Thermochimica Acta, 184 (1991) 131–139
Elsevier Science Publishers B.V., Amsterdam

Thermogravimetric analysis of organometallic films

Galo Cárdenas T. [a,1] and L.H. Tagle D. [b]

[a] *Departamento de Química, Facultad de Ciencias, Universidad de Concepción, Casilla 3-C, Concepción (Chile)*

[b] *Departamento de Química Orgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 6177, Santiago (Chile)*

(Received 31 October 1990)

Abstract

The thermal behaviour of organometallic films was studied by thermogravimetric analysis (TGA) between 25 and 550 °C at 10 °C min^{-1}. From the kinetic data obtained by TGA, it was found that the thermostability of these metal films depends on the metal and solvent. For palladium films the stability decreases in the following order: acetone, 2-butanone, dimethylformamide (DMF), 2-propanol, dimethyl sulphoxide (DMSO), tetrahydrofuran (THF), ethanol. For germanium films the stability decreases in the order acetone, 2-propanol, DMF, ethanol, 2-butanone, THF. For indium films the order of decreasing stability is DMF, ethanol, acetone, 2-butanone, DMSO, THF, 2-propanol.

The variation in thermal stability is discussed in relation to the various solvents used and comparisons are made with poly(methyl methacrylates) containing the same metals; the activation energies of the thermal degradation are comparable within certain limits for the palladium, germanium and indium films. The reactions were found to be zero order for the thermal decomposition of these films. The pre-exponential factors and decomposition temperatures were determined.

INTRODUCTION

The thermal stability of palladium, germanium and indium thin films is very important owing to their potential applications as semiconductors [1] and in solar cell devices [2].

By studying the thermal behaviour of these films of low carbon content as a function of the weight loss and the temperature of the system, it is possible to obtain information about their stability. Another relevant feature is related to the preparation of the films; so far, most of them have been prepared by sputtering and/or laser methods [3].

---

[1] Author to whom correspondence should be addressed.

0040-6031/91/$03.50 © 1991 – Elsevier Science Publishers B.V.

Thermogravimetric analysis has been used as a method to determine the activation energy and pre-exponential factor; a simple mechanism is assumed so that an uncomplicated rate expression can be used [4]. The activation energy values are within the range of those of metal poly(methyl methacrylates) [5] and also those of polystyrene and poly(α-methylstyrene) [4]. The stabilities are important in the synthesis of new materials for solar cells and optical sensors [6].

This is a new approach to the preparation of metal films with carbonaceous species from colloidal sols. The sols of palladium, germanium and indium were prepared with solvents such as acetone, 2-butanone, dimethylformamide (DMF), dimethyl sulphoxide (DMSO), tetrahydrofuran (THF), ethanol and 2-propanol.

EXPERIMENTAL

Colloid synthesis

The colloid was prepared by the previously reported chemical liquid deposition technique [7–9].

Metal films

The metal-like films were prepared by slowly dripping the corresponding colloidal sols onto a substrate. To increase the speed of solvent evaporation, a vacuum of 10^{-3}–10^{-4} Torr was used over 3 h. The dried films were analysed and their carbon content ranged between 1 and 5%.

Thermogravimetric analysis

The thermogravimetric data were obtained using a Perkin–Elmer TGS-1 thermobalance with a Perkin–Elmer UU-1 temperature program control. Samples (2–5 mg) were placed in aluminium pans and heated under nitrogen flow (50 ml min^{-1}) at 10 °C min^{-1} between 298 and 823 K.

RESULTS AND DISCUSSION

The synthesis of thin metal films by evaporation of colloidal sols has been recently reported [7–9]. The films showed a high metal content (85–90%) and they are easily prepared:

