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HUGGINS CONSTANT OF POLYSTYRENE IN BINARY

SOLVENTS

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ABSTRACT

Continuing of our programe dedicated the behaviour of polystyrene (PS, subscript 2) in mixed solvents(1-5), measurements of the Huggins constant, k, were made at $34.5^{\circ}C$ on solutions of PS dissolved in different conditions of solvent and molecular weight of polymer, Θ-conditions were included so that the expansion factor α could be determined in each case. Viscosity slope constants (K_{calc}) calculated according to an expression of Sakai were plotted as a function of α^3 and were compared with the corresponding curves in terms of experimental values of K. An expression (due to Imai) was examined in order to establish a unique value of the slope constant K_{Θ} under Θ - condition by an extrapolation procedure.

A constant value of K_{Θ} was not found for PS. We tested the equation relating $K \alpha^4$ to $SM^{1/2} \alpha^{-1}$ which we have proposed (1). A unique line under all conditions with reasonable linearity was obtained.

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INTRODUCTION

Several years ago Bohdanecky(6) has reported on the behaviour of $\underline{K}$ in relation to varying solvent power of the medium expressed in terms of the viscometric expansion factor α.

In the present communication we have examined the effect of the K introduced by varying the nature of solvent and the molecular weight of polymer.

At $34.5^{\circ}C$, cyclohexane (CH subscript 3) is a Θ - solvent for PS, whereas tetralin (TET, subscript 1) is thermodynamically good solvent for the polymer (1-5). Hence by altering the composition of the TET/CH binary mixtures, it is possible to effect changes in overall solvent power at constant temperature. The chain expansion factor α is obtained as ($[\eta]$ / $[\eta]_{\Theta}$) $1/3$ where $[\eta]$ and $[\eta]_{\Theta}$ are the intrinsic viscosities in the particular solvent and in CH respectively.

EXPERIMENTAL

<u>Materials</u>: CH and TET were dried over sodium wire, each solvent was distilled at its boiling point under atmospheric pressure. Five PS samples were obtained from polymer Laboratories, Church Stretton, Shropshire, England.
The quoted molar masses M were 1.06×10^5, 2.94×10^5, 4.20×10^5, 6.40×10^5 and 9.60×10^5.

In the same order these samples are denoted as PS1, PS2, PS3, PS4 and PS5. The polydispersity indices M_w/M_n being $\leq$ 1.09.

<u>Techniques</u>: The densities of pure and mixed solvents of several different composition O_3 (where O denotes volume fraction of CH) were measured dilatometrically at $20^{\circ}C$ and $34.5^{\circ}C$.

The mixed solvents prepared volumitrecally with $\phi_3 = 0.2$, 0.4, 0.6, 0.8, and 0.9. The solution viscosity was measured in an ubbelohde viscometer with a provision for filtration in situ. Kinetic energy and end-effect corrections were verified to be negligible and the temperature control was mentioned at $34.5 \pm 0.05^{\circ}C$.

RESULTS AND DISCUSSIONS

The intrinsic viscosity and viscosity slope constant, obtained from Huggins eq.(7).

$$\eta_{SP}/C = [\eta] + K [\eta]^2 C \tag{1}$$

where K is the viscosity slope constant (Huggins constant). These values are tabulated in table 1 and 2.

For the Five PS samples in all the solvent media, experimental values of K are shown as data points in Fig.1 as a function of α^3. The full curve represents the variation of K with α^3 according to least squares fitting of the data. This curve is of similar form to the broken curve in Fig.1. which has been calculated from eq.2 due to Sakai (8)

$$K_{calc.} = 0.05 + \bar{v}_2/(2 [\eta]) - 3(\alpha^2 - 1)/4 \alpha^4 \tag{2}$$

Here $[\eta]$ has the same units as the partial specific volume of polymer in solution, v_2. For the later a literature value(9) of 0.9387 $cm^3 g^{-1}$ relating to the specific volume of amorphous PS was used. Eq.2 indicates that under Θ-conditions a unique value of 0.5 should hold for K (i.e. K_Θ), which is exceeded only if $[\eta]$ is very small, i.e. at low M. Bohdanecky (6) has shown that for PS the viscosity slope constant is 0.5 at the Θ- temperature and does not depend on the nature of the solevent, and on the molecular weight.

