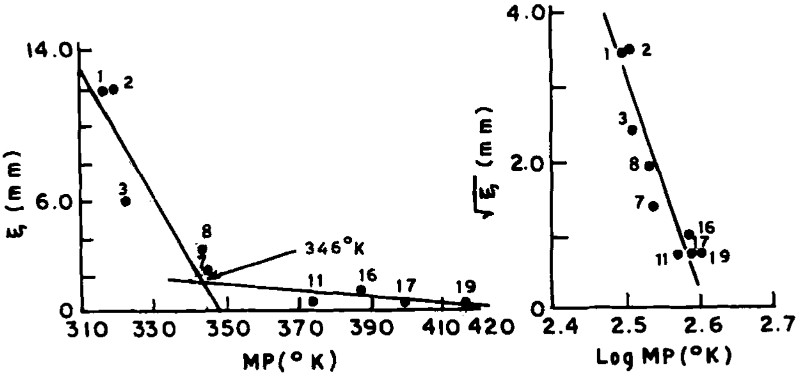

FIGURE 3(a) Plot of ξ vs. melting point (*Mp*) for the reaction of 9 with various organic compounds at 313°K after 4 hours.

FIGURE 3(b) Plot of $\sqrt{\xi}$ vs. log *Mp* for the reaction of Figure 3(a).

than 200° below the melting range and there was likely to be considerable reaction if the reaction temperature was 100° below the melting range. Huttig[7] related the reactivity to the melting point, the maximum reactivity corresponding with the same fraction of the melting point. Link and Wood have not explained their results and they have not postulated any relation between the reactivity and the melting point. According to Tammann[9] for additively reacting systems the reaction temperatures often coincide approximately with the temperature at

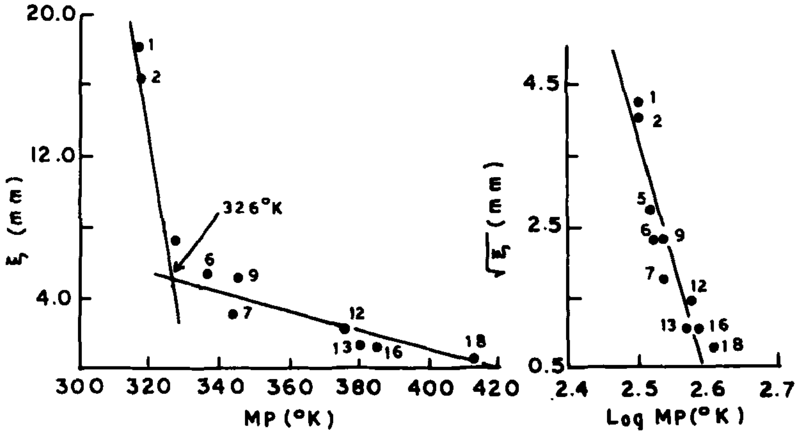

FIGURE 4(a) Plot of ξ vs. melting point (*Mp*) for the reaction of 3 with various organic compounds at 313°K after 3 hours.

FIGURE 4(b) Plot of $\sqrt{\xi}$ vs. log *Mp* for the reaction of Figure 4(a).

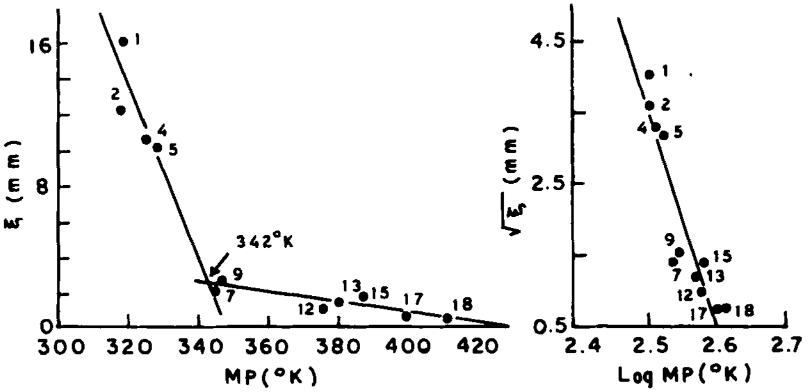

FIGURE 5(a) Plot of ξ vs. melting point (Mp) for the reaction of 8 with various organic compounds at 313°K after 3 hours.
FIGURE 5(b) Plot of $\sqrt{\xi}$ vs. log Mp for the reaction of Figure 5(a).

which self diffusion becomes appreciable with one of the reactants. A relation of the temperature of measurable self diffusion to the absolute temperature was first proposed by Tammann and Mansuri.[10] The ratio between two temperatures is approximately 0.3 for metals, 0.5 for inorganic substances and 0.9 for organic compounds.

It is not possible for us to derive Eq. (1) from theoretical consideration but a rough qualitative picture is given below. According to the simplified theory of Lennard-Jones[8] at $T = 0$ the lattice executes zero point vibrations about positions of equilibrium. With progressive rise in temperature the amplitudes increase until a point is reached when an atom moves out of its vibrating region and its place is taken up by another atom. The re-arrangement from a state of order to state of disorder is identified with fusion and corresponds to maximum reactivity. Thus the mobility is decreased as we move away from the melting point of an organic solid. For instance, if an organic solid-state reaction is studied at 40°C with the same substrate then a reactant whose melting point is 50°C will be more reactive than a substance whose melting point is 60°C. The rate of reaction is determined by the thickness of the colored boundary and this depends upon two independent factors: (1) The number of mobile species of B, C, D or E (2) The diffusion of the mobile species through the product layer. Both factors decrease with increase in melting point. If one assumes that each factor

$$\alpha \log \frac{1}{Mp} \text{ it follows that } \xi = K\left[\log\left(\frac{1}{Mp}\right)\right]^2 + C. \qquad (2)$$

It is possible that A may also diffuse but since we are comparing the reactivity of B, C, D, E etc. with A the diffusion of A is a common parameter which may not be considered in this comparative study.

Acknowledgment

The authors thank Prof. W. Rahman for research facilities, C.S.I.R. (India) is thanked for financial assistance to Mr. P. M. Qureshi.

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