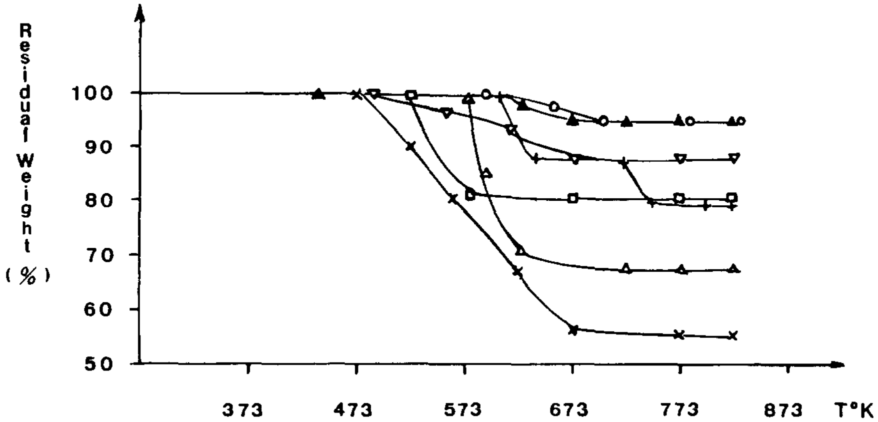
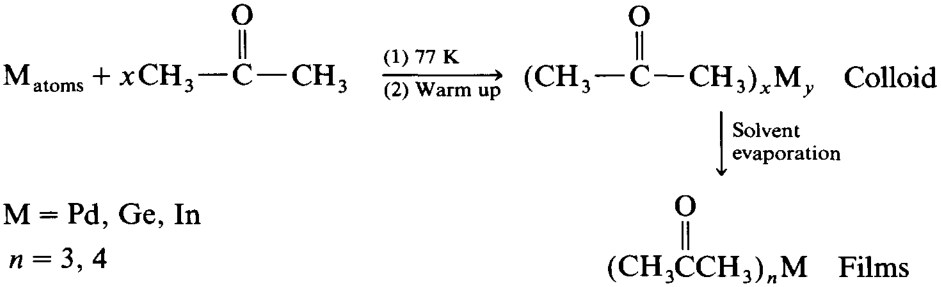


Fig. 1. Thermogravimetric curves of palladium films at a heating rate of 10 °C min^{-1}: △, Pd–acetone; □, Pd-2-butanone; +, Pd–DMF; ×, Pd–DMSO; o, Pd–THF; ▲, Pd–ethanol; ▽, Pd-2-propanol.



$$M_{\text{atoms}} + xCH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[\text{(2) Warm up}]{\text{(1) 77 K}} (CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3)_xM_y \quad \text{Colloid}$$

$$\downarrow \text{Solvent evaporation}$$

$$(CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3)_nM \quad \text{Films}$$

M = Pd, Ge, In

$n = 3, 4$

The most common feature accounting for the similarities in carbon content is the formation of chemical bonds between the metal and the solvents. The mass spectrometry data indicate that small (two or three unit) clusters of solvent are attached to the metal [10]. Figure 1 shows the change in sample weight as a function of time and temperature when palladium films are heated from 298 to 823 K. Figures 2 and 3 show the thermograms of germanium and indium films respectively. In Table 1 are listed the thermal decomposition kinetic parameters for each film obtained from the first marked change in the slope of the TG curves.

The palladium films degrade in one stage with a thermal decomposition temperature T_D of around 550 K. The Pd–THF, Pd–DMF and Pd-2-propanol films are very stable (see Fig. 1): Pd–THF displays 10% of the total weight loss at 823 K. Only Pd–DMF gives a higher activation energy, but this is still lower than for the ketones. Apparently, the ketones are strongly bonded to the metal which results in higher activation energies. However, Pd–DMSO, which has the lowest T_D, also has the lowest E.

Germanium films have similar T_D values but their E values are higher than those of palladium films. It appears that because of the greater

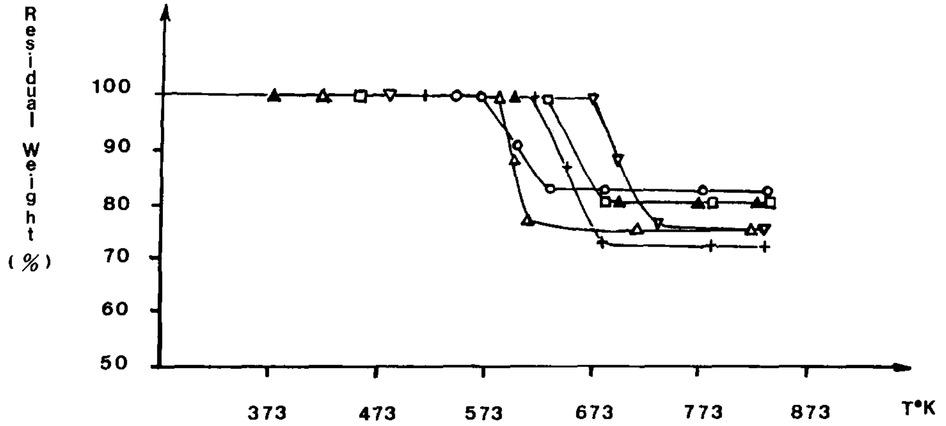


Fig. 2. Thermogravimetric curves of germanium films at a heating rate of 10 °C min^{-1}: △, Ge–acetone; □, Ge-2-butanone; +, Ge–DMF; ○, Ge–THF; ▲, Ge–ethanol; ▽, Ge–2-propanol.