Higher values can also be found in the literature (10) for cyclohexane at M < 50 x 10^3 and M > 2 x 10^6. However, a constant value of K was not found for PS under Θ - condition.

A unique value of K_Θ has been predicted theoretically by Imai (11) who derived the expression.

$$K \alpha^4 = K_\Theta + C_0 (\alpha^4 - \alpha^2) \tag{3}$$

where C_0 is numerical constant.

Plots of $K \alpha^4$ VS (α^4 - α^2)., shown in Fig.2, displays only moderate scatter, least squares analysis yielding $K_\Theta = 0.49$ and $C_0 = 0.393$. For the corresponding plot invoking $K_{calc.}$ in place of K, there is exact linearity with no scatter, least squares analysis yielding $K_\Theta = 0.49$ and $C_0 = 0.388$. In the original treatment by Imai, a value of 0.45 was predicted for K_Θ and this was asserted to be unique value independent of temperature, nature of solvent and polymer, and molecular weight of polymer.

The values of K_Θ and C_0 obtained by the method of least squares analysis of the experimental results lie midway between the set of values obtained for solutions of PS in TET/3-methyl cyclohexanol (1), $K_\Theta = 0.58_0$ and $C_0 = 0.45$

and those for solutions of PS in a series of cyclic Ketons (6)
($K_\theta = 0.5$ and $C_O = 0.31$)

We have indicated previously (1) the restrictive nature of
the plot due to Imai (10) in which K is correlated with $\propto$
and proposed instead the following relationship

$$K \propto^4 = K_\theta + CSM^{\frac{1}{2}} \propto^{-1} \tag{4}$$

Here C is a factor which includes the unperturbed dimensions.
Since the latter are independent (5) of the composition of
the binary solvent, C is constant. The factor S is the slope
of the stockmayer-Fixman plot (12) of $[\eta] M^{\frac{1}{2}} VS M^{\frac{1}{2}}$.
This factor depends on the nature of the solvent.

The plot according to eq.4 is shown in Fig.3. Reasonably,
good linearity is seen to hold and intercept represents
$K_\theta = 0.43$.

CONCLUSIONS

1. Studying the dependence of the viscosity slope constant,
   K, on the expansion factor, $\propto$, showd that K is
   rather insensitive criterion of solvent power.

2. An obvious dependence of K on M was shown only in
   moderately good solvent while no discernible influence
   of M on K of PS dissolved in ideal and nonideal solvents
   could be detected.

3. The experimental values of K shows much scatter than the
   calculated ones.

4. The new equation for the viscosity slope constatnt which
   we have proposed (1), found to accord well with the
   experimental data.

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TABLE 1

Intrinsic Viscosities at 34.5°C For PS Samples of

Different Molecular Weight[*] in TET/CH Mixtures

Solvent Composition	($Cm^3 g^{-1}$)				
	PS 1	PS 2	PS 3	PS 4	PS 5
0.00	52.7	119	159	225	304
0.20	52.1	116	154	218	290
0.40	49.3	107	144	200	270
0.60	44.0	945	124	173	233
0.80	380	74.0	95.3	129	174
0.90	33.8	62.9	79.7	105	139
1.00	28.1	46.6	55.7	68.7	84.2

*   For molecular weights of samples PS 1 - PS 2, see the

experimental section.