difference in electronegativity between germanium and oxygen, than between palladium and oxygen, the Ge–O bond is more polarized than the Pd–O bond. The most stable film is Ge–THF with a total weight loss of 20% (see Fig. 2). Finally, indium films are also stable, In–2-propanol showing behaviour similar to that of Pd–THF. Most of the films, following a decomposition, display a 70% weight loss. In addition, the solvents containing carbonyl or sulphonyl groups have the highest E values. It seems likely that carbonyl groups are attached more strongly to the metals by M–O coordination.

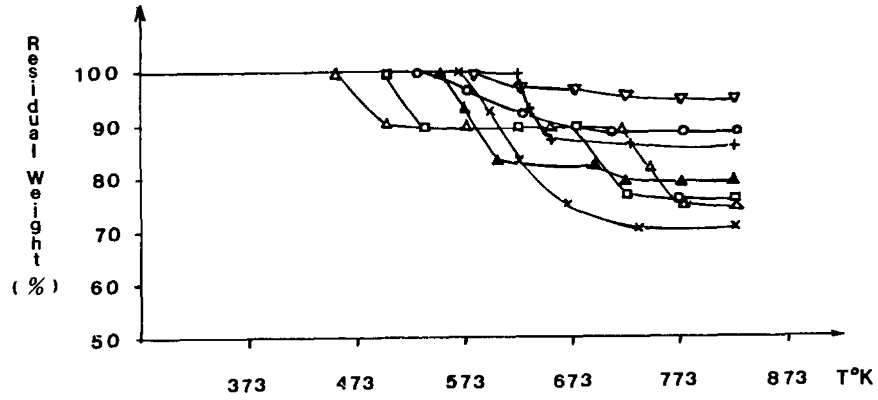


Fig. 3. Thermogravimetric curves of indium films at a heating rate of 10 °C min^{-1}: △, In–acetone; □, In–2-butanone; +, In–DMF; ×, In–DMSO; ○, In–THF; ▲, In–ethanol; ▽, In–2-propanol.

TABLE 1

Kinetic parameters for organometallic films

Films	n	E_a (kJ mol^{-1})	A (s^{-1})	T_D (K)
Pd–acetone	0	184.56	4.66	588
Ge–acetone	0	448.05	32.53×10^{10}	593
In–acetone	0	194.31	16.85×10^{6}	723
Pd–2-butanone	0	176.93	10.70	543
Ge–2-butanone	0	122.17	72.21×10^{4}	653
In–2-butanone	0	146.04	25.64×10^{6}	683
Pd–DMF	0	99.78	8.44	623
Ge–DMF	0	150.12	17.15×10^{7}	643
In–DMF	0	280.63	37.09×10^{10}	643
Pd–DMSO	0	27.44	3.01	533
In–DMSO	0	101.40	91.12×10^{3}	613
Pd–THF	0	26.83	1.98	656
Ge–THF	0	86.63	19.58×10^{2}	613
In–THF	0	74.57	6.58×10^{2}	673
Pd–ethanol	0	16.72	2.44	638
Ge–ethanol	0	122.17	72.22×10^{4}	653
In–ethanol	0	271.45	17.26×10^{10}	583
Pd–2-propanol	0	46.29	8.00	648
Ge–2-propanol	0	364.83	52.62×10^{8}	688
In–2-propanol	0	32.00	9.3	648

Considering that the decomposition reaction is irreversible, the rate-dependent parameters such as activation energy and reaction order may be calculated from a single experimental curve [11]. The specific rate constant k can be expressed in the Arrhenius form

$$k = Z \exp(-E/RT) \qquad (1)$$

where Z is the frequency factor, E the activation energy, R the gas constant and T the absolute temperature.

The thermal decomposition kinetics of the thermogravimetric weight loss can be described in terms of the following kinetic equation:

$$-\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(1-\alpha)^n \qquad (2)$$

where α is the fraction of the sample weight reacted at time t, n is the reaction order and k is the specific rate constant. The reaction rate $\mathrm{d}\alpha/\mathrm{d}t$ was calculated using a differential technique with a heating rate of 10 °C min^{-1} and temperature vs. sample weight-fraction data [12]. After combining eqns. (1) and (2) and incorporating v, the following expression can be obtained:

$$\beta = \ln\left[-\frac{\mathrm{d}\alpha/\mathrm{d}t}{v(1-\alpha)^n}\right] = \ln A - \frac{E}{RT} \qquad (3)$$

Assuming a first-order reaction model, a multiple regression program was used to plot β vs. $1/T$; a straight line should be obtained (see Fig. 4), and E and Z can be calculated from the slope and intercept respectively.

For all the metal films the linear relationship obtained suggests that the order of the decomposition reaction is zero. The coefficients of linear correlation vary from 0.917 to 0.997. The kinetic parameters E and Z calculated from these plots are summarized in Table 1.

In general, palladium, germanium and indium films prepared with solvents containing carbonyl groups exhibit higher E values which are similar to those reported by MacCallum for polystyrene [4]. Of course, each metal

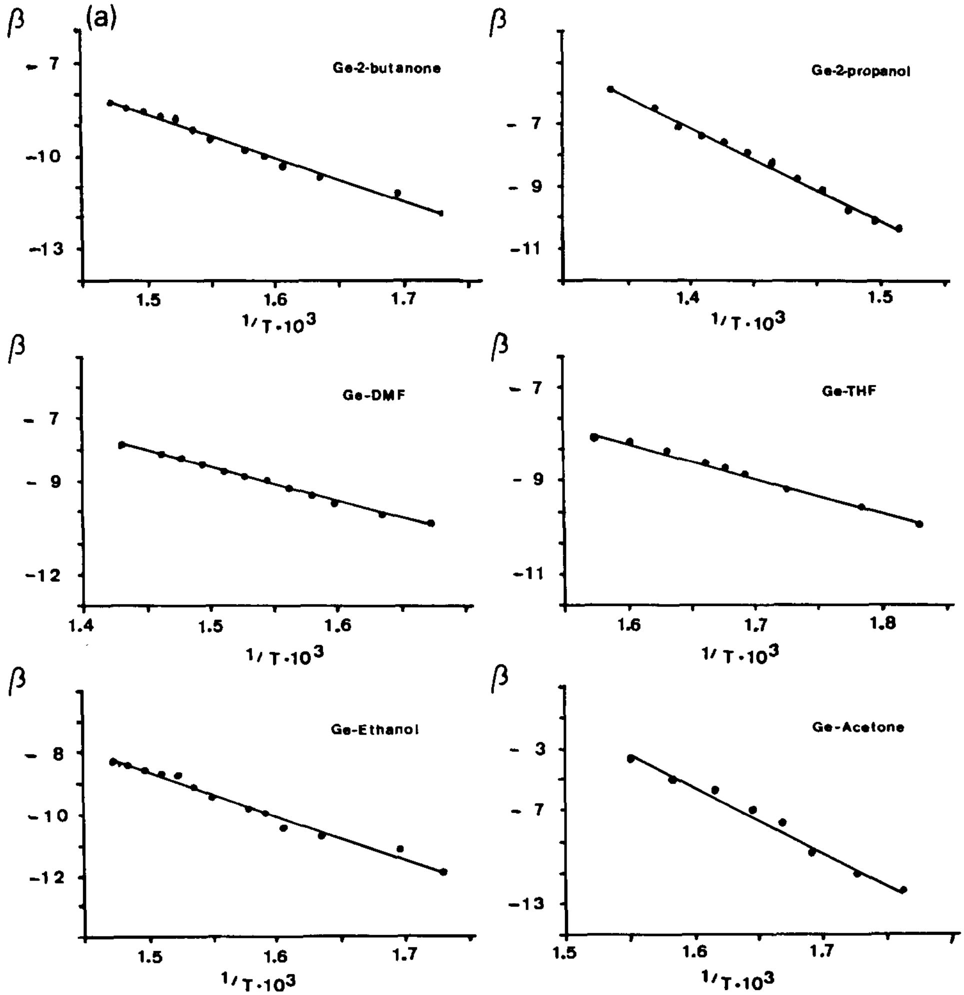


Fig. 4. Arrhenius plot for the thermal decomposition of thin metal films according to eqn. (3): (a) germanium thin films; (b) indium thin films; (c) palladium thin films.

behaves somewhat differently with each solvent, depending on the stability of the original colloid.

The order of the decomposition reaction for all the thin metal films is zero. This is the first report of the kinetic parameters related to the decomposition of thin metal films prepared from colloidal sols.