TABLE 2

Experimental and Calculated Viscosity Slope Constants For PS Samples

in TET/CH Binary mixtures at 34.5°C

| Solvent Composition	PS 1		PS 2		PS 3		PS 4		PS 5	
	K	K_{cal}	K	K_{cal}	K	$K_{cal.}$	K	K_{cal}	K	K_{cal}
0.00	0.333	0.340	0.319	0.317	0.328	0.315	0.312	0.316	0.336	0.318
0.20	0.335	0.341	0.320	0.318	0.330	0.316	0.315	0.314	0.317	0.317
0.40	0.348	0.348	0.342	0.321	0.329	0.318	0.328	0.315	0.334	0.316
0.60	0.389	0.367	0.357	0.329	0.339	0.322	0.339	0.316	0.341	0.315
0.80	0.400	0.405	0.388	0.360	0.375	0.347	0.352	0.334	0.350	0.325
0.90	0.445	0.437	0.425	0.346	0.416	0.381	0.402	0.369	0.387	0.315
1.00	0.538	0.517	0.558	0.510	0.557	0.508	0.576	0.507	0.564	0.506
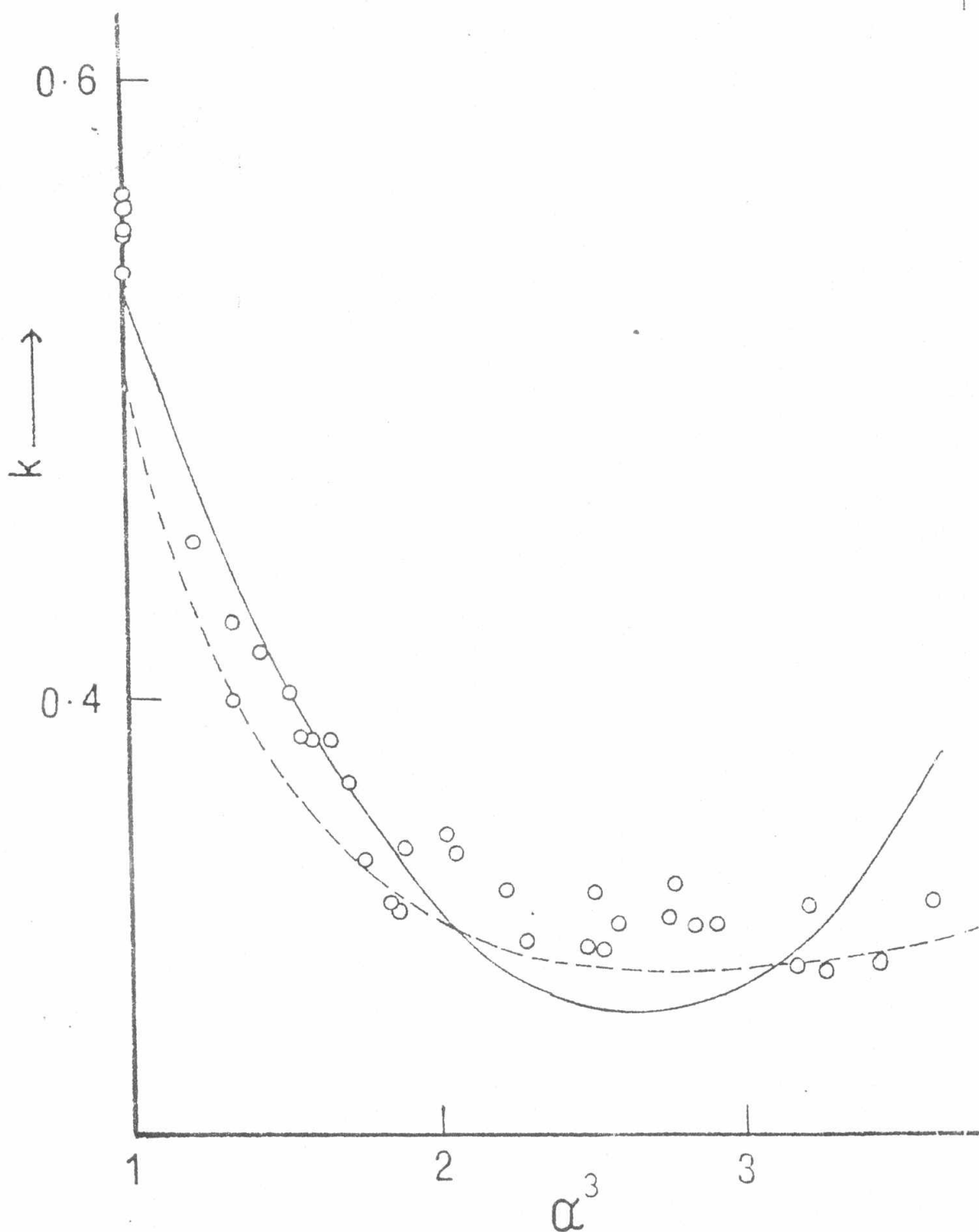
Fig.1   Variation of viscosity slope constant with
        solvent power, expressed as α^3 .
        Experimental values – data points; full
        curve according to least squares analysis
        of experimental data; broken curve-slope
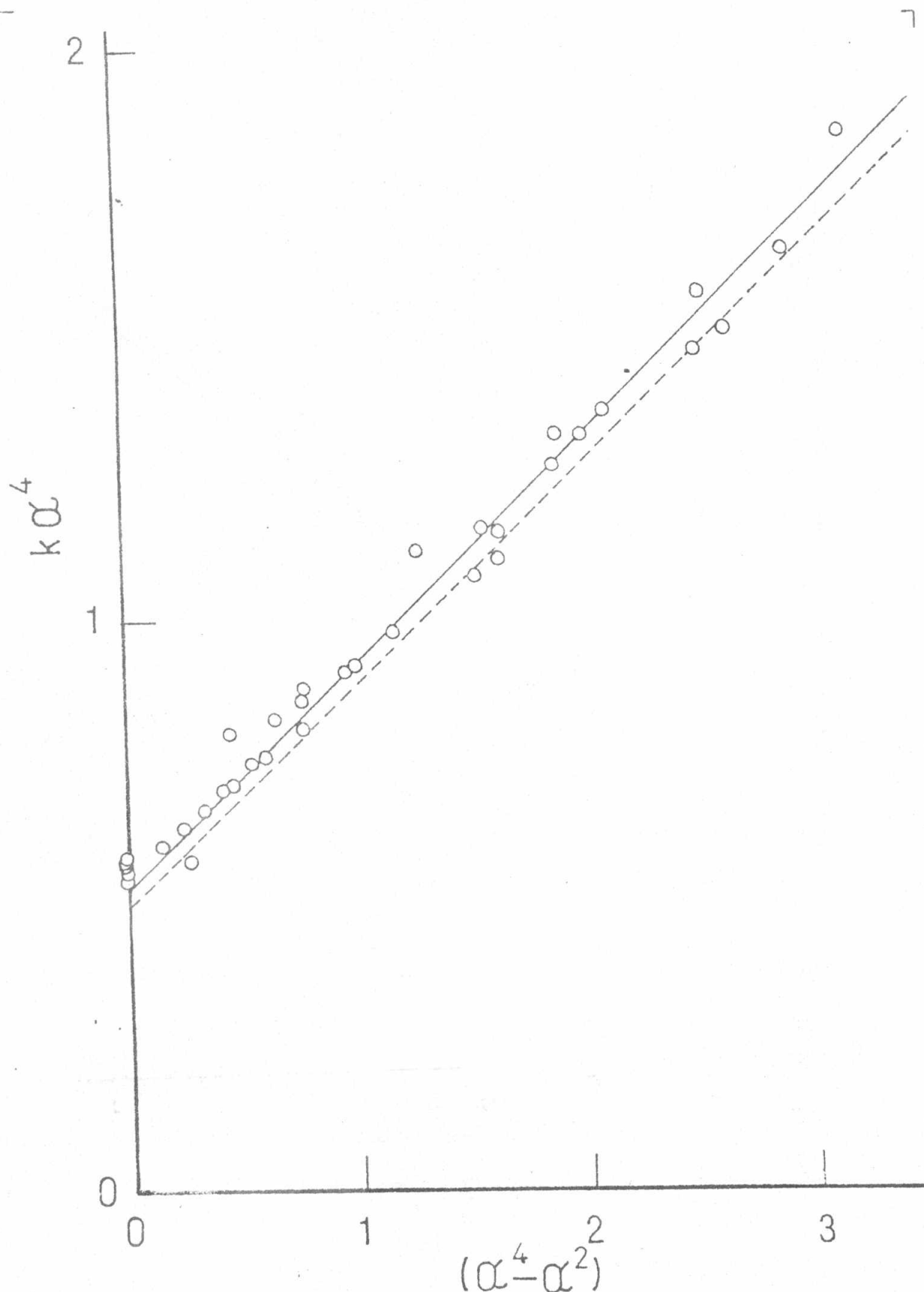   constants Calculated Via eq. 2.