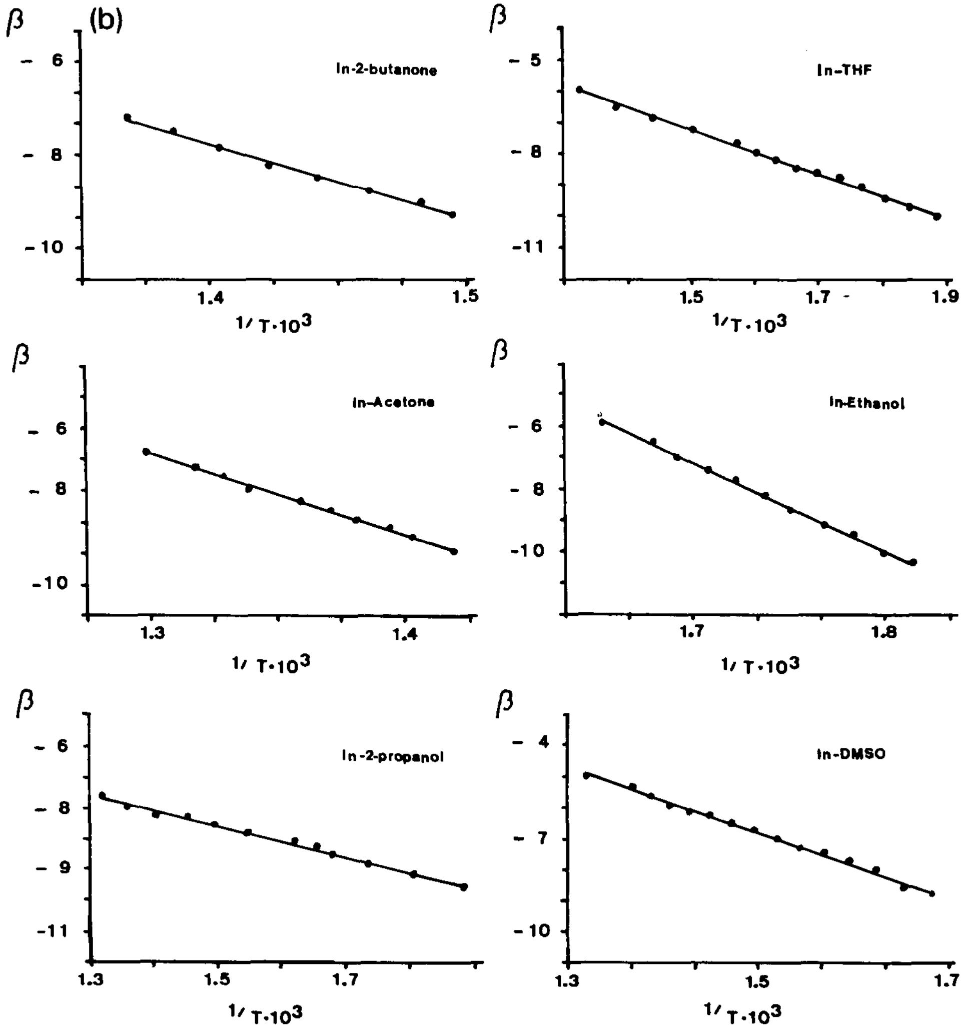


Fig. 4 (continued).

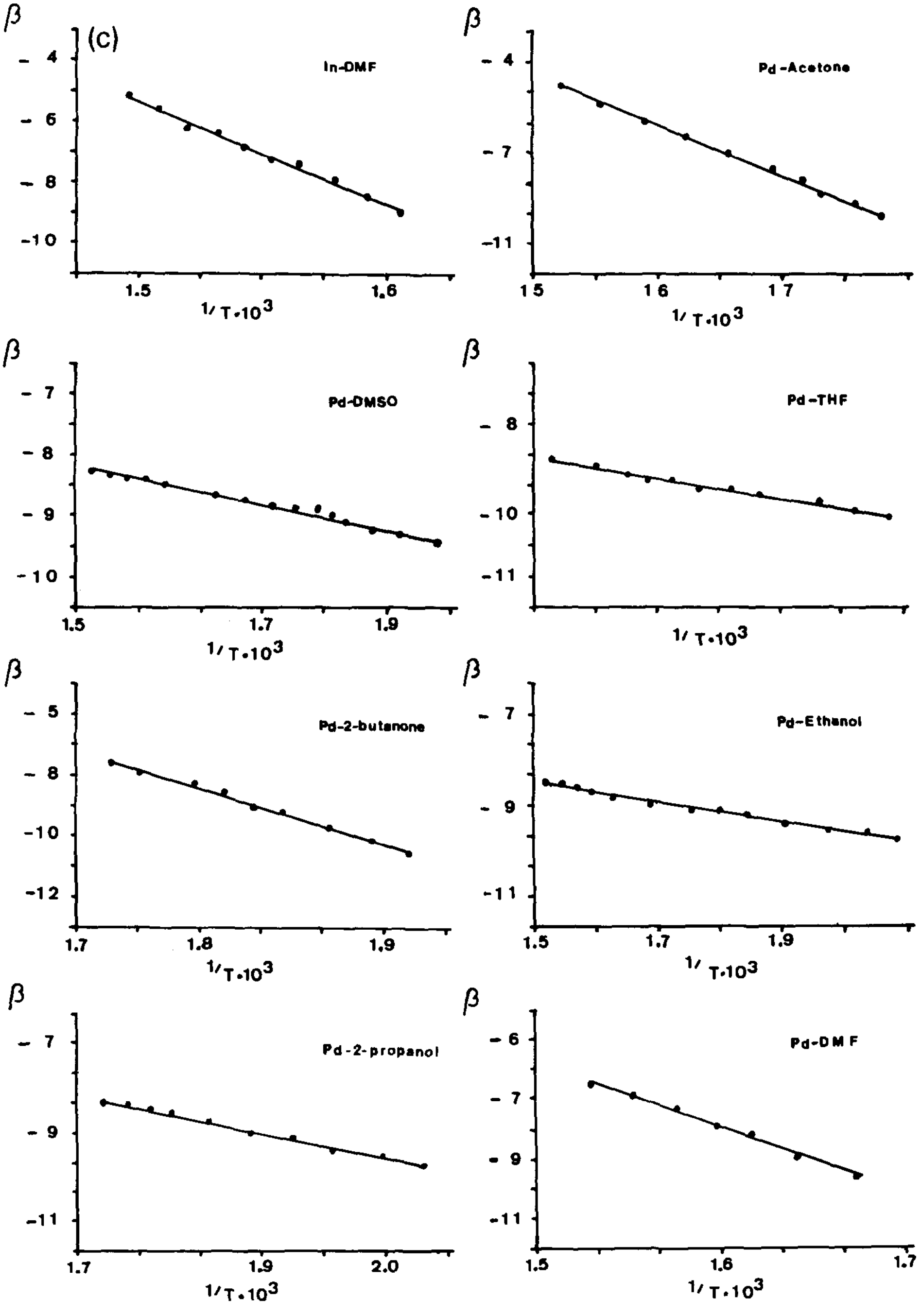


Fig. 4 (continued).

ACKNOWLEDGEMENTS

The support of Fondecyt (Grant 89/0702) and Dirección de Investigación from Universidad de Concepción (Grant 20.13.63) is acknowledged with gratitude.

REFERENCES

1 R.J. Temkin, G.A.N. Connell and W. Paul, Solid State Commun., 11 (1972) 1591.
2 R.J. Temkin and W. Paul, in J. Stuke and W. Brenig (Eds.), Amorphous and Liquid Semiconductors, Taylor and Francis, London, 1974, p. 1193.
3 I.G. Herman, Chem. Rev., 89 (1989) 1323.
4 J.R. MacCallum, in G. Allen (Ed.), Comprehensive Polymer Science, Vol. 1, Pergamon, London, 1989, p. 905.
5 G. Cárdenas T., C. Retamal C. and L.H. Tagle D., Thermochim. Acta 176 (1990) 233.
6 I. Chambouleyron, F.C. Marques, J.P. de Souza and J.R. Baumvol, J. Appl. Phys., 63 (1988) 5596.
7 G. Cárdenas T., K.J. Klabunde and E.B. Dale, Langmuir, 3 (1987) 986.
8 G. Cárdenas T., K.J. Klabunde and E.B. Dale, Proc. SPIE-Int. Soc. Opt. Eng., 821 (1987) 206.
9 G. Cárdenas T., M. Alvial J. and K.J. Klabunde, Bol. Soc. Chil. Quím., 35 (1990) 277.
10 G. Cárdenas T. and K.J. Klabunde, Bol. Soc. Chil. Quím., 33 (1988) 163.
11 E.S. Freeman and B. Carroll, J. Phys. Chem., 621 (1958) 394.
12 W.Y. Wen and J.W. Lin, J. Appl. Polym. Sci., 22 (1978) 2285.