Fig. 2   Influence of excluded volume parameter
$\alpha^4 - \alpha^2$ on (a) slope contant K and (b)
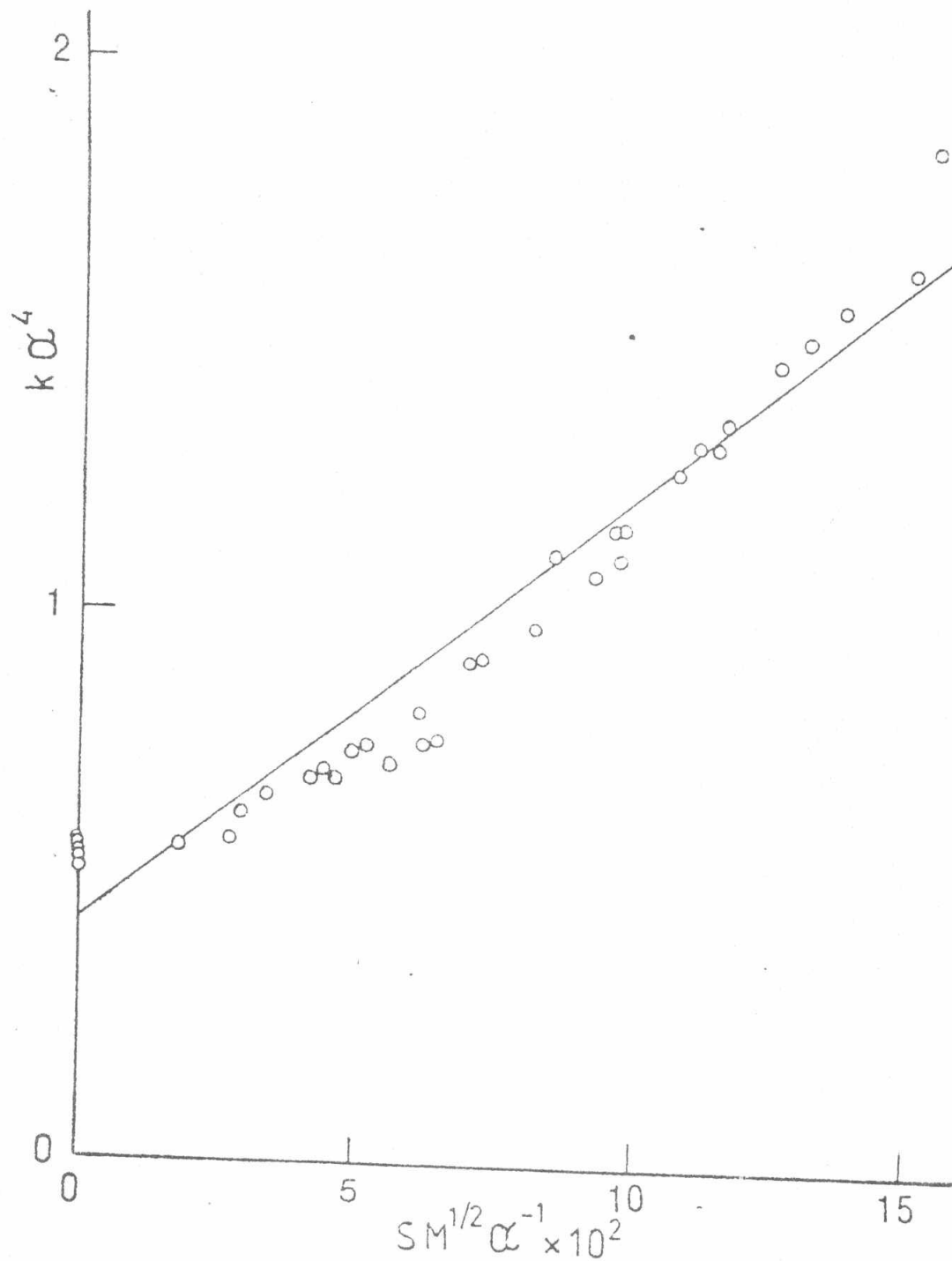K_{calc} according to eq. 3.

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Fig. 3   Plot according to eq. 4.